

Ingenious Engineering of Phosphorus and Nitrogen-enriched Nickel/Iron Bimetallic Phyllosilicates: Forging Multifunctional Epoxy Composites with Excellent Toughness, Self-lubrication, Wear Resistance and Flame Retardancy

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Electronic Supplementary Information

Abstract Epoxy resin (EP) is one of the most promising thermosetting resins used in engineering applications; however, its intrinsic drawbacks of poor abrasion resistance and flame retardancy limit its long-term application in harsh environments. In this study, to improve the comprehensive properties of EP, a prospective four-in-one strategy was proposed to prepare composites by rationally introducing multifunctional nanofillers. First, phosphorus- and nitrogen-enriched nickel/iron bimetallic phyllosilicates (PN-NiFePS) were facilely synthesized and subsequently incorporated into EP to prepare high-performance composites. The results indicate that PN-NiFePS nanoparticles display unique rice-grain-shaped morphologies with rough surfaces, as numerous PN-NiFePS nanosheets were vertically grown on the crystalline surface of the metal-organic framework. The chemically grafted P/N-containing pendant chains enabled well-bonded polymer-filler interfaces and homogeneous dispersion, significantly enhancing the mechanical properties. With the increase filler concentration, the wear rate exhibits a trend of initial decrease followed by subsequent increase, reaching a minimum of $1.19 \times 10^{-6} \text{ mm}^3/(\text{N} \cdot \text{m})$ by adding 1% PN-NiFePS, which is 72% lower than pure EP. The incorporated PN-NiFePS endowed the composites with improved flame retardancy, leading to a steady increase in the limiting oxygen index and excellent self-extinguishing during combustion. This study provides an ingenious engineering strategy for constructing cross-function-integrated polymer composites suitable for harsh environments.

Keywords Nickel/iron bimetallic phyllosilicate; Four-in-one strategy; Cross-performance integration; Flame retardancy; Wet-sliding performance

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INTRODUCTION

Among commercial polymeric materials, epoxy resin (EP) is the most widely used thermosetting resin owing to its outstanding adhesion, excellent chemical inertness, superior mechanical properties, and facile processability.^[1] However, owing to the high crosslink density, cured EP tends to crack and undergo severe wear under harsh operating conditions.^[2] Additionally, like most organic polymers, EP is highly flammable in air, releasing large amounts of toxic smoke and molten droplets, which poses a serious threat to people's lives and property. Therefore, im-

proving the wear resistance and flame retardancy of EP is a key focus of the current research. This is of great importance for the design of high-performance EP-based composites and for expanding their application prospects in structural and functional materials.

Over the past decades, researchers have proposed various methods to improve the comprehensive properties of EP, and incorporating functional nanofillers into the EP matrix to form composites has proven to be one of the most useful strategies. Among these, the use of lamellar nanofillers has attracted intensive attention owing to their unique structure, consisting of atoms within the same atomic layer bonded by covalent bonds and forming a monolayer structure with high modulus and high strength.^[3] Many types of lamellar nanomaterials, including graphene oxide,^[4] molybdenum disulfide (MoS_2),^[5] and nanoclay^[6] have imparted excellent tribo-

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logical responses to EP because the relatively weak van der Waals forces between adjacent atomic layers allow easy sliding between layers and adhesion to the contact surface during friction, thereby reducing the direct contact between the sample and the friction pair. Other reports have demonstrated that some lamellar nanofillers, such as layered double hydroxide (LDH)^[7] and MXene^[8], show great potential for improving the flame retardancy of EP composites owing to their tremendous nanosheets participating in the generation of robust and condensed char layers, effectively hindering heat transfer and flame spread, and protecting the underlying bulk resin from damage during combustion.^[1] To simultaneously improve the tribological properties and flame retardancy of EP composites, researchers in related fields have made considerable efforts, and they generally used multicomponent nanofillers to prepare nanohybrids, improving the tribological properties and flame retardancy simultaneously. For example, in the research reported by Zou *et al.*^[9] phosphorus (P) and nitrogen (N) co-doped MoS₂ was used as a template to grow cobalt borate (Co-Bi) to construct dual sheets of PN-MoS₂@Co-Bi, which was found to simultaneously improve the flame retardancy and tribological properties at a filler concentration of 2%, reducing the peak heat release rate (PHRR) and total heat release (THR) by 28.0% and 27.9%, and lowering the friction coefficient and wear rate by 18.7% and 46.1%, respectively. Hou *et al.*^[10] used MoS₂-based binary compounds (MB) to reduce the heat release and enhance anti-wear properties, and they demonstrated that by adding 1% MB, the PHRR and THR were decreased by 22.0% and 21.8%, respectively, while the wear rate was lowered more than 56% compared with the control sample. However, achieving the cross-functional integration of wear resistance and flame retardancy in EP composites, thereby effectively realizing the integrated construction of flame-retardant and wear-resistant functions, remains challenging because the strong synergistic improvement in the comprehensive properties of EP composites is largely limited by the synergistic effect of the respective components of the resulting hybrids, especially their interfacial bonding and modification efficiency.^[11] To date, few reports have been published on the integrated synthesis of multifunctional single-component nanofillers and their application in the fabrication of robust, wear-resistant, and flame-retardant EP composites.

Phyllosilicates are a representative class of two-dimensional layered nanomaterials in which silicon-oxygen tetrahedra are linked to two-dimensional sheets *via* shared oxygen atoms. These sheets are further stacked and arranged in a well-defined manner, with octahedral sheets composed of metal cations and their hydroxides or oxides.^[12] Owing to their distinctive structural characteristics and the remarkable versatility in tailoring their outstanding properties,^[13] phyllosilicates have attracted extensive attention from researchers, rendering them highly attractive in those applications of catalysis^[14] and lithium-ion batteries.^[15] In our previous work, we employed various synthesis routes to prepare a series of phyllosilicates, including nickel phyllosilicate,^[16] nickel/iron^[17] and nickel/cobalt^[18] phyllosilicates, and found that these phyllosilicates played a significant role in improving the tribological properties of EP composites under both

dry and water-lubricated conditions, suppressing the wear rate by 92.0% in dry sliding^[18] and 70.6% in wet sliding^[17] at a filler concentration of 1%–3%. In addition, the added phyllosilicates also helped to increase the mechanical properties and enhance the thermal stability, presenting great potential in the preparation of cross-functional integrated EP composites.^[17,18] However, they failed to improve the flame retardancy of the EP. In this study, a P/N-enriched nickel/iron bimetallic phyllosilicate (PN-NiFePS) was proposed and synthesized *via* a concise strategy, wherein a nickel/iron metal-organic framework (NiFe-MOF) was utilized as both a template and a reactive precursor. Compared with conventional nanofillers, the as-synthesized PN-NiFePS not only retains the structural merits of NiFe-MOF but also possesses abundant tiny inorganic nanosheets grown *in situ* on the basal planes of NiFe-MOF, constructing uniform hierarchical architectures that remarkably enhance interfacial bonding. Furthermore, numerous organic pendant chains functionalized with P/N-containing groups were covalently grafted onto the phyllosilicate-based structure, further improving the interfacial compatibility with the epoxy resin matrix. By incorporating various mass fractions of the as-prepared PN-NiFePS into the EP matrix, noticeable improvements in the mechanical responses, thermal stability, and flame retardancy of the EP composites were carefully evaluated. Subsequently, the significance of the tribological properties of the tribological properties was thoroughly assessed using a wet sliding method in aqueous environments. Finally, based on chemical and morphological analyses, the wear resistance mechanism of the EP/PN-NiFePS composites was revealed. This study provides an ingenious engineering approach to the rational design and preparation of cross-functional integrated polymer composites.

MATERIALS AND METHODS

Reagents and Chemicals

All reagents and chemicals were used as received from commercial sources and their details are provided in the electronic supplementary information (ESI).

Sample Preparation

The entire sample preparation process was schematically illustrated in Fig. 1 and generally includes the following key steps:

(1) Synthesis of DOPO-*g*-KH550. 10.81 g of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was added to a three-neck flask containing tetrahydrofuran (30 mL), and the system was sealed. The mixture was refluxed by stirring at 70 °C for 30 min. Subsequently, KH550 (11.68 mL) was added to the flask and stirred. Next, formaldehyde (1.84 mL) was slowly added dropwise to the above reaction mixture, followed by gentle stirring for an additional 1 h. Finally, DOPO-grafted KH550 (DOPO-*g*-KH550) was dried under vacuum at 70 °C for 12 h to yield a white powder.

(2) Synthesis of NiFe-MOF. Weighed H₂BDC (0.285 g), NiCl₂·6H₂O (0.307 g), and FeCl₃·6H₂O (0.115 g) were dissolved in *N,N*-dimethylformamide (20 mL). After vigorous stirring for 10 min, an ethanol/H₂O solution (8 mL, 1/1, V/V) was added dropwise. The resulting mixture was transferred to a Teflon-lined autoclave (50 mL) and subjected to a solvothermal reaction at 130 °C for 3 h. Brown NiFe-BDC powder was collected

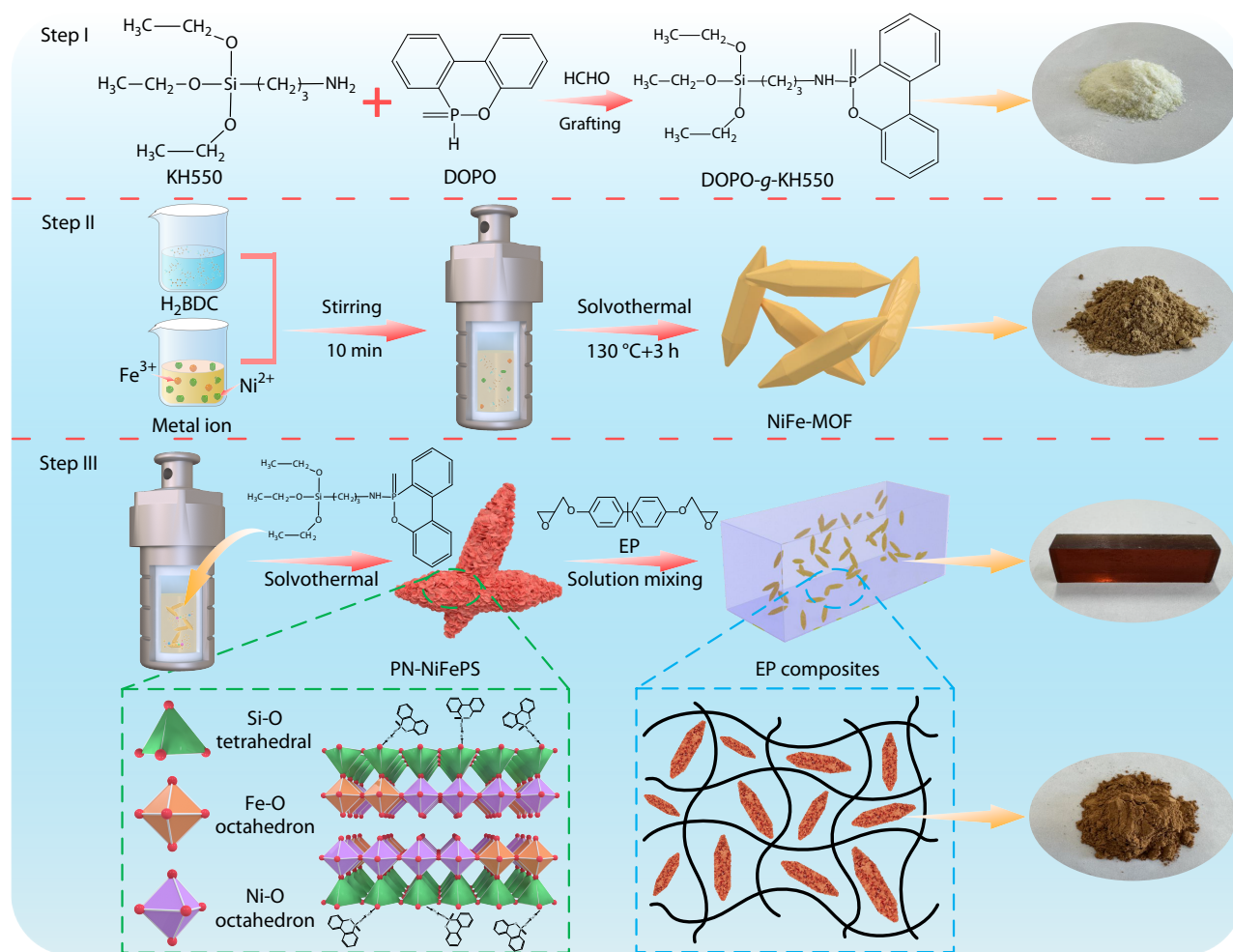


Fig. 1 Schematic illustration of the entire preparation process of EP/PN-NiFePS composites.

by repeated washing with deionized water and ethanol, followed by centrifugation and vacuum drying at 70°C overnight.

(3) Synthesis of PN-NiFePS. DOPO-g-KH550 (1.8 g) and NiFe-MOF (0.8 g) were dispersed in methanol (60 mL), followed by slow dropwise addition of deionized water (60 mL) under vigorous stirring. The pH of the homogeneous suspension was then adjusted to approximately 11.3 using 1 mol/L NaOH solution, and the mixture was sonicated for an additional 30 min. The resulting suspension was transferred to a Teflon-lined stainless-steel autoclave (200 mL), sealed, and hydrothermally reacted at 160°C for 15 h. After naturally cooling to room temperature, the precipitate was collected by centrifugation and washed alternately with anhydrous ethanol and deionized water. The product was dried overnight under vacuum at 70°C to yield a brown powder, denoted as PN-NiFePS.

(4) Preparation of EP/PN-NiFePS composites. EP composites with various mass fractions of PN-NiFePS were prepared via a typical solution mixing method. Taking 1% PN-NiFePS as an example, PN-NiFePS (0.15 g) was dispersed in acetone (15 mL) and sonicated for 1 h to obtain a homogeneous suspension. This suspension was added dropwise to EP (15 g) followed by vigorous stirring at 70°C for at least 4 h. After re-

moving excess acetone, DEDDM (4.8 g) was added, and the mixture was stirred for another 5 min. The resulting mixture was poured into a preheated mold made of silicon rubber and degassed under vacuum at 70°C for 40 min to remove the air and residual acetone. Finally, the EP composites were cured at 100°C for 2 h and at 150°C for another 4 h.

Characterization

Detailed analysis technologies and measurements were provided in ESI.

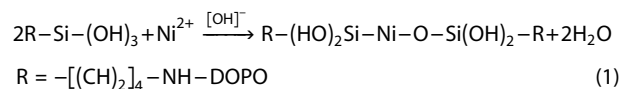
RESULTS AND DISCUSSION

Characterizations of PN-NiFePS

As shown in Fig. 1, DOPO-g-KH550 was successfully synthesized via a traditional solution-phase grafting reaction, in which a phosphorus-containing compound, DOPO, was grafted onto the silane coupling agent KH550. Meanwhile, a rice-granular bimetallic NiFe-MOF was synthesized via a chemical reaction between Ni/Fe ions and organic ligands of H_2BDC , using a facile and well-known solvothermal method, which has been well described elsewhere.^[19] A facile hydrothermal method was used to synthesize PN-NiFePS, following the copolymerization mechanism of trialkoxysilane and Ni(Fe) ions.^[20] Specifically, under ba-

sic conditions, the silane molecules of DOPO-*g*-KH550 were hydrated and act as organic silicon sources, which can react with the fully activated metal-organic framework with metal ions. Simultaneously, many tiny phyllosilicate nanosheets formed and grew *in situ* on the relatively large crystal planes of NiFe-MOF, with the H₂BDC ligands substituted by organic silicon molecules. During this process, Ni ions and hydrated silane molecules first undergo condensation with dehydration to form a unit, as shown in Eq. (1), and then polymerization reactions occur with each other *via* —O—Ni—O— linkages.^[20] Because of the strong tendency of Ni ions to adopt octahedral coordination with six oxygen atoms, these connected units generate oc-

tahedral sheets, forming smectite-type phyllosilicate crystals.^[21] For this purpose, a cross-scale architecture was ultimately obtained by integrating a larger rice-grain-shaped skeleton with numerous finer phyllosilicate nanosheets. To confirm the statements made above, the target product's morphology and composition were characterized carefully through various tests, and the results are presented in Fig. 2.



The detection of the phase structure of PN-NiFePS based on powder diffraction measurements is shown in Fig. 2(a).

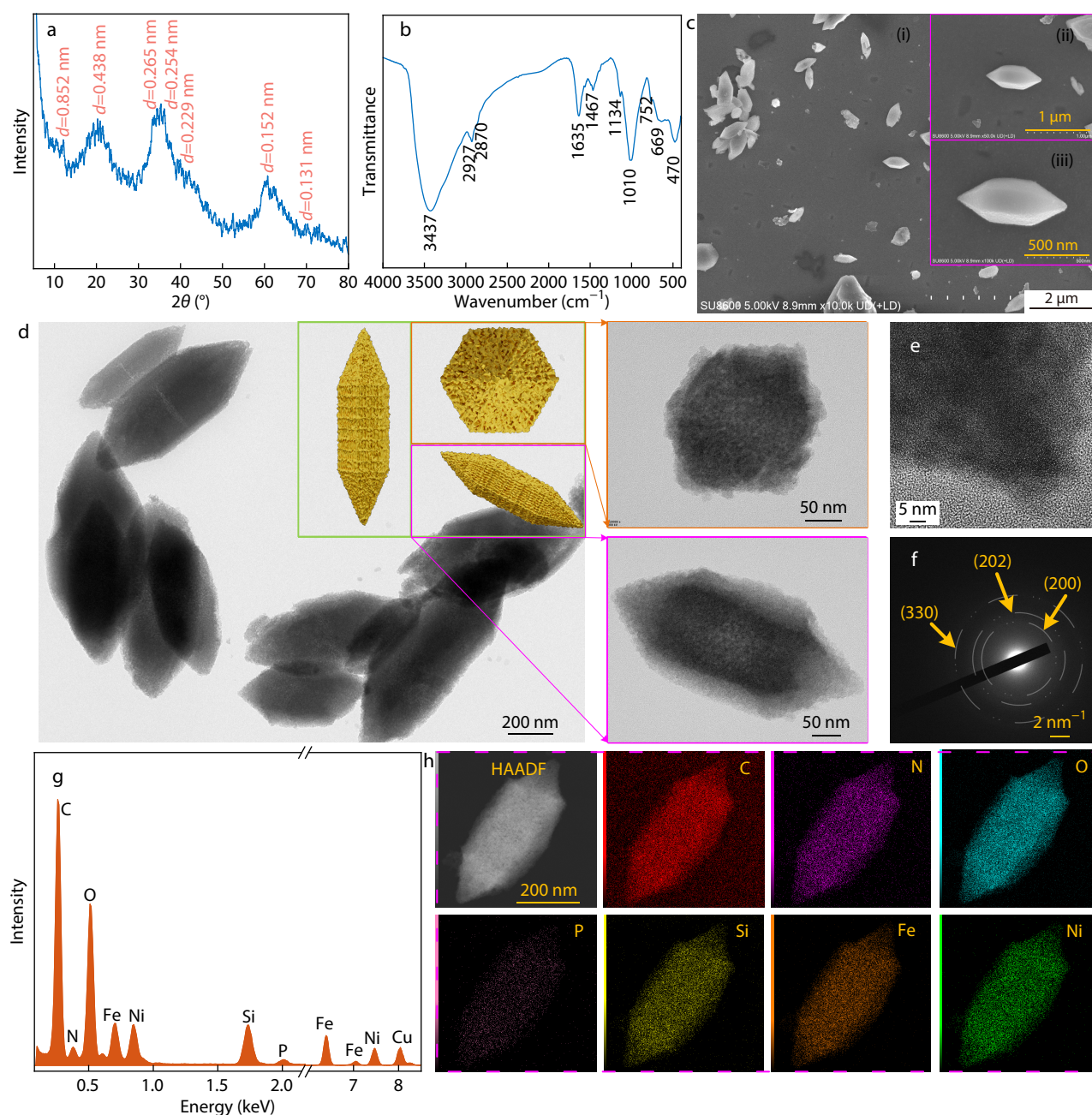


Fig. 2 (a) XRD pattern, (b) FTIR spectrum, (c) SEM images with varied magnifications: (i) $\times 10\text{k}$, (ii) $\times 50\text{k}$, (iii) $\times 100\text{k}$, (d) TEM images, (e) high-resolution TEM image, (f) SAED pattern, (g) EDS spectrum and (h) elemental mappings of PN-NiFePS.

There are several prominent peaks characterized by (00 l) lines and ($hk0$) bands are observed in the diffraction pattern of PN-NiFePS, which can be indexed to the crystal planes of (001), (020), (200), (122), (202), (330) and (410), respectively. These diffractions belong to the pure orthorhombic structure of nepouite phyllosilicates with the chemical formula $\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4$,^[22] which generally exhibits a hydromagnesite-type lamella containing octahedrally coordinated Ni(II) and a lamella containing linked tetrahedral $[\text{SiO}_4]^{2-}$ units.^[23] Such a diffraction pattern is clearly different from that of pristine NiFe-MOF but very similar to that of NiFePS demonstrated in our previous report.^[19] These diffractions clearly present typical (00 l) and ($hk0$) bands and are in line with the characteristics of a layered structure,^[23] confirming that the product possesses a lamellar structure. The diffraction peaks corresponding to $d=0.152$ and 0.254 nm reflect the presence of a trioctahedral smectite structure belonging to PN-NiFePS^[24] and the reflection at $d=0.45$ indicates the formation of phyllosilicate rather than turbostratic nickel (iron) hydroxides.^[23] Moreover, the low-angle reflection of (001) plane suggests the layered structure with a basal spacing of 0.852 nm, which is much lower than the values demonstrated by Chen *et al.* wherein a different MOF precursor was employed.^[18] It is well known that the basal spacing depends on the nature of phyllosilicate, which is briefly affected by the silicon and Ni sources, supporting substrates, and the pH value of the reaction solution.^[13] Similar to those reported elsewhere,^[22,25] the diffraction belonging to Fe-containing phyllosilicate is not clearly observed at an angle of approximately 30° due to the relatively low intensity, which suggests that the doped Fe(III) ions lead to a negligible change in the present phyllosilicate structure; however, the somewhat broadened and weakened characteristic signals indicate the ill-crystallized PN-NiFePS particles, which generally arise from intralayer and stacking disorder due to the insertion of organic chains in the interlamellar regions and the smaller particle diameters of the synthetic solids as well.^[26]

Fig. 2(b) displays the infrared spectrum of PN-NiFePS, and for comparison, the spectra belonging to DOPO-*g*-KH550 and NiFe-MOF are shown in Figs. S1 and S2 (in ESI), respectively. It is found that, the characteristic signals that emerged in the spectra of DOPO-*g*-KH550 and NiFe-MOF are well in line with those results reported by Li.^[27] In contrast, the spectrum of PN-NiFePS is distinctly different from that of NiFe-MOF but similar to that of pristine NiFePS.^[19] The prominent band at 3437 cm^{-1} primarily originates from the overlapped antisymmetric stretching vibrations of the hydroxyl and amino groups, while the sharp peak at 1635 cm^{-1} is caused by the bending vibrations of $\text{H}-\text{O}-\text{H}$ in water molecules, confirming the presence of intramolecular hydrogen bonds and N-rich organic pendant chains contained in the interlayer structures of PN-NiFePS.^[28] The doublet peaks located at 2927 and 2870 cm^{-1} are the symmetric and asymmetric stretching vibrations of $-\text{CH}_2-$, respectively, which mainly originate from the introduced organic pendants. The P-related characteristic signals appearing at approximately 752 , 1134 and 1467 cm^{-1} are associated with the stretching vibrations of the $\text{P}-\text{O}-\text{Ph}$, $\text{P}-\text{O}-\text{C}$, and $\text{P}-\text{Ph}$ bonds,^[29] confirming that P-rich organic pendants were successfully incorporated into the

lamellar structures of phyllosilicate *via* DOPO-*g*-KH550. A relatively weak band at 470 cm^{-1} originates from the $\text{Si}-\text{O}$ stretching vibration,^[30] whereas the second prominent peak located at 1010 cm^{-1} is assigned to the $\text{Ni}-\text{O}-\text{Si}$ stretching vibrations, which, together with the stretching signal of the $\text{Ni}-\text{OH}$ lattice at 669 cm^{-1} , strongly confirms the successful formation of phyllosilicate.^[31]

Fig. 2(c) presents the SEM images of PN-NiFePS particles, which are characterized by rice-granular shapes and are approximately $600\text{--}800\text{ nm}$ in length, generally retaining the original morphology of pristine NiFe-MOF, as shown in our previous study.^[19] The TEM images in Fig. 2(d) reveal that the edges are not smooth and exhibit somewhat zigzag morphologies, implying that the surface of PN-NiFePS is relatively uneven owing to the *in situ* development of PN-NiFePS nanosheets. The inserted top and side views further demonstrate that PN-NiFePS maintains the integrity of the metal-organic framework structure during the growth process, with a radial dimension of approximately 200 nm . Although the high-resolution TEM image in Fig. 2(e) exhibits alternating bright and dark features, they do not clearly show distinct nanosheet edges, and no distinct lattice fringes are observed, which is quite different from our previous results, where an inorganic silicon source was adopted.^[18] Such divergence is attributed to the presence of a large number of organic pendants that hindered the growth of phyllosilicate nanosheets to generate imperfect crystals during the hydrothermal process. Nevertheless, the selected area electron diffraction (SAED) image of Fig. 2(f) shows three distinct diffraction rings at 0.154 , 0.213 and 0.264 nm , corresponding to (135), (220), and (200) crystal planes, respectively, as is consistent with XRD detection. The chemical composition of the PN-NiFePS was easily determined from the EDS spectrum shown in Fig. 2(g). The elements of carbon (C) and oxygen (O) present two prominent peaks at 0.26 and 0.51 keV , respectively, indicating their abundant loading within the PN-NiFePS. By contrast, the N and P elements exhibit the very low signals at around 0.38 and 2.01 keV , respectively, implying their relatively low concentration. Both the transition metal elements of Fe and Ni show multiple peaks, appearing at $0.71/6.39/7.05\text{ keV}$ and $0.84/7.46\text{ keV}$, respectively. Furthermore, the elemental maps depicted in Fig. 2(h) clearly demonstrate that all elements were uniformly distributed throughout the rice-granular framework, which is consistent with the elemental composition of PN-NiFePS. These observations, together with the above analysis, provide robust support for the successful synthesis of PN-NiFePS.

To further verify the valence states of each element within the PN-NiFePS, the XPS test results are shown in Fig. 3. From the fully scanned spectrum in Fig. 3(a), all characteristic elements detected in EDS measurements were observed, with their relative atomic concentrations of 39.71% (C 1s, 284.53 eV), 5.11% (N 1s, 399.34 eV), 33.8% (O 1s, 530.65 eV), 6.18% (Ni 2p, 855.26 eV), 5.57% (Fe 2p, 710.90 eV), 1.99% (P 2p, 132.31 eV), and 7.64% (Si 2p, 101.61 eV). The N 1s and P 2p core-level spectra depicted in Figs. 3(b) and 3(c) exhibit the characteristic P/N related bonds at 399.4 , 401.6 , 134.5 , 133.3 and 132.5 eV , respectively indicating the formation of $\text{N}-\text{P}$,^[32] $\text{P}-\text{NH}-\text{CH}_2$,^[33] $\text{P}-\text{O}/\text{P}-\text{N}$,^[32] and $\text{P}-\text{O}-\text{C}$ bonds,^[34] pro-

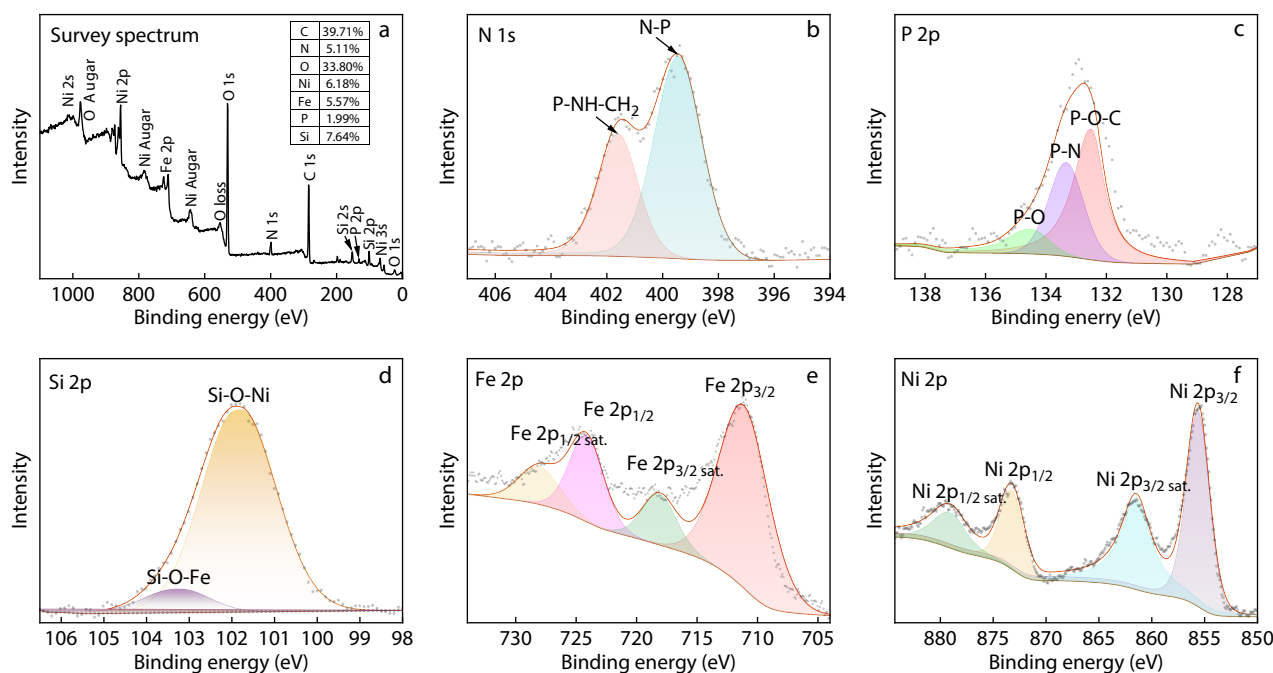


Fig. 3 XPS analysis of PN-NiFePS: (a) survey scan, core-level spectra of (b) N 1s, (c) P 2p, (d) Si 2p, (e) Fe 2p and (f) Ni 2p.

viding solid evidence for the molecular inheritance of DOPO-g-KH550 in PN-NiFePS. Fig. 3(d) shows the two deconvoluted peaks in the Si 2p spectrum, of which the prominent at 102.1 eV is assigned to the Si—O—Ni bond^[35] while another one at 103.3 eV with relatively low intensity can be assigned to the Si—O—Fe bond,^[36] further demonstrating the successful synthesis of phyllosilicates.^[22] The Fe 2p spectrum in Fig. 3(e) includes two main peaks at binding energies of 724.8 and 711.1 eV due to spin splitting, corresponding to the Fe 2p_{1/2} and Fe 2p_{3/2} orbitals, respectively, while the other two peaks at 728.5 and 718.4 eV are their respective satellite signals.^[37] The peak separation (*i.e.*, $2p_{1/2}-2p_{3/2} = 13.7$ eV) is very similar to that reported for Fe₂O₃, indicating that the Fe element in the present PN-NiFePS is in the trivalent state.^[37] Ni 2p shows a core-level spectrum analogous to that of Fe 2p, as shown in Fig. 3(f). The two major spin-split orbitals centered at 873.4 and 855.8 eV correspond to Ni 2p_{1/2} and Ni 2p_{3/2}, along with their satellites at 879.5 and 861.8 eV, respectively. The difference in the binding energy was 17.6 eV, indicating the presence of divalent Ni.^[38] Besides, Coenen has pointed out that the difference in binding energies between Ni 2p_{3/2} and Si 2p (defined as ΔBE_{Ni-Si}) is another indicator to distinguish whether a Ni-containing compound is a phyllosilicate, and ΔBE_{Ni-Si} value located within the range of 753.2–753.8 eV belongs to phyllosilicate structure whereas a remarkably suppressed value usually implies other Ni species.^[39] In the present study, the ΔBE_{Ni-Si} value (*i.e.*, Ni 2p_{3/2}–Si 2p_{Si-O-Ni}) was 753.7 eV, which provides solid proof to support the above inference, validating the successful synthesis of PN-NiFePS *via* the present route.

Observations of Fracture Surfaces for EP Composites

To examine the dispersion behavior of PN-NiFePS and its interfacial compatibility with the EP matrix, Fig. 4 displays SEM micrographs at different magnifications (500× and 3000×) of the

fractured surfaces of pure EP and its composites after tensile testing. It is well known that during tensile fracture, crack propagation in pure EP generally depends on the location of the stress concentration within the matrix. Thus, as expected, the fracture surface of the pure EP in Fig. 4(a) shows no distinct features, and we can observe a step-like structure formed by regularly arranged fractures, known as river patterns, which indicate the propagation path of the main cracks. The high-magnification image reveals very smooth areas between the steps, implying that pure EP exhibits weak resistance to crack initiation, propagation, and deflection, exhibiting representative characteristics of a typical brittle fracture mode.^[40] However, as PN-NiFePS particles were introduced, significant changes occurred in the morphological structure of the fracture surface, as shown in Figs. 4(b)–4(e). For all composite samples, the regularly arranged steps disappeared, and instead, uneven fracture surfaces with new morphologies with many small protrusions and depressions emerged. This is caused by the tortuous crack propagation paths induced by the added second-phase particles, that is, the existing PN-NiFePS particles not only act as rigid sites to arrest cracks but can also branch and deflect the propagation paths of cracks within the resin matrix. For this reason, the crack propagation paths are significantly prolonged, with numerous crack intertwining points formed in the process. Furthermore, the higher the filler content, the more points there are, because fillers tend to block propagating cracks and induce their intertwining. It was confirmed that both the extension of the crack propagation paths and the increase in the intertwining points directly indicated greater energy dissipation during fracture. This enhanced energy-dissipating capacity enables EP composites to resist rapid crack propagation more effectively than pure resin, which is highly beneficial for improving the macroscopic properties.^[41] As shown in the corresponding high-magnification SEM images, no interfacial debonding was ob-

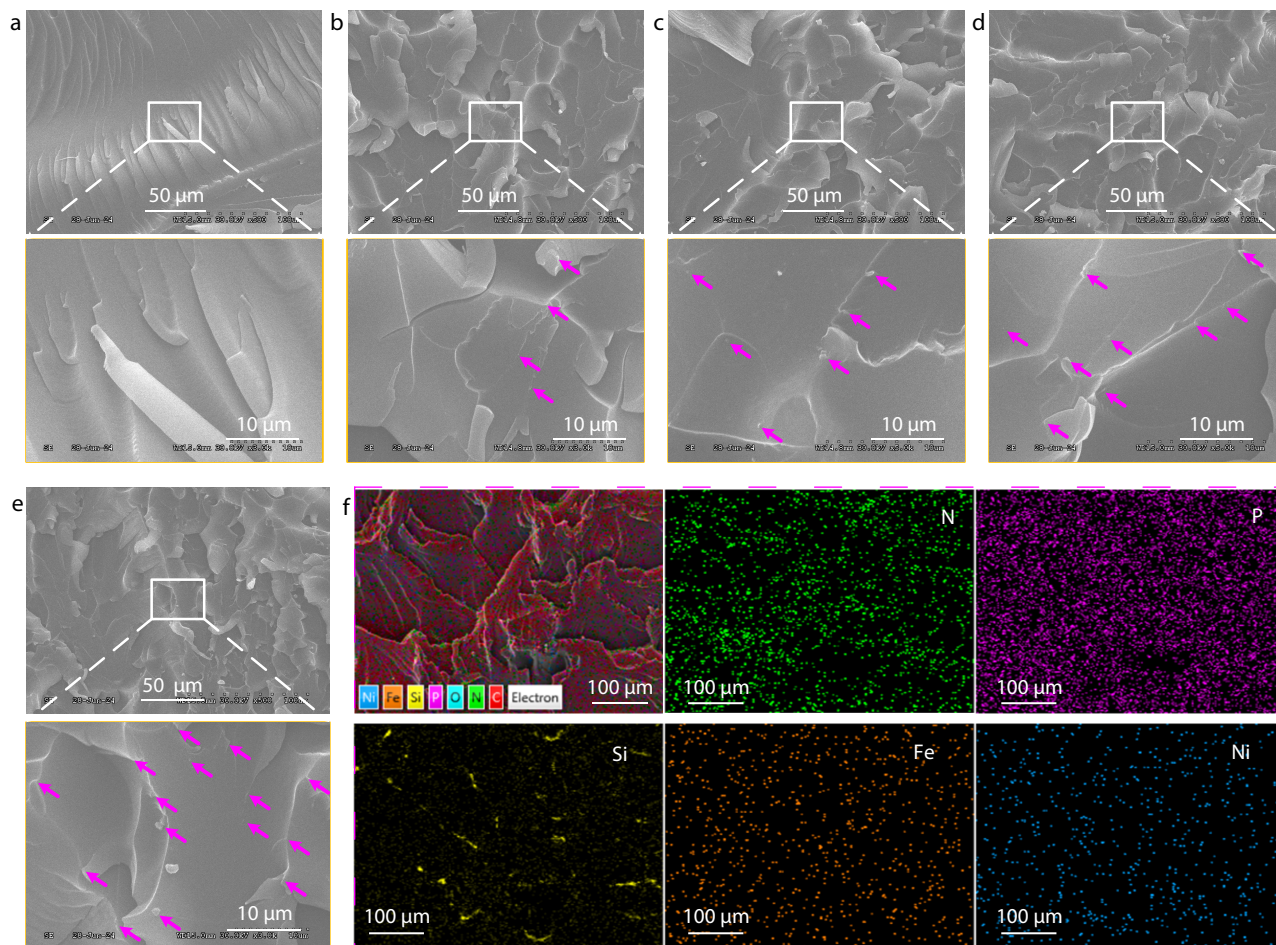


Fig. 4 SEM micrographs of fractured surfaces for EP/PN-NiFePS composites after tensile tests: (a) 0%, (b) 0.25%, (c) 0.5%, (d) 1%, (e) 3%, and (f) EDS elemental mapping images of the sample containing 1% PN-NiFePS.

served between the added PN-NiFePS particles and EP matrix, which directly demonstrates the excellent interfacial compatibility between the incorporated filler and resin matrix. Such compatibility plays a dual role in governing the microstructures of composite systems, not only effectively preventing the agglomeration of PN-NiFePS into large aggregates, but also ensuring uniform particle dispersion within the EP resin, existing temporarily in the form of fine clusters. From the elemental mappings depicted in Fig. 4(f), all the characteristic elements were found to be homogeneously dispersed throughout the fracture surface, providing further strong evidence for the homogeneous distribution of PN-NiFePS within the EP matrix. As presented in the aforementioned discussion, the as-synthesized PN-NiFePS is characterized by a rough surface with numerous organic pendant chains, which not only provide abundant active sites to firmly form interfacial interactions and achieve forced compatibilization but also enhance interfacial compatibility with the matrix resin through the organic modification of pendant chains. Additionally, the uniformly dispersed reactive groups (e.g., hydroxyl and amine groups) on the surface of PN-NiFePS further promote the curing reaction of the EP-amine system, increase the density of cross-linking points, and are therefore expected to be beneficial to the mechanical properties of EP composites.^[42]

Mechanical Properties of EP Composites

To determine the positive influence of various mass fractions of PN-NiFePS on the mechanical properties of EP composites, the measurement results of the tensile properties and hardness for all investigated samples are shown in Fig. 5. Typical stress-strain curves from quasi-static uniaxial tensile tests reveal that pure EP exhibits a hard and brittle stress-strain response, featuring a high modulus and strength, low ductility, and abrupt failure with no evident yielding, as depicted in Fig. 5(a). This is mainly due to the highly crosslinked structure of EP, which endows it with difficulty in deformation under stress but causes it to fracture rapidly once the critical stress is exceeded. The incorporation of PN-NiFePS had no significant influence on the nearly linear tensile stress-strain curves without any obvious yielding plateau or necking phenomenon in the composite samples. Nevertheless, a slight deviation from linearity emerges in the stress-strain curves with the addition of different amounts of PN-NiFePS. As shown in Fig. 5(b), when the filler content was increased, the elongation at break first increased and then decreased. The slight incorporation of 0.25% PN-NiFePS increased elongation at break from 6.4% for pure EP to 11.17% for EP composites, representing a significant improvement of about 74.5%. Although further addition of 0.5% and 1% of PN-NiFePS leads to a decrease in elongation at break, the corresponding

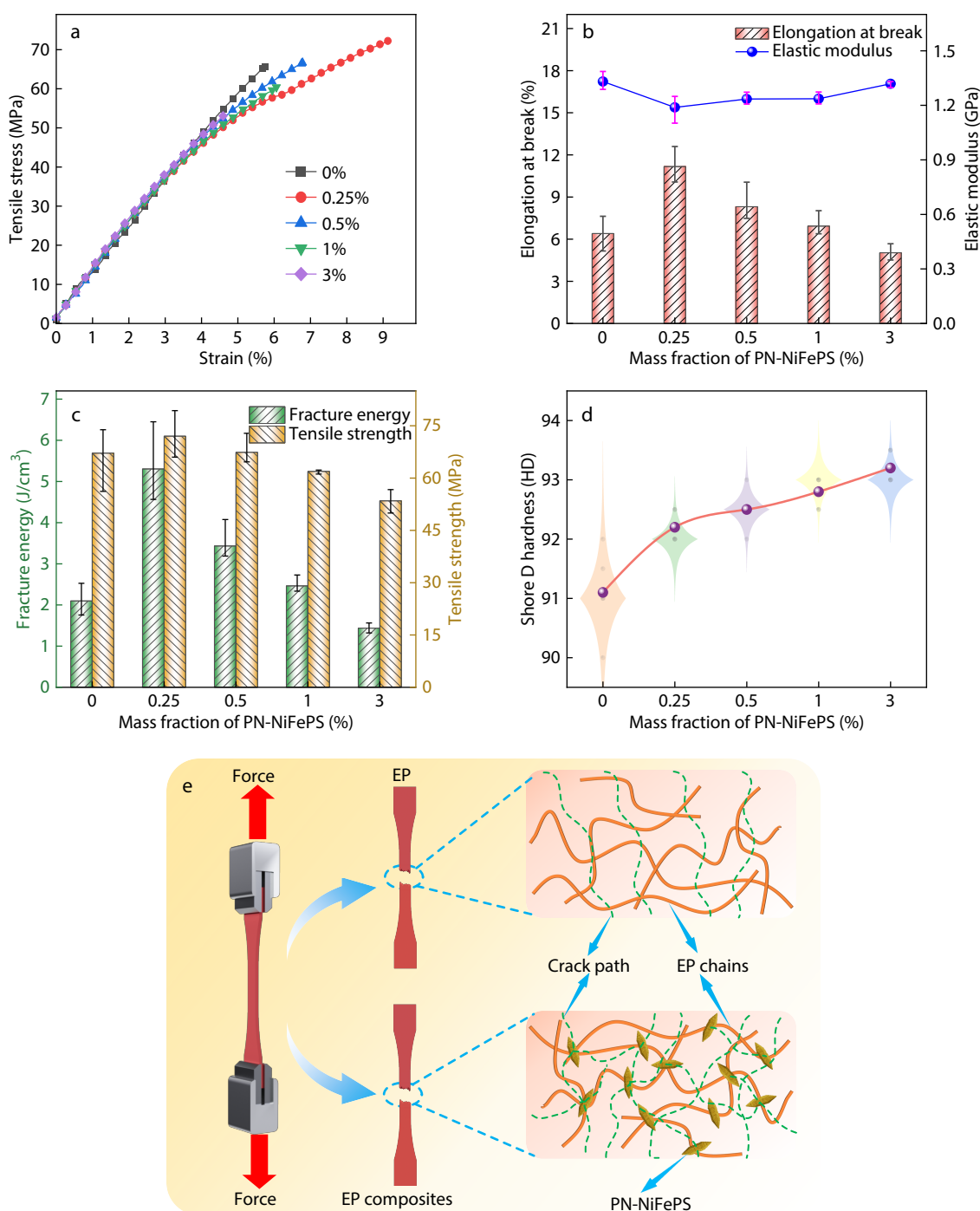


Fig. 5 Mechanical properties of EP/PN-NiFePS composites: (a) representative tensile stress-strain curves, (b) elongation at break and elastic modulus, (c) fracture energy and tensile strength and (d) Shore D hardness as a function of increased PN-NiFePS content; (e) The possible strengthening and toughening mechanism of EP/PN-NiFePS composites.

values of 8.31% and 6.93% are still obviously higher than the control sample. Furthermore, our observations indicate that relative to pristine NiFePS,^[19] the as-prepared PN-NiFePS is more effective at improving the toughness of EP composites at the same addition level, achieving a notably higher elongation at break. In contrast, the elastic modulus showed an opposite trend to that of the elongation at break. This fact suggests that the as-synthesized PN-NiFePS tends to improve ductility at a rel-

atively low concentration of 0.25%–1% while tends to enhance the stiffness at a higher content of 3%. These findings are similar to those of our previous reports regarding pristine NiFePS^[19] but differ from those of other phyllosilicates, where the elongation at break usually decreases steadily with increasing filler concentration.^[43] It is well known that both elongation at break and elastic modulus are closely related to the mobility of polymer chains under external forces, and the existing inorganic

fillers have dual functions of occupying the space between molecular chains to weaken the interactions between chains, form entanglements with molecular chains, and restrict chain mobility. These two functions are competitive, and the dominant effect depends on filler loading. When the PN-NiFePS content was low, the plasticizing effect dominated, exhibiting a relatively high elongation at break, whereas brittleness gradually became dominant in the tensile measurements as the filler content increased to 3%. The fracture energy, defined as the integral area under the stress-strain curve, presents a similar variation trend to elongation at break in Fig. 5(c), i.e., it is first elevated from 2.1 J/cm³ to 5.3 J/cm³, approximately 152% higher than that of pure resin, at a low content of 0.25%, and then declined gradually with the further added filler concentration. Such elevated fracture energies intuitively indicate much higher energy dissipation, as is closely related to the well-dispersed PN-NiFePS particles that provide tortuous paths for crack propagation during the entire tensile process. This fact reveals the significant improvement of the added PN-NiFePS in the toughness of the EP composites, supporting the above SEM observations.

The tensile strength of the EP/PN-NiFePS composites with increasing filler content is presented in Fig. 5(c). The incorporation of 0.25% PN-NiFePS increased tensile strength to a maximum of 72.01 MPa, which is approximately 7.16% higher than that of pure EP. Though the further added PN-NiFePS leads to a mild decrease in the tensile strength, it still remains relatively high, ranging from 53.48 MPa to 67.40 MPa. This phenomenon indicates that the current PN-NiFePS is not effective in significantly improving the tensile strength; instead, it only slightly reduces the tensile strength when the filler content is relatively high. Similar results have been demonstrated by Verma^[44] and Qi^[45] for EP-based composites with other fillers, whereas our previous investigations confirmed that the incorporated phyllosilicate nanoflowers and whiskers could boost the tensile strength more efficiently.^[16,46] Generally, as the added reinforcing fillers scatter widely and uniformly within the resin matrix, they form a rigid network with abundant polymer-filler interfaces throughout the polymer matrix, forcing crazes to propagate along tortuous paths and simultaneously dissipate substantial energy prior to the fracture of the material. Meanwhile, owing to the effective interfacial stress transfer between PN-NiFePS and the EP matrix, external loads were largely borne by the harder PN-NiFePS particles, thereby significantly improving the tensile strength of the composite. At the micro level, as the content of PN-NiFePS increased, a trade-off emerged between the chain mobility and microcrack aggregation.^[45] When the filler content is low, microcracks remain isolated and dissipate energy effectively, and increase the tensile strength accordingly, whereas a higher filler concentration tends to trigger microcrack agglomeration, reduce the interparticle distance, and eventually lead to a decline in the tensile strength of the EP composite.^[47] Nevertheless, the decrease in tensile strength was not significant, with the lowest retention of 79.58% for the case containing 3% PN-NiFePS, which is sufficient to meet most engineering application requirements. However, we also note that the present PN-NiFePS exhibits a better tensile strength enhancement than pristine NiFePS,^[19] and this superiority is closely associated with the adhered organic pendant

chains, which introduce π - π stacking between aromatic rings as well as intermolecular interactions between the hydroxyl groups in PN-NiFePS and epoxide macromolecules. These interactions facilitate uniform stress transfer within the composites, effectively avoiding stress concentration and thus contributing more efficiently to the improved mechanical strength of the EP composites.^[48] In light of the above descriptions, a potential toughening and reinforcement mechanism for EP/PN-NiFePS composites is proposed and illustrated in Fig. 5(e). Besides, It was also found that incorporating PN-NiFePS into resin matrix at loadings ranging from 0.25% to 3% modifies the surface characteristics by enhancing the Shore D hardness of EP composites, as illustrated in Fig. 5(d), where the average hardness increases steadily from 91.1 HD for neat EP to 93.2 HD for the composites a PN-NiFePS content of up to 3%. Generally, the highly densely distributed NiFePS not only enables dense packing of the composite but also provides extensive surface coverage, thereby imparting exceptional stiffness and hardness to the EP composites *via* large surface area coverage and replacement.^[49] Nevertheless, careful consideration is required when formulating EP composites with high concentrations of inorganic nanofillers to prevent excessive brittleness. Increased brittleness tends to induce tensile stress within the material, which can initiate fatigue cracking on its surface.

Thermal Stabilities of EP Composites

Because the friction of materials is inherently a heat-generating process, investigating the thermal stability of epoxy composites is crucially important. The thermogravimetric results obtained under a nitrogen atmosphere are presented in Fig. 6, with the relevant characteristic data included in Table S1 (in ESI). Based on the weight-loss dependent plots in Fig. 6(a), the thermogram for each specimen shows a single-step decomposition behavior with a linearly increasing temperature, indicating that the addition of PN-NiFePS has little effect on the decomposition behavior of EP. The single sharp peak that appears in each plot of the weight loss rate versus temperature implies that the weight loss occurs within a relatively narrow temperature range, and the decomposition reaction follows a typical first-order reaction.^[50] Briefly, the entire thermal decomposition process can be divided into three distinct periods. During the first stage, ranging from room temperature to approximately 350 °C, the weight of all the samples remained almost unchanged, indicating that the EP composites maintained their structural integrity during this stage. When the temperature increased to 350–500 °C, the samples began to decompose, and the main weight loss corresponded to random chain scission reactions and the pyrolysis of the network structure within the matrix resin,^[51] including the cleavage of C—C, aromatic C=C, C—O, and C—N bonds.^[52] The decomposition temperatures ($T_{5\%}$ and $T_{\max}$) for pure resin are 356.4 and 404.1 °C, respectively, while the added PN-NiFePS generally reduces the initial and maximum thermal decomposition temperatures of the EP composite. This may be due to the early decomposition of phosphorus-based pendant chains, producing acidic species such as phosphoric acid and polyphosphates, which accelerate the structural decomposition of the EP matrix.^[53] Moreover, the loss of physically bound water in the phyllosilicates of PN-NiFePS also contributed significantly to the earlier decomposition of EP composites than that

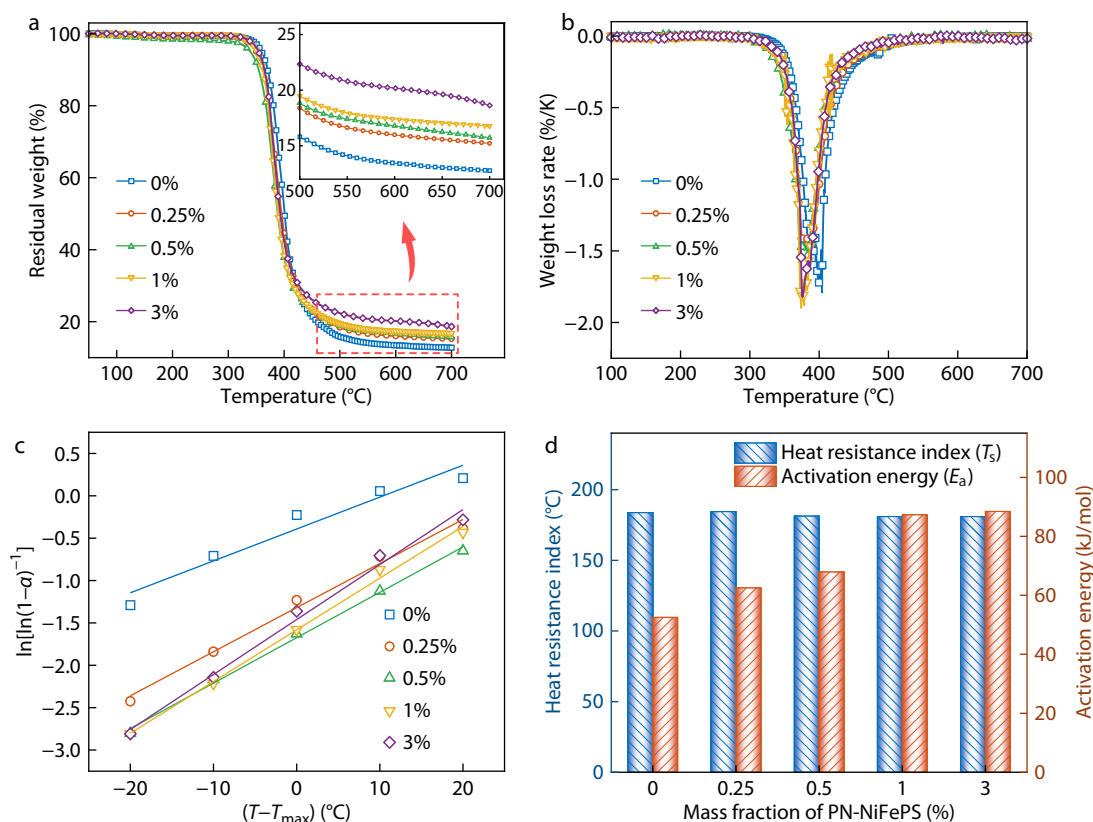


Fig. 6 Thermal stabilities of EP/PN-NiFePS composites: (a) residual weight, (b) weight loss rate, (c) linear fitting plots of $\ln[\ln(1-a)-1]$ versus $(T-T_{\max})$ and (d) variations of T_s and E_a as a function of PN-NiFePS content.

of the resin matrix.^[19] As the temperature continued to rise above 500 °C, the pyrolysis process entered the third stage, during which the weight of the samples stabilized because the organic components and physically bound water in the fillers were fully removed. The char content is only 12.8% for pure EP, while steadily rising up to 14.7%–18.4% for the composite samples, *i.e.*, a higher PN-NiFePS loading leads to higher residual char at the end temperature of 700 °C. This is primarily because the inorganic components contained in PN-NiFePS are difficult to decompose at high temperatures in an inert atmosphere, ultimately leading to an increasingly elevated char content. This is promising because a higher char content can provide more efficient protection to the underlying resin against further thermal destruction, making it more suitable for high-temperature or flame-exposed environments.

According to Figs. 6(c) and 6(d) and Table S1 (in ESI), neat EP shows the lowest activation energy (E_a), 52.5 kJ/mol, among all samples, suggesting that it is most likely to decompose when exposed to high temperatures.^[54] In contrast, E_a values of the composites increased continuously with increasing PN-NiFePS content. Specifically, as the filler concentration increased from 0.25% to 3%, the E_a values are accordingly elevated from 62.5 kJ/mol to 88.4 kJ/mol, with a maximum improvement of about 68.4% achieved when 3% PN-NiFePS was added. Although the existing PN-NiFePS showed a slight suppression of the decomposition temperatures of the EP matrix, it remarkably increased the activation energies of the EP composites. This finding is closely related to the widely

and uniformly distributed PN-NiFePS particles forming a stable inorganic network within the matrix, which acts as a physical barrier against the volatilization of low-molecular-weight substances by providing tortuous diffusion pathways, thus significantly inhibiting the diffusion and penetration of pyrolysis products during the thermal decomposition process.^[55] Moreover, it should also be noted that the extensive entanglement interactions formed between the resin molecules and the surface of PN-NiFePS play a key role in significantly restricting the mobility of the molecular chains, thus offering another important contribution to the higher E_a values of EP-based composites.^[56] Nevertheless, the presence of PN-NiFePS does not change the statistical heat resistance index (T_s) remarkably. Notably, pure EP exhibits a T_s value of 183.7 °C, while the composites present the T_s values ranging from 180.0 °C to 184.4 °C, showing an average value of (181.9 ± 1.7) °C. This small decline in the T_s value is mainly attributed to the early decomposition triggered by PN-NiFePS; however, it is almost negligible in practical applications owing to the inherently high thermal resistance of EP. Clearly, studies focusing on thermal stability will provide useful information to support later investigations of how these substances perform in terms of flame retardancy.

Tribological Properties of EP/PN-NiFePS Composites

Although materials with excellent mechanical strength and surface hardness usually possess superior resistance to wear, their tribological properties cannot be determined directly from their mechanical responses.^[57] To determine the impact of the PN-

NiFePS content on the tribological performance of EP composites, wet sliding measurements were carried out using an ice/water mixture as the lubricant and coolant. The results of the friction curves, average friction coefficients, wear rates, and tem-

peratures throughout the entire process are shown in Fig. 7 and Fig. S3 (in ESI). From the time-dependent dynamic friction profiles of the EP/PN-NiFePS composites presented in Fig. 7(a), the instantaneous friction coefficient reaches equilibrium rapidly as

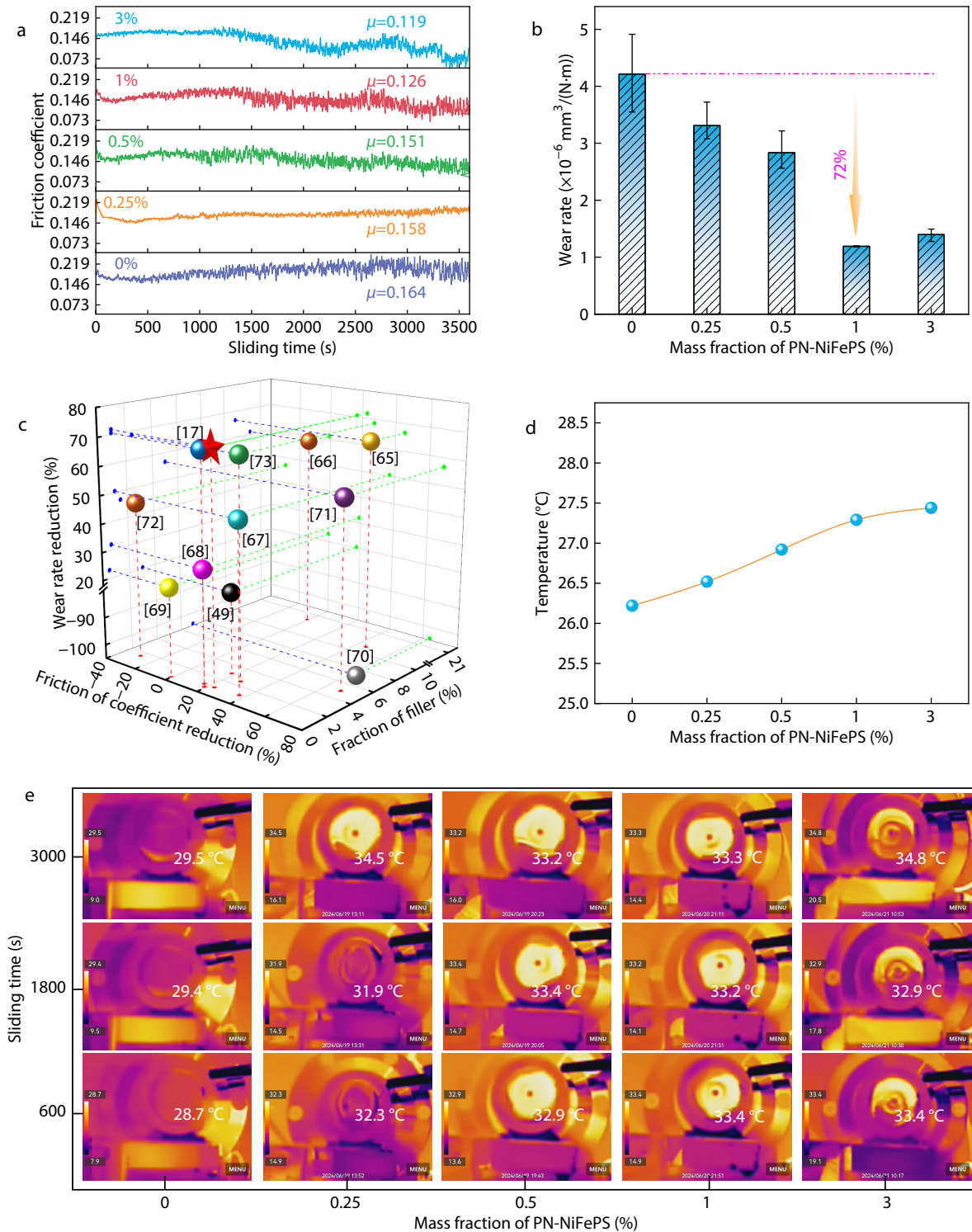


Fig. 7 Wet-sliding properties of EP/PN-NiFePS composites: (a) representative curves of instantaneous friction coefficient, (b) wear rates, (c) comparison of wear rates and friction coefficients, (d) mean temperatures along with PN-NiFePS content and (e) infrared thermographs at varied time intervals.

the friction action occurs, presenting an exceptionally short running-in stage for all the investigated samples. This phenomenon is quite different from the tribological responses of EP composites under conditions of insufficient lubrication, where the friction processes are usually characterized by a relatively long running-in period.^[18] The main reason for this discrepancy is the water film formed in time on the contact interfaces of the friction pairs, which acts partially as a transfer film before full formation.^[58] As the frictional test proceeded, the real-time friction coefficient of pure EP exhibited a steady upward trend; however, the curve fluctuation gradually intensified as the sliding time increased. This is generally because the tribofilm fails to form properly within the contact area; instead, it undergoes repeated formation, adhesion to the counterpart, and detachment throughout the friction process.^[59] In comparison, the incorporation of 0.25% PN-NiFePS did not significantly alter the friction curve, but it led to an obvious reduction in the instantaneous friction coefficient—with the curve exhibiting less prominent fluctuations. When PN-NiFePS content ranged from 0.5% to 3%, however, the friction profiles of EP composites exhibited a distinct zigzag downward trend. This observation suggests that the PN-NiFePS particles provide some lubrication at the contact interface, thus reducing the direct abrasive contact between the friction pairs. The average friction coefficient (μ) values for all tested samples are presented in Fig. 7(a). Pure EP exhibited the highest μ value of 0.164, which was consistent with our expectations. The incorporation of PN-NiFePS, however, significantly reduced the μ values of the EP composites, with a clear negative correlation, that is, a higher PN-NiFePS content resulted in a lower μ . Specifically, as the filler content increased, the μ value gradually decreased to 0.158, 0.151, 0.126, and 0.119 for samples containing 0.25%, 0.5%, 1%, and 3% PN-NiFePS, respectively, showing a maximum reduction of about 27.44% relative to neat EP. This is a promising result, which is different from the effect of pristine NiFePS reported in our previous work, where the excessive addition of NiFePS heightened the friction coefficient again,^[17] but very similar to the results reported elsewhere.^[58,60] The probable reason for this could be attributed to the exposed inorganic filler concentrated in the wear region, which blocks direct surface contact between the sample and rubbing counterpart.^[61] Moreover, sample surface properties also contribute significantly to the reduced μ values, as Bajwa^[62] and Upadhyay^[63] stated that hydrophilic samples yield better wet-sliding performance. The water contact angles (WCAs) of the EP composites are shown in Fig. S3 (in ESI) are suppressed steadily with the elevated PN-NiFePS content, switching the surface from hydrophobic (103.76° for pure EP) to hydrophilic (71.58°–88.85° for the composites). This enhanced hydrophilicity allows the composites to readily absorb water molecules and form an effective water film in the friction zone, which, in turn, reduces the friction coefficient and improves their frictional properties.^[60]

The variation in the wear rate as a function of the PN-NiFePS content is shown in Fig. 7(b). Clearly, the neat resin showed the highest wear rate, indicating the poorest wear resistance among all the investigated samples. However, the introduction of a series of mass fractions of PN-NiFePS remarkably reduced the wear rate of the EP composites, implying that the mass loss caused by severe friction could be greatly

reduced. In fact, by adding only 0.25% PN-NiFePS, the wear rate decreases significantly from $4.23 \times 10^{-6} \text{ mm}^3/(\text{N} \cdot \text{m})$ for pristine EP to $3.32 \times 10^{-6} \text{ mm}^3/(\text{N} \cdot \text{m})$ for the composites, while a further increase in PN-NiFePS leads to a continuously decreased wear rate for the composite samples. The lowest wear rate of $1.19 \times 10^{-6} \text{ mm}^3/(\text{N} \cdot \text{m})$ was obtained when 1% PN-NiFePS was added, representing a reduction of about 72% compared with neat EP. This is certainly related to the well-dispersed PN-NiFePS particles within the matrix resin with strong filler-polymer interactions owing to their rough surface morphology and relatively large specific area, thereby making the matrix sufficiently robust to resist fatigue failure during the dynamic rubbing process.^[64] Such an improvement in the wear resistance of PN-NiFePS is also superior to that of pristine NiFePS reported in our previous report,^[17] which is closely associated with the anchored abundant organic pendants that improve filler-polymer interfacial compatibility and inhibit craze propagation more effectively when subjected to repeated abrasive actions, contributing to the positive effect on the elevated wear resistance. Although a further increase in PN-NiFePS loading results in a slightly elevated wear rate of $1.41 \times 10^{-6} \text{ mm}^3/(\text{N} \cdot \text{m})$ owing to filler agglomeration and subsequent third-body abrasion, the value remains markedly lower than that of the control sample, providing convincing evidence for the significant positive effect of PN-NiFePS on enhancing the wear resistance of EP composites under the present water-lubricated conditions.

With the aim of more distinctly demonstrate the superiority of PN-NiFePS in improving the wet-sliding performance, a comprehensive and meticulous comparison of the reductions in both friction coefficient and wear rate is painstakingly conducted using the EP composite with 1% PN-NiFePS as the reference object. The results are presented in Fig. 7(c) and Table S2 (in ESI), which incorporate the experimental data from publicly available reports^[65–73] and our previous studies.^[17,49] Although EP composites modified with various wear-resistant fillers exhibit promising tribological properties in their optimized formulations, they typically either demand a relatively high filler concentration^[49,65,66] or attain the reported wear rates only under substantially low applied loads.^[65–69] Notably, the addition of nanoclay enables EP composites to exhibit a remarkable reduction in the wear rate; however, this comes at the cost of an elevated friction coefficient.^[69] In contrast, the current PN-NiFePS particles exert a considerable "dual reduction" effect on both the friction coefficient and wear rate at a relatively low filler concentration, reflecting a notably high-efficiency reinforcing effect compared to those reported in the existing literature, which is also superior to some non-EP materials.^[70–73] This results illustrate the importance and competitive advantages of the functionalized bimetallic phyllosilicate of PN-NiFePS in regulating the friction coefficient and wear rate, thus highlighting its prospects for broader utilization and deeper investigation in the field of material tribology.

Because heat generation is inherent to the friction process, even under ice-water lubrication, which may compromise the material's mechanical strength, thereby reducing wear resistance and increasing the friction coefficient, it is essential to account for the temperature variation of the material

throughout the entire friction process. The representative instantaneous temperature profiles of the contact surface for all the investigated samples as a function of sliding time are shown in Fig. S4 (in ESI), whereas the average values with an increased mass fraction of PN-NiFePS are shown in Fig. 7(d). It is clear that pure EP exhibits significant temperature variations during the early and late friction stages, suggesting that it fails to form a thermally stable tribofilm. This is likely because pure EP itself has relatively low strength, causing the film to be damaged by the rubbing pair. In contrast, with the addition of PN-NiFePS, the temperature profiles of the EP composites became gentler and flatter, providing further evidence for the facilitation of PN-NiFePS in the formation of a well-formed tribofilm between the abrasive pairs. Moreover, the gradual addition of PN-NiFePS led to a continuous increase in the average temperatures of the EP composites. This is consistent with our expectations, as the added inorganic particles intensify interactions within the abrasion region, and such intensification leads to more frequent occurrence of microscale flash temperatures and their probable accumulation, which in turn elevates the average temperature accordingly.^[18] However, given its considerably higher thermal conductivity and specific heat capacity, the steel rubbing pair reaches a relatively higher temperature, as detected by an infrared thermal imager at different time intervals, as shown in Fig. 7(e). Nevertheless, the temperatures are somewhat lower than those obtained under dry sliding, which is clearly a result of the cooling effect exerted by the ice/water mixture during friction.^[74]

To clearly visualize the mass loss after wear, the wear trajectories for all the investigated samples were examined using a 3D profilometer, showing the 3D surface pictures and corresponding cross-sectional profiles in Fig. 8. Macroscopically, all wear trajectories appear nearly identical in overall appearance, exhibiting distinctly semicircular concave grooves, but considerable differences exist in volume loss during the friction process. Pure EP showed the most severe wear damage, with the groove width (X) and depth (Z) reaching the highest values of 2.42 mm and 29.31 μm , respectively, as depicted in Fig. 8(f). In comparison, the addition of PN-NiFePS steadily reduced the volume loss of the composites and gradually decreased the wear trajectories narrower and shallower. Notably, the EP composite sample containing 1% PN-NiFePS has the lowest X and Z values, *i.e.*, 1.54 mm and 10.76 μm , respectively, representing reductions of about 36.36% and about 63.29% relative to neat EP. Even when the PN-NiFePS content was increased further, leading to wider and deeper wear tracks, the wear trajectory was still far less extensive than that of pure EP. This phenomenon is consistent with the aforementioned discussion regarding the variations in the wear rate, providing further solid proof to ascertain the significant positive effect on the anti-wear performance.

Analysis of Friction and Wear Mechanisms of EP Composites

To better understand why PN-NiFePS effectively improved the tribological properties, the surface topographies of the wear trajectory for all investigated samples were carefully characterized, and the captured images are shown in Fig. 9. Based on the SEM images shown in Fig. 9(a), the worn surface of neat EP exhibited

severe damage with obvious scratches in the low-magnification image ($\times 500$), while the high-magnification ($\times 5000$) observation revealed prominent scratches, accompanied by abundant debris and some micro-holes on the worn surface. This phenomenon indicates that neat EP suffers severe abrasive and adhesive wear under ice-water lubrication, and the lack of reinforcing phases results in poor resistance to friction-induced shearing and deformation, resulting in resin detachment and surface breakdown. Additionally, it is noted that fatigue-induced resin debris appears not only in the resin-detached region but also within the scratches, suggesting that the main wear mechanisms are adhesive wear and fatigue fracture.^[75] This is primarily because of the continuous traction exerted by the rigid counterpart on the soft resin surface, which induces continuous shear failure and limits the formation of an effective interpair tribofilm.^[76]

In contrast, the added 0.25% PN-NiFePS partially improved the integrity of wear trajectory compared to pure EP, yet obvious damage still occurred. Although the addition of a small amount of PN-NiFePS provided some mechanical support, the loading was insufficient to fully suppress wear damage, resulting in obvious scratches and debris. As the PN-NiFePS content increased, the load-bearing capacity and wear resistance of the composites were gradually enhanced, and the well-scattered inorganic fillers effectively hindered scratch propagation and reduced resin detachment, thus mitigating abrasive wear. For this, the wear trajectory morphology was further improved, indicating that the abrasion damage was reduced gradually. Significantly, when the PN-NiFePS loading increased up to 1%, the wear trajectory became relatively smooth with only a small amount of scattered debris and no obvious scratches or holes. This is mainly because the optimal PN-NiFePS loading forms a continuous and effective reinforcement network, which not only improves the mechanical properties of the EP substrate but also promotes the formation of a stable lubricating film under ice-water lubrication.^[17] Certainly, this synergistic effect significantly reduces abrasive and adhesive wear, resulting in minimal surface damage. This finding was also verified by the variations in the surface roughness depicted in Fig. 10(a), where the highest surface roughness (S_a) of 10.48 μm belongs to pure EP, which clearly reflects the occurrence of severe abrasion damage during the friction process. In contrast, the S_a values gradually decrease to 7.79 μm and then 6.74 μm , finally obtaining the lowest value of 3.64 μm for the composites with 1% PN-NiFePS. Typically, a decrease in the surface roughness is associated with a reduction in the wear rate, and the trends identified in the present work align with this correlation. Although the wear trajectory integrity was slightly deteriorated by excessive filler concentration, a few microvoids and debris appeared within the abrasion zone. However, the worn surface is still much smoother than that of the pure resin, which is evidenced by the relatively low S_a value of 3.89 μm , demonstrating that PN-NiFePS significantly contributes to the improvement in the wet-sliding properties.

To further explore the wear mechanism, the wear trajectory of EP composites with 1% PN-NiFePS was also subjected to chemical analysis, and the corresponding results are shown in Fig. 10. From the EDS result in Fig. 10(b), the most significant

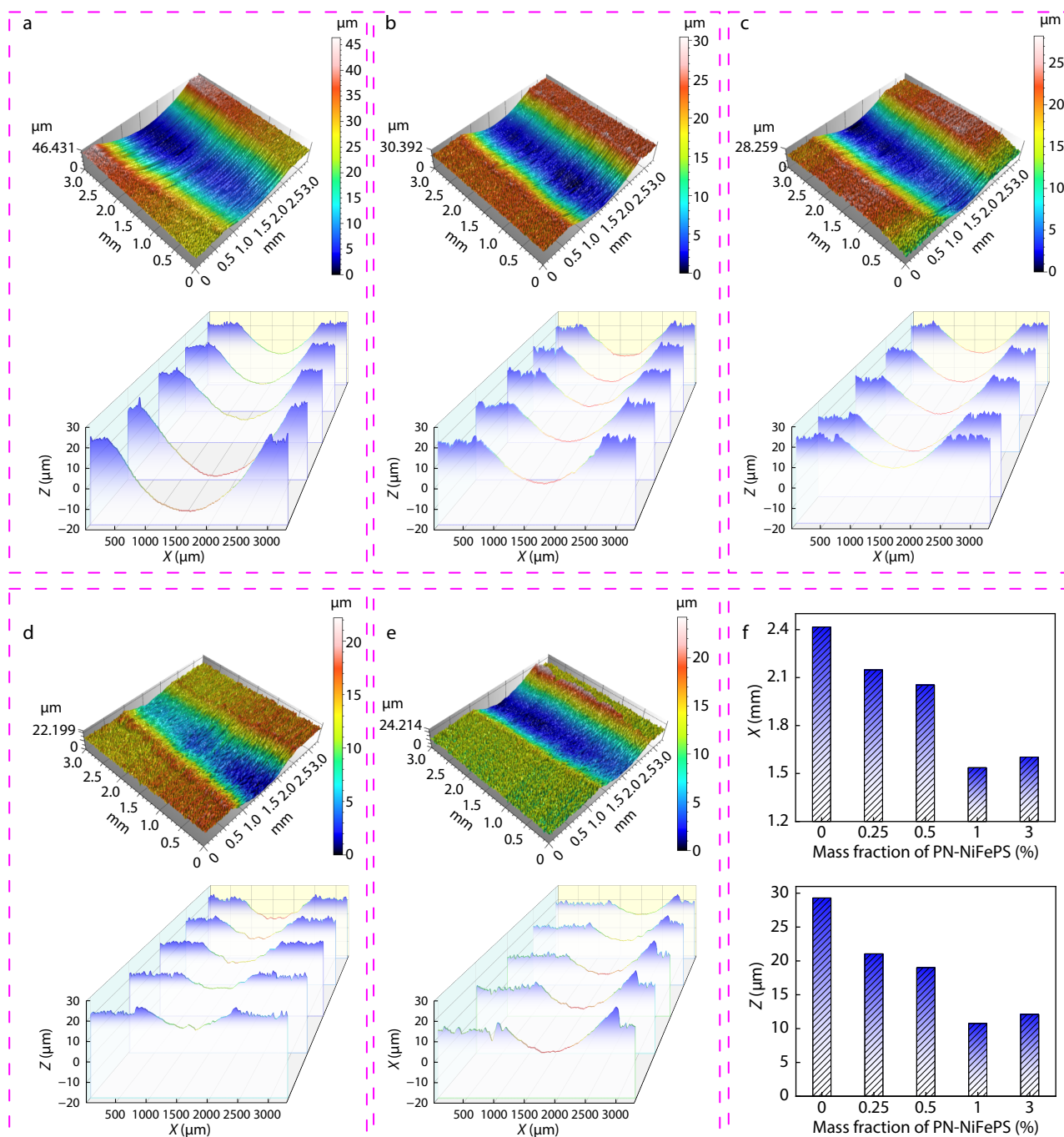


Fig. 8 3D pictures with enclosed cross-sectional profiles of wear trajectories for EP/PN-NiFePS composites: (a) 0%, (b) 0.25%, (c) 0.5%, (d) 1% and (e) 3%; (f) variations in width (X) and depth (Z) of wear trajectories.

peak located at 0.27 keV of course belongs to C elements, indicating its abundant presence in the wear trajectory. The other visible signals for N, O, and Si elements appear at 0.38, 0.52 and 1.65 keV, respectively, originating from both the matrix and the added PN-NiFePS, while the Fe and Ni elements exhibit weak signals at approximately 6.42 and 7.36 keV due to their low content. In addition, the relative proportion of Fe implies that it comes not only from the added PN-NiFePS, but also from the steel rubbing pair owing to the fierce interactions, where Fe-containing particles are readily detached and

captured simultaneously within the wear trajectory during the friction process, which is consistent with our previous research findings.^[17,19] The XPS full-scan spectrum in Fig. 10(c) further confirms the existence of characteristic elements, in which the prominent peaks at 531.94, 398.76 and 284.40 eV correspond to O 1s, N 1s, and C 1s, whereas the weak peaks at 862.46, 710.50, and 153.73/102.82 eV correspond to Ni 2p, Fe 2p, and Si 2s/2p, respectively, which is consistent with the EDS results. Although some elements are difficult to detect via EDS, the elemental mappings clearly demonstrate their

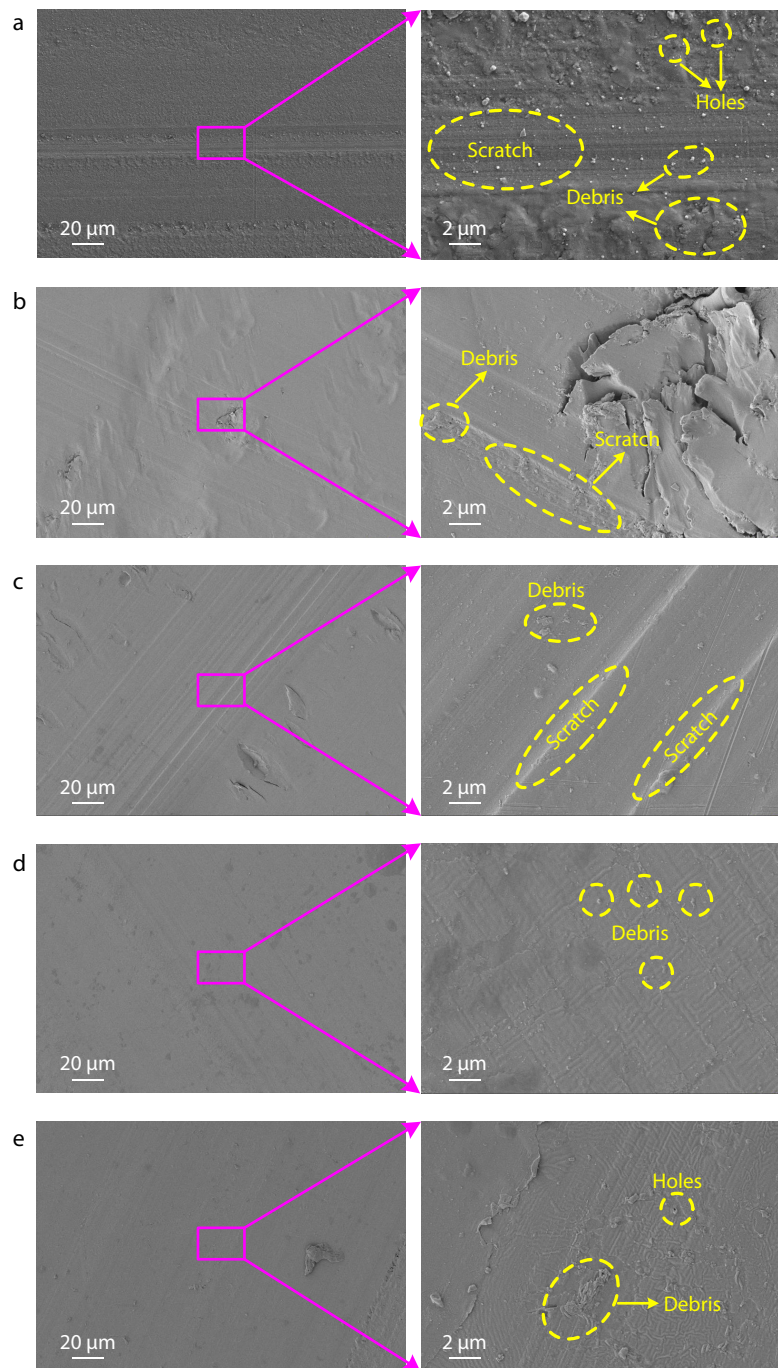


Fig. 9 Surface topographies of wear trajectory for EP/PN-NiFePS composites: (a) 0%, (b) 0.25%, (c) 0.5%, (d) 1% and (e) 3%.

presence and distribution in Fig. 10(d), where the characteristic elements derived from both the EP matrix and PN-NiFePS are evenly distributed within the wear trajectory without obvious aggregations, which significantly enhances the friction and wear performance of the composites. From the preceding descriptions, it is reasonable to conclude that the added PN-NiFePS, in conjunction with the trapped Fe-containing particles, is critical for forming a high-quality tribofilm between rubbing pairs, which substantially improves the friction and wear performance of the EP/PN-NiFePS composites under wet sliding conditions.

Based on the aforementioned analysis and descriptions, the significant positive effect exerted by the incorporated PN-NiFePS on the enhanced anti-friction property and wear resistance was clearly confirmed. To further elaborate on the beneficial role of PN-NiFePS in improving the wet-sliding properties, a plausible mechanism governing the friction and wear behavior is schematically illustrated in Fig. 11. Generally, pure EP is widely acknowledged to possess a densely crosslinked network structure; when exposed to frictional actions, it is prone to volume loss owing to the breakdown of intrinsic intermolecular bonds. Simultaneously, the wear debris is easily

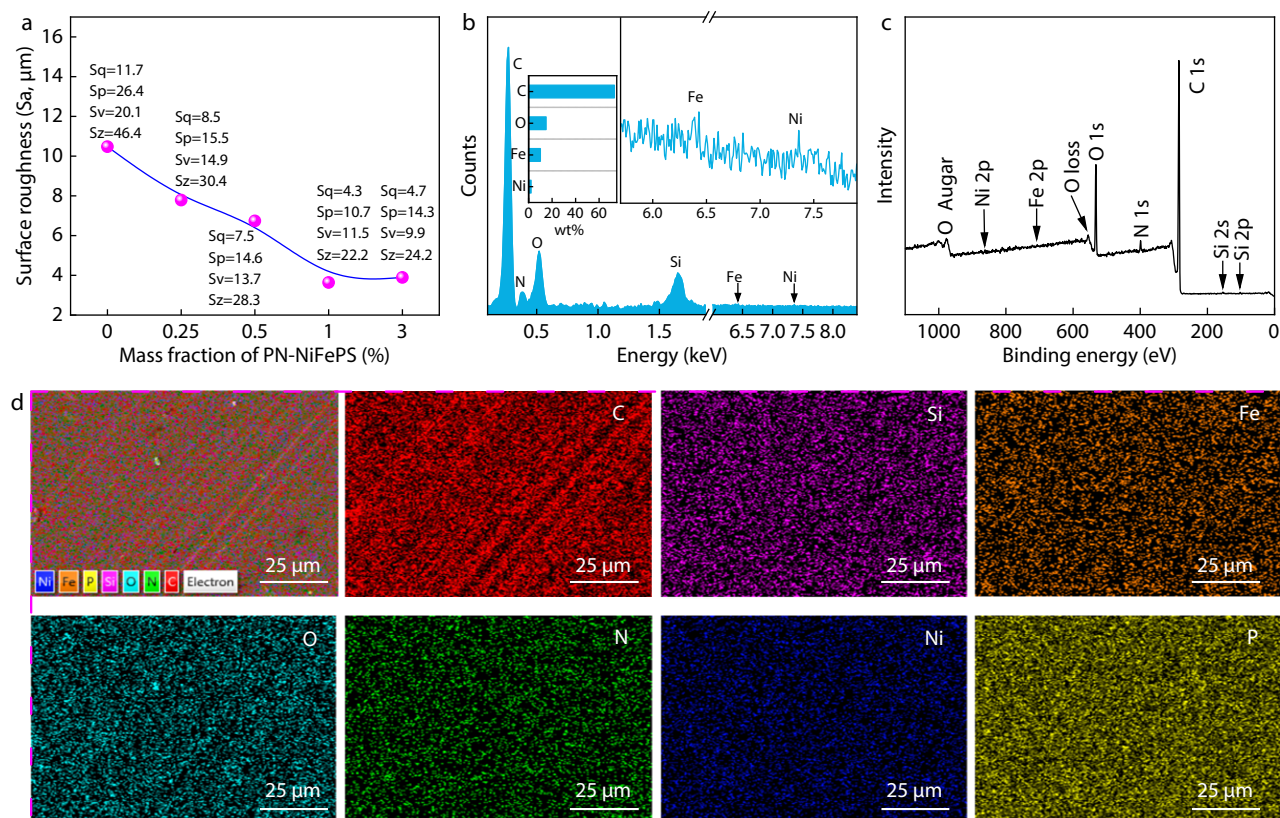


Fig. 10 (a) Surface roughness with increased PN-NiFePS content; (b) EDS result, (c) XPS survey scan and (d) elemental mappings of EP composites with 1% PN-NiFePS.

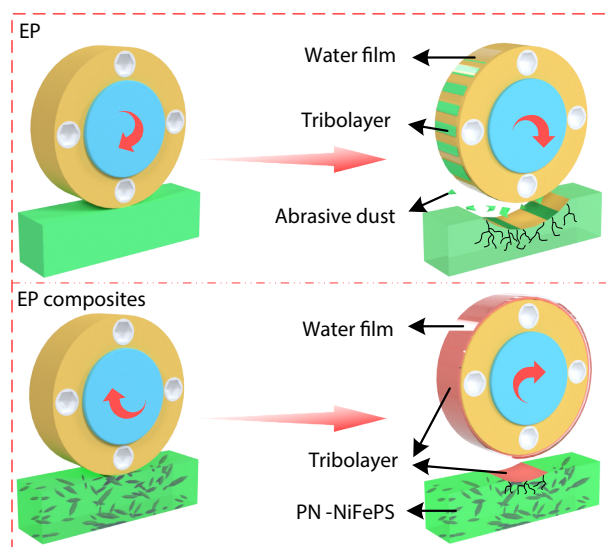


Fig. 11 The possible friction and wear mechanisms of EP/PN-NiFePS composites.

detached from the bulk sample during the rubbing process and causes continuous wear damage to the matrix. In addition, pure resin exhibits a water contact angle higher than 90° , leading to low surface energy and high residual stress^[77] such strong hydrophobicity makes it difficult to form a continuous water film between the rubbing pairs, resulting in poor boundary lubrication. Under such circumstances, molec-

ular bond breakage occurs in the frictional region, which leads to fatigue wear.^[63] Consequently, among the investigated samples, pure EP exhibited severe wear damage and a markedly roughened wear trajectory.

However, with adequate incorporation of PN-NiFePS, the situation changed significantly. According to the above descriptions, this positive effect is closely associated with the multiple roles of the PN-NiFePS particles. First, the proper incorporation of PN-NiFePS brings results in a comprehensive enhancement of the mechanical performance. The notably improved strength and stiffness endowed the composites with excellent deformation resistance, which greatly inhibited plastic deformation under compressive and shearing forces, and concurrently reduced the actual contact region in the frictional zone throughout the friction process.^[78] In addition, the markedly increased toughness and thermal stability enhance the tolerance to fatigue damage, making the composites far less susceptible to fracture under repeated abrasive interactions while producing considerably fewer resin fragments than pure EP. Second, the as-synthesized PN-NiFePS particles, featuring a rough surface and large specific surface area, were dispersed uniformly throughout the matrix after incorporation, providing abundant active sites for polymer chain adsorption and entanglement on the filler surface. This interaction facilitates the formation of robust and well-distributed filler-matrix interfaces, which not only effectively impedes rapid crack propagation and mitigates residual stress^[77] but also concurrently diminishes the likelihood of forming closed-loop structures within the EP composites.^[78] More importantly, when abrasive actions occurred between

the rubbing pairs, the surface resin layer of the EP composites was worn away, and the pre-dispersed PN-NiFePS particles were exposed, releasing abundant inorganic nanosheets that migrated to the surface and accumulated within the frictional region. The residual inorganic nanosheets, in conjunction with the Fe_2O_3 particles dislodged from their counterparts, together contribute to the formation of a PN-NiFePS-containing tribofilm, which not only improves the surface compactness of the composites, but also deposits a protective layer on the counterpart. Consequently, the primary locus of frictional engagement shifts from between the heterogeneous composite and counterpart pairs to the interface between the homologous tribofilms^[79] thereby effectively protecting the composite matrix from wear damage. Finally, the incorporation of PN-NiFePS endowed the EP composites with excellent hydrophilicity, which enabled the formation of a complete and continuous water film during friction, together with the PN-NiFePS-containing tribofilm, creating a mixed lubrication effect during friction. Consequently, the underlying matrix provides highly efficient safeguarding against wear-induced damage, exhibiting excellent tribological performance under wet sliding conditions.

Flame Retardancy of EP/PN-NiFePS Composites

As an organic coating material, flame retardancy is of great significance for its safe service. The flame-retardant properties of the EP/PN-NiFePS composites were carefully evaluated, and the results are shown in Fig. 12. From the captured digital images of UL-94 testing in Figs. 12(a)–12(e), neat EP burns rapidly upon ignition with heavy smoke release, and molten droplets ignite the underlying cotton and cause secondary flame spread, with a total burning time of 298 s until complete burnout. This observation indicated that pure EP exhibited high flammability and no self-extinguishing ability. In contrast, the incorporated PN-NiFePS remarkably improved the flame retardancy of EP composites, not only by gradually reducing the burning time and in-

tensity, but also by providing excellent self-extinguishing behaviors. As the PN-NiFePS concentration reached 1% and above, no molten droplets were produced to ignite the cotton, the samples remained intact during combustion, and the shortest burning time was only 41 s (Table S3 in ESI), much lower than that of neat EP. The positive effect of the incorporated PN-NiFePS on flame retardancy was further verified by the limiting oxygen index (LOI), as shown in Fig. S5 (in ESI), where the LOI values increased steadily from 23.7% for pure EP to 25.6% for the composite with a filler content of 3%. Consistent with this observation, the heat release behaviors as a function of temperature, illustrated in Fig. 12(f) and summarized in Table S4 (in ESI), reveal that neat EP shows the highest peak heat release rate (PHRR) and total heat release (THR) among all the tested samples, with values of 626.3 W/g and 29.9 kJ/g, respectively, and the PHRR is attained at a temperature of 422.9 °C. Nevertheless, with the incremental increase in the loading of PN-NiFePS, both the PHRR and THR of the composite specimens display a steady declining tendency, and when the filler content reaches 3%, the minimum values of 477.9 W/g and 22.5 kJ/g are achieved, presenting the remarkable reductions of 23.7% and 24.7%, respectively, relative to pure EP. These experimental observations clearly demonstrate a significant inhibitory effect of added PN-NiFePS on heat release throughout the combustion process, and such favorable flame-retardant performance is closely related to the *in situ* formation of a robust, dense char layer that can efficiently hinder heat transfer and act as a protective barrier shielding the underlying matrix from additional thermal degradation or structural damage during combustion.^[80] This hypothesis can be well demonstrated by the SEM images of the residual char shown in Fig. 12(g), where neat EP leaves only a porous char layer with many through-thickness voids after combustion, failing to form a compact and continuous structure. These pores provide pathways for thermal exchange between the internal and external thermal environments, thereby in-

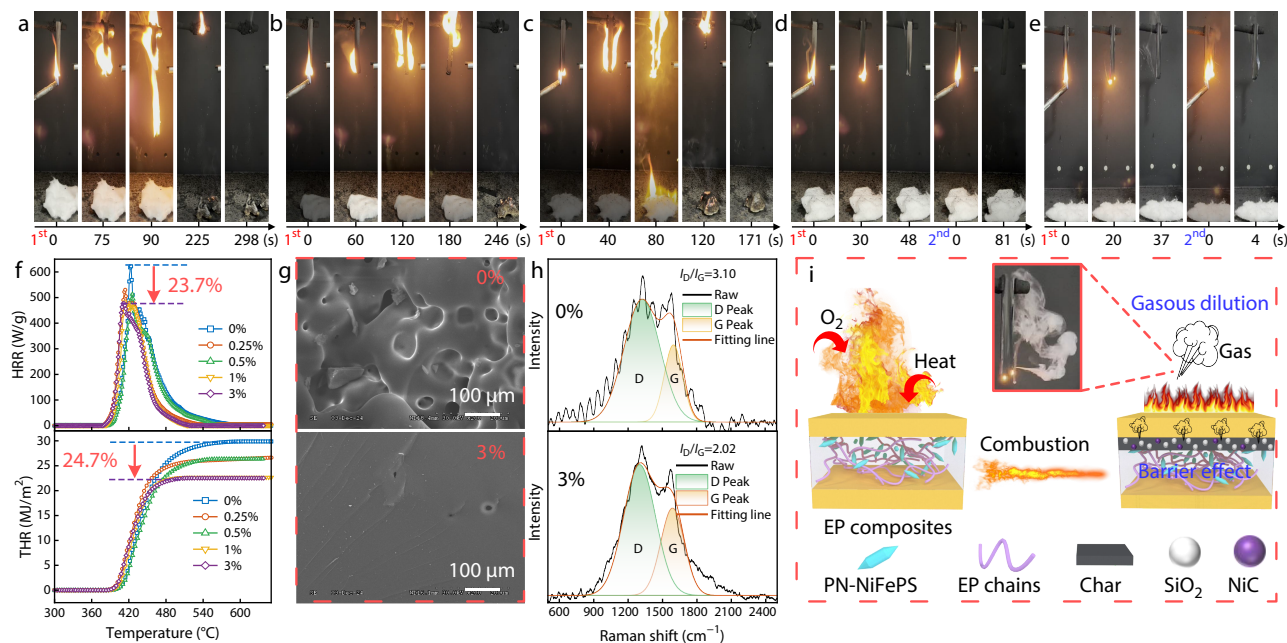


Fig. 12 Digital pictures captured from vertical burning measurements: (a) 0%, (b) 0.25%, (c) 0.5%, (d) 1% and (e) 3%; (f) HRR and THR profiles versus temperature, (g) SEM images of residual char, (h) Raman spectra and (i) suggested flame-retardant mechanism of EP/PN-NiFePS composites.

creasing the combustion intensity and leading to poor flame retardancy.^[45] In contrast, the addition of PN-NiFePS improved the char layer structure, allowing the dense char to effectively encapsulate the matrix and block the transport of heat, oxygen, and combustibles, providing a strong barrier against flames.^[81] Such an enhanced char layer is closely related to the reinforcement by the inorganic decomposition products of PN-NiFePS, as identified by XRD detection in Fig. S6 (in ESI), and moreover, the graphitization degree of residual char affects the thermal stability and further affects the transfer of heat and pyrolysis products. From the Raman analysis presented in Fig. 12(h), the EP composites exhibited a relatively lower D/G band intensity ratio (I_D/I_G), implying more graphitic carbon formation, favoring the formation of a char layer with high thermal stability and heat resistance during combustion. The existing PN-NiFePS particles play dual synergistic roles in improving the flame retardancy of EP composites; their main role is to promote a robust, compact, and continuous char layer to protect the underlying matrix from being destroyed, and the other is to release non-combustible gases to effectively dilute the concentration of flammable gas in the combustion zone, as illustrated in the inset of Fig. 12(i), thereby achieving excellent flame retardancy. Based on the above analysis, the proposed flame-retardant mechanism of PN-NiFePS in EP composites is mainly ascribed to the synergistic effect between the organic and inorganic components. As schematically illustrated in Fig. 12(i), the P/N-containing organic pendant chains facilitated the formation of a compact and stable char layer during combustion, which acted as a physical barrier to isolate oxygen, heat, and combustible volatiles. Meanwhile, the NiFe-based inorganic components exert reinforcing and catalytic carbonization effects, promoting the release of nonflammable gases and suppressing flame spread and smoke emission.

CONCLUSIONS

In this study, a novel PN-NiFePS featuring a homogeneous hierarchical architecture was successfully synthesized *via* a facile hydrothermal route, with NiFe-MOF serving as both a template and reactive precursor, and DOPO-*g*-KH550 acting as the organic silicon source. The effect of PN-NiFePS loading on the mechanical properties, thermal stability, tribological performance under wet sliding conditions, and flame retardancy of EP composites was systematically investigated. The key findings are summarized as follows.

(1) Structural and compositional characterizations verified that PN-NiFePS not only inherited the rice-granular-like morphology of NiFe-MOF but also enabled *in situ* growth of abundant ultrathin phyllosilicate nanosheets on its surface. Meanwhile, dense P/N-containing organic pendant chains were chemically grafted onto the phyllosilicate structure, which significantly enhanced the interfacial interactions between the PN-NiFePS and EP matrix.

(2) The incorporation of PN-NiFePS effectively regulates the mechanical properties of EP. At a filler loading of 0.25%, the elongation at break of EP/PN-NiFePS composites reached 11.17%, corresponding to a 74.5% improvement relative to neat EP. Meanwhile, the fracture energy and tensile strength were elevated by 152% and 7.16%, respectively, at the same loading. Although the tensile strength exhibited a slight re-

duction at higher filler loadings, it remained above 53 MPa, retaining approximately 79.6% of that of neat EP. In addition, the Shore D hardness increased steadily from 91.1 HD for neat EP to 93.2 HD for the composite with 3% PN-NiFePS, verifying the balanced toughness and stiffness of the resultant composites.

(3) Although PN-NiFePS slightly lowered the decomposition temperatures of EP owing to the early pyrolysis of the anchored organic pendant chains, it significantly increased the residual char yield and activation energy (E_a) over the entire thermal decomposition process. With the addition of 3% PN-NiFePS, the residual char content increased from 12.8% to 18.4%, and activation energy was enhanced by approximately 68.4%, increasing from 52.5 kJ/mol to 88.4 kJ/mol. At a filler loading of only 3%, the LOI increased from 23.7% to 25.6%, and the PHRR and THR were reduced by 23.7% and 24.7%, respectively. Furthermore, the incorporation of PN-NiFePS significantly improved the flame retardancy of the EP composites by imparting excellent self-extinguishing behavior and eliminating molten droplets during combustion.

(4) Under water lubrication, PN-NiFePS significantly reduced the friction coefficient (μ) and wear rate of the composites with optimal tribological properties at a filler loading of 1%. Specifically, the μ value decreased from 0.164 to 0.126, and the wear rate dropped from 4.23×10^{-6} mm³/(N·m) to 1.19×10^{-6} mm³/(N·m), corresponding to reductions of 27.4% and 72%, respectively, relative to neat EP. This enhancement was attributed to the incorporated PN-NiFePS, which not only reinforced the substrate, but also facilitated the formation of a PN-NiFePS-containing tribofilm and a more stable water film, which acted synergistically to provide superior lubrication and significantly enhanced wear resistance.

This study provides a novel strategy for the design of high-performance multifunctional polymer composites with promising applications in harsh environments that require excellent wear resistance and fire safety.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

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Data Availability Statement

The data supporting the findings of this study are available from the corresponding author upon reasonable request.

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Graphical Abstract

Ingenious Engineering of Phosphorus and Nitrogen-enriched Nickel/Iron Bimetallic Phyllosilicates: Forging Multifunctional Epoxy Composites with Excellent Toughness, Self-lubrication, Wear Resistance and Flame Retardancy

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This work ingeniously designed and synthesized rice-like hierarchical PN-NiFePS derived from NiFe-MOF, which integrates *in situ* grown inorganic nanosheets and covalently grafted P/N-containing organic chains, significantly enhancing the comprehensive properties and providing a novel strategy for multifunctional EP composites.



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