metals

MDPI

Article

Enhanced Environmental Durability of an AlN-Modified Aluminium Phosphate Binder Through PVA Incorporation

Yaojian Ren [1], Xinyi Wu [1], Taike Zhang [2], Jiawei Yang [1], Qingkun Meng [1], Fuxiang Wei [1], Yanwei Sui [1,*], Wenqing Wei [3,*] and Jiqiu Qi [1,*]

[1] School of Materials and Physics, China University of Mining and Technology, Xuzhou 221116, China
[2] Guangdong Bay Area Communications Construction and Investment Co., Ltd., Guangzhou 511462, China
[3] Shandong Key Laboratory of Intelligent Manufacturing Technology for Advanced Power Equipment, Weifang University, Weifang 261061, China
* Correspondence: suiyanwei163@163.com (Y.S.); hitweiwenqing@126.com (W.W.); flower_cumt@outlook.com (J.Q.)

Abstract

Aluminium phosphate binders have attracted considerable attention due to their high-temperature resistance and environmental friendliness. However, curing-related shrinkage and cracking, together with moisture-induced degradation, can adversely affect their structural integrity and bonding performance. In this study, polyvinyl alcohol (PVA) was incorporated into a previously developed aluminium nitride (AlN)-modified aluminium phosphate binder to investigate the effects of polymer content on its microstructure, mechanical properties, thermal behaviour, and environmental durability. The results show that the binder containing 3 wt% PVA (PHAP3) exhibits the highest room-temperature shear strength of 3.06 MPa, representing a 14.6% increase compared with the PVA-free AlN-modified reference binder (PHAP0, 2.67 MPa). After 20 days of water immersion, UV irradiation, and humid–heat ageing, PHAP3 retains 61.1%, 67.2%, and 58.8% of its initial shear strength, respectively. Under water immersion, this retention rate is higher than the 37.8% recorded for PHAP0. Microstructural observations reveal that PVA incorporation improves the continuity and compactness of the binder surface, while FTIR and XPS analyses indicate changes in phosphate-related vibrations and the local chemical environments of the constituent elements, suggesting interactions between PVA and the phosphate matrix. These results demonstrate that an appropriate PVA content can improve the bonding performance and environmental durability of AlN-modified aluminium phosphate binders, with 3 wt% PVA providing the most favourable overall performance among the investigated formulations. This study provides an approach for improving the environmental durability of inorganic phosphate binders through controlled polymer incorporation.

Keywords: aluminium phosphate binder; polyvinyl alcohol; aluminium nitride; organic–inorganic hybrid; environmental ageing

Received: 15 October 2026
Revised: 9 November 2026
Accepted: 11 November 2026
Published: 16 November 2026

Copyright: © 2026 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license.

1. Introduction

With the increasing demand for reliable bonding materials in aerospace, transportation, and fire-protection applications, the development of high-performance inorganic ad-

hesives has attracted considerable attention. Among these materials, aluminium phosphate binders are widely investigated because of their excellent thermal stability, chemical resistance, and compatibility with metallic and ceramic substrates [1]. However, their practical applications remain restricted by several limitations. During curing, condensation and dehydration reactions may cause volume changes and the formation of microcracks, which adversely affect the structural integrity and bonding performance of the adhesive layer. In addition, the presence of hydrophilic P-OH groups contributes to moisture absorption, making aluminium phosphate binders susceptible to water-induced degradation under humid environments. Wang et al. [2] investigated the influence of the P/Al molar ratio on the thermal evolution and hygroscopic behaviour of acid aluminium phosphate systems, demonstrating that the chemical composition plays an important role in determining their moisture resistance. Further studies by Wang et al. [3] elucidated the reaction mechanisms and hygroscopic behaviour of aluminium phosphate adhesives, highlighting the relationship between hydroxyl-containing phosphate species and moisture sensitivity. These findings indicate that improving the structural integrity and environmental durability of aluminium phosphate binders remains an important research objective.

To address these limitations, considerable efforts have been devoted to modifying phosphate-based adhesives through the incorporation of inorganic fillers. Recent studies have demonstrated that the composition, distribution, and interfacial interactions of fillers can substantially influence the phase evolution and bonding performance of phosphate matrices. Huo et al. [4] developed a modified multicomponent phosphate adhesive for joining 316L stainless steel by incorporating modified B_4C, TiO_2, and low-melting-point glass powders. The formation of interfacial chemical bonds and phosphate-based network structures contributed to improved bonding performance, with a maximum tensile strength of 8.73 MPa at 500 °C. Similarly, Li et al. [5] investigated the effects of Si and B_4C additions on aluminium phosphate adhesives for quartz-glass joining. Their results showed that these additives altered the decomposition behaviour and phase evolution of phosphate species, helping to improve the compositional stability of the adhesive matrix. Liu et al. [6] further demonstrated that zirconium incorporation could regulate the thermal expansion characteristics and high-temperature bonding performance of aluminium phosphate adhesives. More recently, Wang et al. [7] developed an inorganic adhesive for alumina ceramic joining using Cu, Si, and B_2O_3 as modifying components, achieving improved bonding performance over a broad temperature range. Although these investigations have established the effectiveness of inorganic modification in regulating the structural and mechanical properties of phosphate-based adhesives, their primary focus has been on high-temperature bonding, phase evolution, and thermal compatibility [8]. The environmental durability of such systems, particularly under prolonged water exposure and combined ageing conditions, remains an important aspect requiring further investigation.

In addition to inorganic filler modification, organic–inorganic hybridisation provides an alternative approach to regulating the mechanical and interfacial properties of phosphate-based materials. Polyvinyl alcohol (PVA), owing to its abundant hydroxyl groups, film-forming ability, and flexible molecular chains, has attracted interest as a potential organic component for modifying inorganic matrices. Previous investigations have explored PVA/aluminium phosphate adhesive systems, including glutaraldehyde-crosslinked PVA/aluminophosphate adhesives and PVA/aluminium phosphate adhesives for wood-based panels [9,10]. These studies established the feasibility of incorporating PVA into phosphate-based adhesive systems. Earlier, Mohamed Saat and Johan [11] prepared partially phosphorylated PVA-$AlPO_4$ composite films and investigated their surface structure and thermal properties. Subsequently, Mohamed Saat et al. [12] investigated the

influence of reaction pH on the physicochemical characteristics of phosphorylated PVA-$AlPO_4$ nanocomposites prepared through a two-step process involving PVA phosphorylation followed by $AlPOO_4$ conjugation. Beyond phosphate-based systems, Song and Han et al. [13] developed hybrid coatings containing PVA, sodium alginate, and reconstructed layered double hydroxides, demonstrating that interactions between organic polymers and inorganic components could regulate the barrier properties of composite films. Nevertheless, the incorporation of polymeric components may also introduce challenges, including increased system viscosity, non-uniform component distribution, and reduced thermal stability at elevated temperatures [14,15]. Therefore, controlling the polymer content and maintaining an appropriate balance between the organic and inorganic phases are essential for achieving desirable mechanical properties and environmental durability.

In our previous work, an aluminium phosphate binder modified with 10 wt% aluminium nitride (AlN) was developed. AlN can participate in the reaction with phosphoric acid during binder preparation. The reaction between AlN and H_3PO_4 promotes the formation of $AlPO_4$ and releases NH_3, thereby influencing the local acid–base environment and microstructural evolution of the binder [16]. The dosage of AlN thus governs the balance between phosphate formation and the generation of pores and defects. Previous investigations have demonstrated that an appropriate AlN content can improve the structural integrity and mechanical performance of aluminium phosphate binders, whereas excessive addition may lead to increased porosity and surface cracking. This AlN-modified system exhibited improved structural integrity and bonding performance compared with the corresponding unmodified system. However, its strength retention after 20 days of water immersion remained approximately 38%, indicating that further improvement in moisture resistance was necessary. Building on this previous investigation, the present study introduces PVA into the AlN-modified aluminium phosphate binder to investigate the influence of polymer incorporation on its microstructure, phase composition, thermal behaviour, mechanical properties, and environmental durability. The AlN content was maintained at 10 wt%, while the PVA content was varied from 1 to 7 wt% to examine its composition-dependent effects. The resulting binders were characterised using scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS). Their mechanical and thermal properties were evaluated through shear testing and thermogravimetric analysis, respectively. Furthermore, water immersion, ultraviolet (UV) irradiation, and humid–heat ageing tests were conducted to assess the evolution of bonding performance under different environmental conditions. By correlating the observed microstructural and chemical changes with the corresponding mechanical properties, this study aims to clarify the influence of PVA incorporation on the performance of AlN-modified aluminium phosphate binders and provide a practical approach for improving their environmental durability.

2. Experimental Procedure

2.1. Preparation of PVA/AlN Modified Aluminum Phosphate Adhesive

Based on the previous optimisation of the AlN-modified aluminium phosphate binder, the AlN content was fixed at 10 wt% in the present study. This formulation provided a favourable balance between the formation of the phosphate matrix and the microstructural integrity of the cured binder. PVA was subsequently introduced at different contents to further investigate its influence on the properties of the AlN-containing system. First, a 60% (*v*/*v*) dilute H_3PO_4 solution is added to a three-neck flask, followed by the slow addition of PVA powder to the H_3PO_4 solution. Two to three drops of tributyl phosphate are added as an anti-foaming agent, and the mixture is stirred gently at temperatures ranging from room temperature to 95 °C. Then, we add urea as a catalyst to promote the esterification reaction and obtain a mixture, designated as PP. Subsequently, the esterified

https://doi.org/10.3390/met16111259

phosphoric acid PP is held at 95 °C for 120 min. $Al(OH)_3$ was weighed out according to the protocol and added to PP. The mixture was stirred at a controlled temperature of 85 °C until the $Al(OH)_3$ had dissolved. Subsequently, B_4C, AlN and ZnO were added to the system in sequence, with continuous stirring until all raw materials were fully dispersed. Once the slurry was uniformly mixed, it was poured into a beaker and allowed to cool naturally to room temperature, thereby producing a PVA/AlN-modified aluminium phosphate binder, denoted as PHAP. PVA/AlN-modified aluminium phosphate binders were prepared by adding 1 wt%, 3 wt%, 5 wt% and 7 wt% PVA, designated as PHAP1, PHAP3, PHAP5 and PHAP7, respectively. Additionally, a 10 wt% AlN aluminium phosphate binder without PVA was prepared and designated as PHAP0 to serve as the control group.

2.2. Structural Characterization

An X-ray diffractometer (XRD, D8 Advance; Bruker AXS GmbH, Karlsruhe, Germany) was used to analyse the phase composition of the modified aluminium phosphate binder. A scanning electron microscope (SEM, SU8010; Hitachi High-Tech Corporation, Tokyo, Japan)) was employed to observe the microstructure of the binder's surface and cross-section. A Fourier transform infrared spectrometer (FTIR, Nicolet iS10; Thermo Fisher Scientific, Waltham, MA, USA) was utilised to analyse the chemical structure and changes in functional groups of the binder following curing. An X-ray photoelectron spectrometer (XPS, K-Alpha; Thermo Fisher Scientific, Waltham, MA, USA) was used to analyse the chemical states and bonding patterns of the elements on the binder's surface.

2.3. Performance Evaluation

The shear strength of the adhesive was determined in accordance with national standards by testing aluminium-to-aluminium bonded specimens using an electronic universal testing machine to evaluate their mechanical properties. Five parallel specimens were tested for each formulation, and the average value was calculated. Thermogravimetric and differential scanning calorimetry (TG-DSC) analyses were performed on the cured binder powder using a simultaneous thermal analyser. The samples were heated from room temperature to 600 °C at a rate of 10 °C/min in an air atmosphere to assess their thermal stability. To evaluate the environmental durability of the modified aluminium phosphate binder, water immersion, UV irradiation, and humid–heat ageing tests were conducted. For the water immersion test, fully cured adhesive specimens were immersed in deionised water at room temperature for up to 20 days and removed at predetermined intervals for mechanical testing. For UV ageing, the specimens were placed in a UV ageing chamber maintained at 60 °C, with an irradiation intensity of 1.55 W/m^2. For humid–heat ageing, the specimens were exposed in a constant-temperature and -humidity chamber at 55 °C and 90% relative humidity. Each ageing test was conducted for up to 20 days, and specimens were collected at predetermined intervals to evaluate changes in their microstructure, phase composition, and shear strength. The environmental durability was assessed by comparing the shear strength before and after ageing.

3. Results and Discussion

3.1. Structural Analysis of the Modified Aluminum Phosphate Adhesive

To investigate the effect of PVA content on the microstructure of the modified aluminium phosphate binder, a series of samples were characterised using SEM, XRD and FTIR. SEM analysis (Figure 1c–f) revealed that, compared with PHAP0 (Figure S1b), the introduction of PVA significantly improved film-forming properties, resulting in a more intact and dense surface. This is attributed to the interaction between PVA and the H_3PO_4 matrix, which promotes the formation of an organic–inorganic hybrid structure. However,

when the PVA content exceeded 5 wt%, the viscosity of the system increased sharply, leading to an uneven reaction between the esterification products and $Al(OH)_3$, and a decline in coating uniformity. XRD analysis (Figure 1a) showed that all samples exhibited diffraction peaks corresponding to residual $Al(OH)_3$, orthorhombic $AlPO_4$, and B_4C after room-temperature curing, indicating the coexistence of unreacted aluminium hydroxide, crystalline aluminium phosphate, and the retained B_4C filler in the cured binder. As the PVA content increased, the intensity of the $Al(OH)_3$ diffraction peak increased. This may be attributed to the reaction between PVA and H_3PO_4, which alters the distribution of phosphoric acid species and consequently affects the dissolution of $Al(OH)_3$. No distinct diffraction peaks attributable to crystalline PVA were detected in the modified samples, suggesting that PVA was dispersed within the binder matrix without forming a detectable independent crystalline phase. FTIR analysis further revealed changes in the chemical structure of the binders (Figure 1b). All samples exhibited absorption bands at approximately 3420 and 1640 cm^{-1}, corresponding mainly to O-H-related vibrations [17]. The characteristic bands at 1121, 718 and 513 cm^{-1} are associated with phosphate-related vibrations, Al-O stretching and P-O bending vibrations, respectively [18]. With increasing PVA content, the Al-O- and P-O-related absorption bands became broader. This broadening suggests changes in the local structural environments of the inorganic phosphate network following PVA incorporation, possibly associated with interactions between the flexible PVA chains and phosphate species.

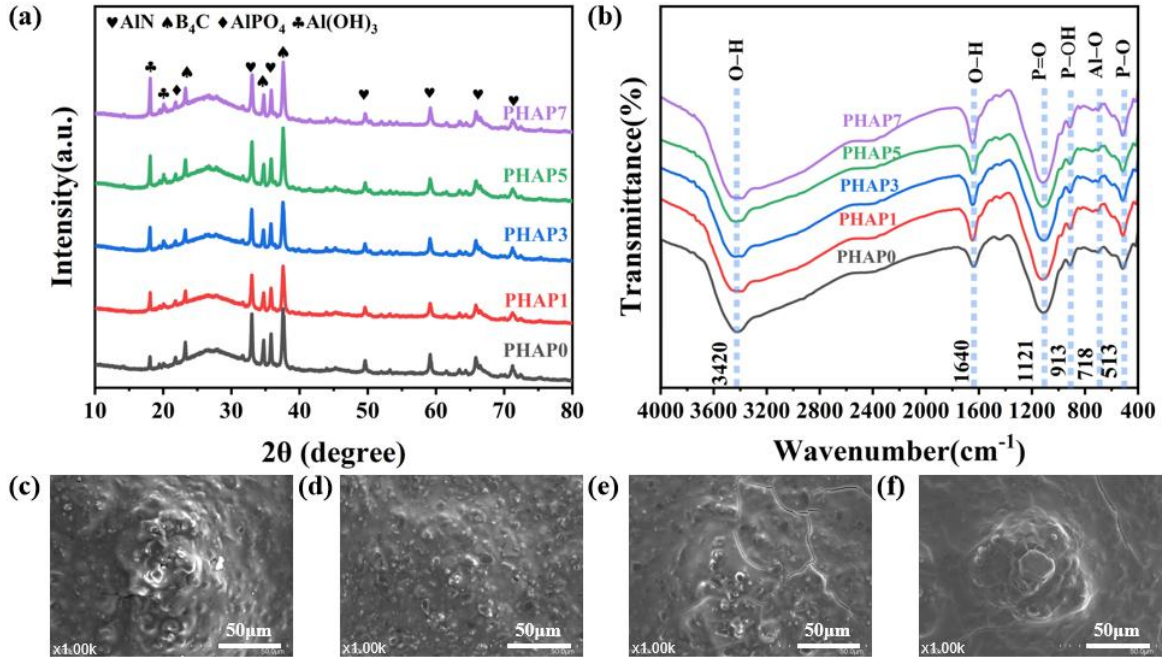


Figure 1. (**a**) XRD patterns, (**b**) FTIR spectra of adhesives modified with different PVA contents, (**c**–**f**) SEM images of the surfaces of PHAP1, PHAP3, PHAP5 and PHAP7 adhesives.

XPS analysis was performed to investigate the chemical environments of the elements in the hybrid binder (Figure 2). A comparison of the C 1s spectra of PVA and PHAP3 reveals that the C-C component at 284.8 eV and the C-O component at 286.33 eV in PVA are attributed to $-CH_2-$ and -CH-OH groups, respectively, accounting for 58.12% and 41.88% of the total C 1s signal [19]. In comparison, the C 1s spectrum of PHAP3 exhibits additional contributions from C-O and C=O species. Notably, the relative contribution of the C-O component decreases from 41.88% in pure PVA to 10.35% in PHAP3. This change indicates that the chemical environment of the hydroxyl-containing carbon groups is altered following the incorporation of PVA into the aluminium phosphate matrix,

which is consistent with the participation of PVA hydroxyl groups in the interaction and esterification reactions with phosphate species [20].

Furthermore, comparison of the high-resolution Al 2p and P 2p spectra of PHAP0 and PHAP3 reveals slight shifts towards lower binding energies following PVA incorporation. The Al 2p peak shifts from 75.14 to 75.02 eV, while the P 2p peak shifts from 134.42 to 134.34 eV [21]. These changes indicate modifications in the local chemical environments of aluminium and phosphorus atoms, which are associated with the interaction between PVA and the inorganic phosphate matrix. Combined with the changes observed in the C 1s and FTIR spectra, the XPS results support the involvement of PVA hydroxyl groups in the formation of the organic–inorganic hybrid structure through interactions with phosphate species.

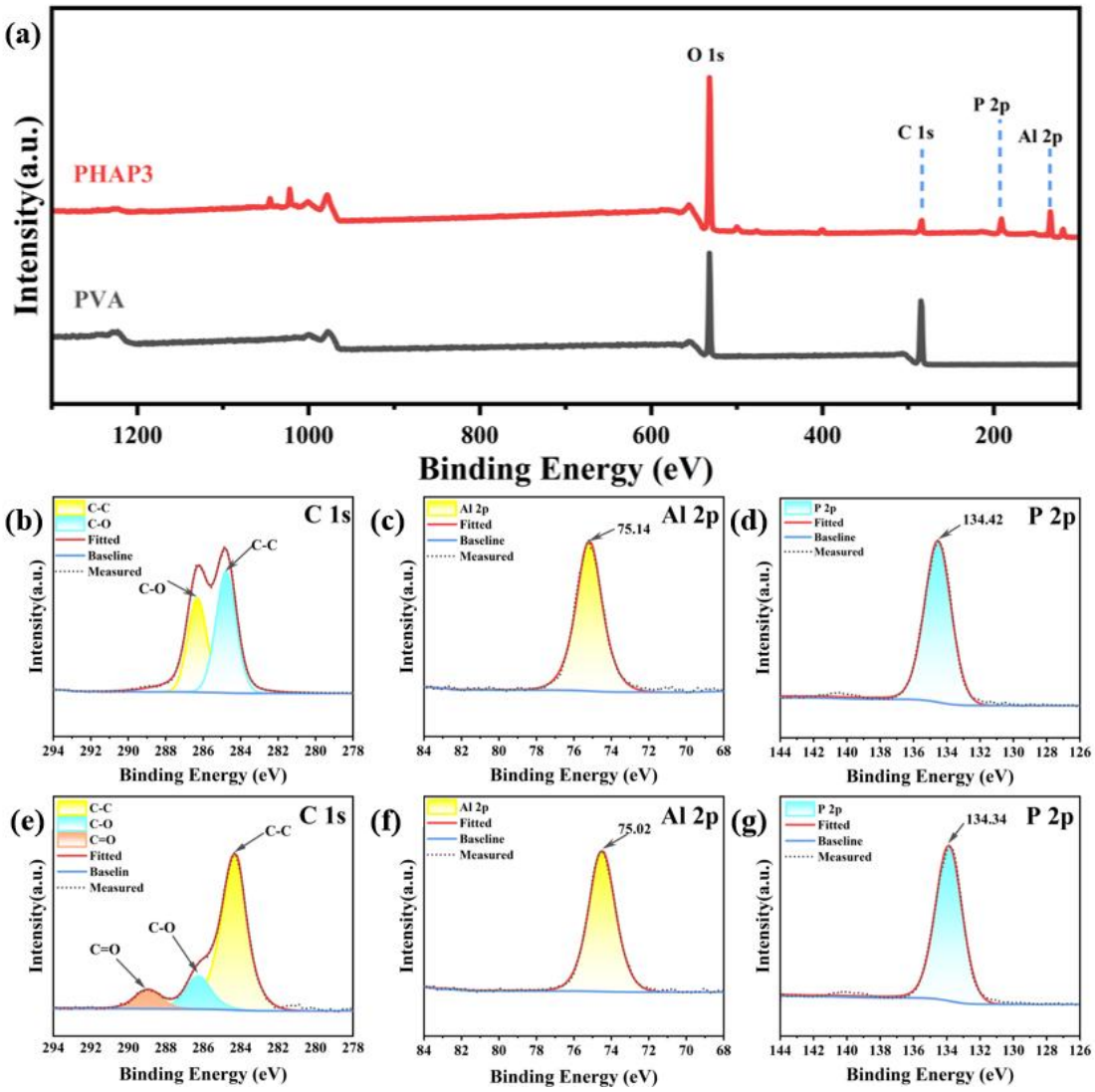


Figure 2. XPS spectra of the PVA, PHAP0 and PHAP3 hybrid binders: (**a**) full spectrum, (**b**) C 1s spectrum of PVA, (**c**,**d**) Al 2p and P 2p spectra of PHAP0, (**e**) C 1s spectrum of PHAP3, (**f**,**g**) Al 2p and P 2p spectra of PHAP3.

3.2. Analysis of the Properties of Hybrid Aluminium Phosphate Binders

The incorporation of PVA significantly influences the mechanical properties of the binder (Figure 3a). The PVA-free reference formulation PHAP0 exhibits a room-temperature shear strength of 2.67 MPa. Following PVA incorporation, the shear strengths of PHAP1, PHAP3, PHAP5 and PHAP7 reach 2.91, 3.06, 2.77 and 2.45 MPa, respectively.

Compared with PHAP0, the corresponding changes are +8.9%, +14.6%, +3.7% and -8.2%. These results demonstrate that PVA incorporation influences the bonding performance of the AlN-modified binder in a concentration-dependent manner. At relatively low PVA contents, the improved film-forming characteristics and interaction between the polymer chains and phosphate matrix contribute to better bonding performance. The highest shear strength is obtained at 3 wt% PVA. However, further increasing the PVA content results in a decrease in shear strength, which may be associated with increased slurry viscosity and the formation of larger residual particles, thereby affecting the uniformity of the binder layer and its contact with the substrate. These findings indicate that an appropriate PVA content is important for balancing the film-forming characteristics and bonding performance of the hybrid binder.

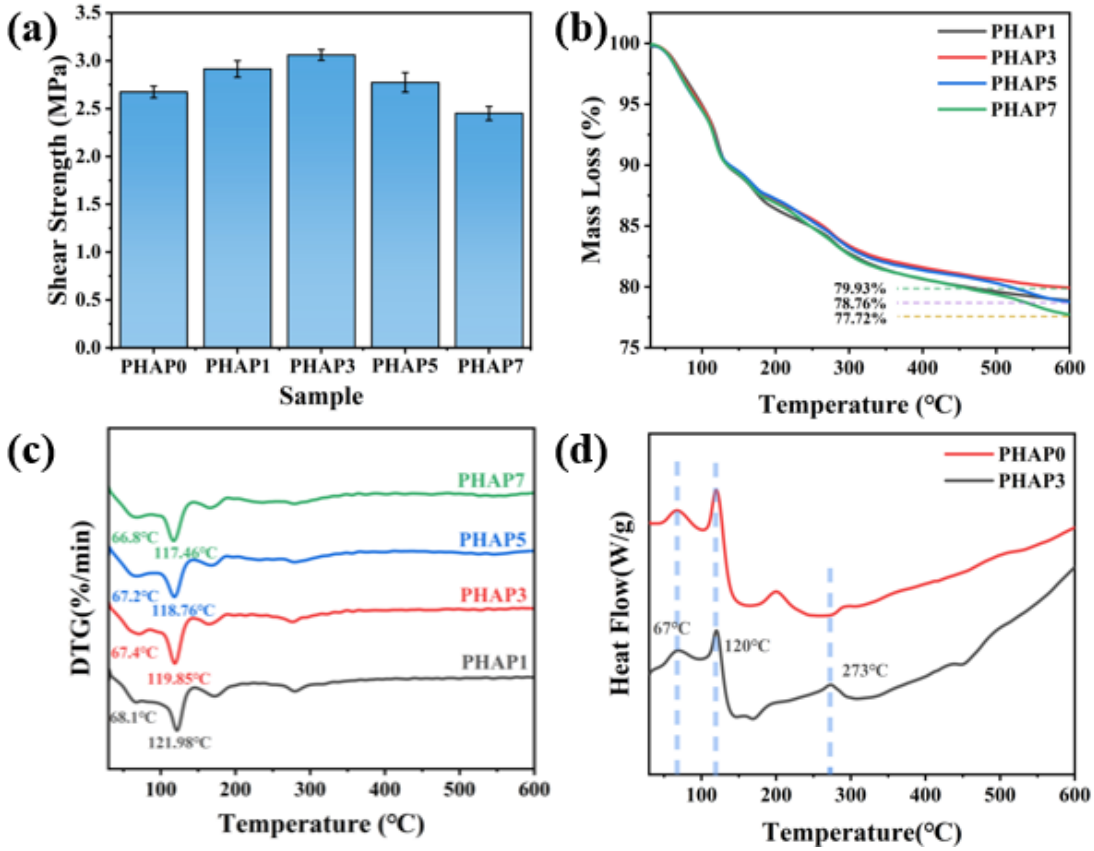


Figure 3. Hybrid aluminium phosphate binder: (**a**) shear properties, (**b**) TGA curve, (**c**) rate of weight change curve, (**d**) DSC curve of PHAP3.

Thermal gravimetric analysis (Figure 3b) can be summarised as comprising two stages. The period from 30–150 °C corresponds to the volatilisation of free water, characterised by significant and rapid weight loss, which corresponds to the rate of mass change at around 118 °C shown in Figure 3c. The 150–600 °C range corresponds to the stage of phosphate condensation and decomposition of the organic components; at 600 °C, the mass retention of PHAP3 reached its maximum value of 79.93%. Compared with the weight residue of 82.35% for the 10 wt% AlN-modified aluminium phosphate binder, the thermal weight loss rate of the PVA-modified binder is higher, attributed to the thermal decomposition of the carbon chains in the PVA organic backbone [22,23]. These results indicate that PVA incorporation increases the mass loss of the binder at elevated temperatures, reflecting the thermal decomposition of the introduced organic component. Therefore, the addition of PVA influences the thermal stability of the modified aluminium phosphate binder, particularly in the higher-temperature range. Combined with DTA analysis,

it is evident that the positions of the main endothermic peaks for PHAP3 and PHAP0 are consistent, indicating that PVA has not altered the intrinsic curing behaviour of the AlN-modified binder; however, PHAP3 exhibits a distinct endothermic peak at approximately 273 °C, corresponding to the thermal decomposition of PVA, the products of which include CO, CO_2, water and olefins. The position of this endothermic peak coincides with the peak in the rate of mass change at approximately 270 °C shown in Figure 3d, confirming that the thermal decomposition of PVA is the primary cause of the increased mass loss of the hybrid binder in the high-temperature range, and revealing the microscopic mechanism behind the reduced high-temperature thermal stability following PVA modification [24,25].

3.3. Evaluation of the In-Service Performance of Hybrid Aluminium Phosphate Binders

To investigate the influence of PVA incorporation on the water resistance of the aluminium phosphate binder, PVA was introduced into the AlN-modified system to regulate its film-forming characteristics and microstructure. Aluminium plates bonded with the PVA-containing aluminium phosphate binders were cured at room temperature and subsequently immersed in water for 5, 10, 15, and 20 days. The morphological and structural changes in the binder during immersion were examined using SEM, XRD, and FTIR. The morphological evolution of the PHAP3 binder layer is shown in Figure 4c,d. After 5 days of immersion, the initially smooth surface began to exhibit pitting and initial cracking, exposing the underlying phosphate and filler particles. By day 20, the surface layer had severely fractured and partially dissolved. Compared with the control system without PVA (Figure S1b), the hybrid adhesive exhibited better film integrity under the same immersion conditions, indicating that PVA incorporation effectively delayed water-induced surface deterioration. This improvement is associated with the interaction between PVA and phosphate species, as well as the enhanced film-forming characteristics of the polymer chains. The resulting more continuous binder structure can reduce the penetration of water through pores and defects, thereby delaying the hydrolysis and cracking of the phosphate matrix [26,27]. XRD analysis (Figure 4a) indicates that characteristic diffraction peaks of $Al(H_2PO_4)_3$ appear in the samples after immersion, with peak intensity increasing as the immersion time increases. The appearance of $Al(H_2PO_4)_3$-related diffraction peaks suggests changes in the phosphate phase composition during water immersion, possibly associated with hydrolysis and subsequent recrystallisation processes [28]. FTIR spectra (Figure 4b) further reveal the structural evolution of the binder during water immersion. As the immersion time increases, changes in the absorption bands at 3420 and 1640 cm^{-1}, associated mainly with O-H stretching and bending vibrations, indicate the increasing involvement of water in the binder structure. Meanwhile, variations in the phosphate-related bands at 1121 cm^{-1}, 718 cm^{-1} and 513 cm^{-1} reflect changes in the chemical environments of the phosphate- and Al–O-containing structures during immersion. Even after 20 days of immersion, residual phosphate-related absorption bands remain observable, indicating that part of the inorganic framework is retained. These observations suggest that PVA incorporation delays the deterioration of the phosphate-containing structure, which is consistent with the improved surface integrity observed by SEM and the higher shear-strength retention of PHAP3. The improved water resistance is therefore associated with the combined effects of polymer incorporation, interfacial interactions and enhanced binder-layer continuity.

When aluminium plates were bonded using the modified aluminium phosphate binder PHAP3, the changes in shear strength following curing at room temperature and immersion in water for varying durations are shown in Figure 5a. The initial shear strength was 3.06 MPa; after 5 days of immersion, it decreased to 2.50 MPa; after 10 days, it further decreased to 2.35 MPa, a 23.2% reduction from the initial value; after 15 and 20

days, it declined to 2.16 MPa and 1.87 MPa, respectively. After 5, 10, 15 and 20 days of immersion, the corresponding values decreased to 2.50, 2.35, 2.16 and 1.87 MPa, respectively. After 20 days of immersion, the strength retention rate remained at 61.1%, which was higher than the 37.8% retention rate of the PVA-free AlN-modified reference binder. This improvement indicates that PVA incorporation enhances the resistance of the binder to water-induced degradation. The improved performance can be associated with the interaction between PVA chains and the phosphate matrix, together with the formation of a more continuous polymer-containing binder layer. These structural characteristics help maintain the integrity of the bonded interface and delay the propagation of cracks during prolonged water exposure [29]. Nevertheless, the gradual decrease in shear strength with increasing immersion time indicates that water penetration and degradation of the phosphate-containing structure still occur [30].

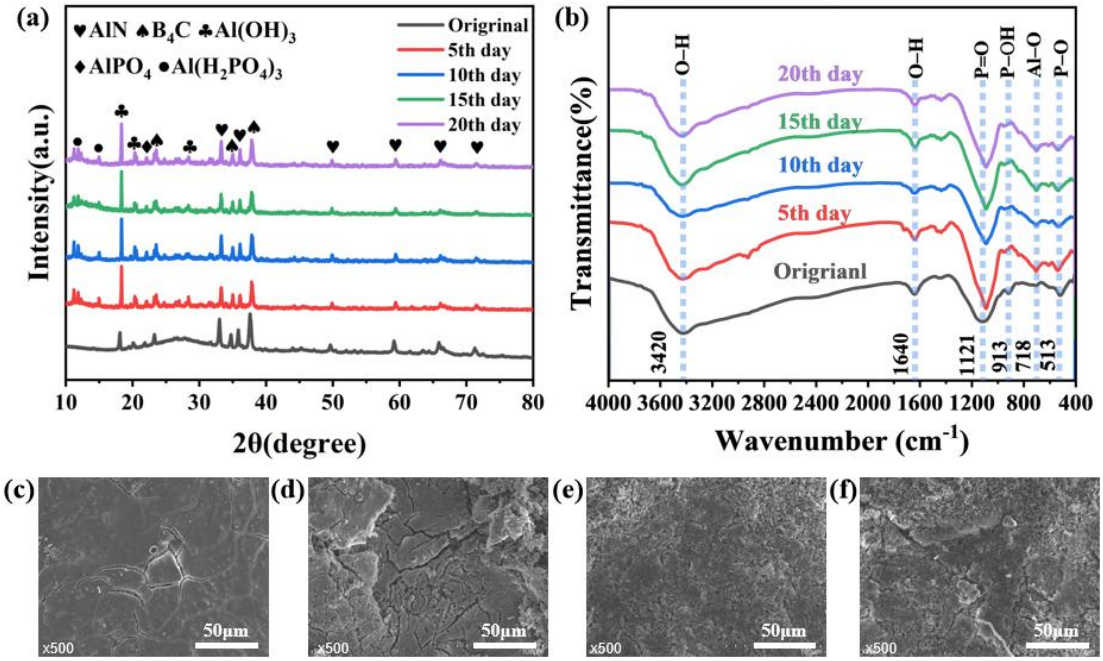


Figure 4. Morphological and structural evolution of the PHAP3 binder following immersion: (**a**) XRD pattern, (**b**) FTIR spectrum, (**c**–**f**) SEM images after 5, 10, 15 and 20 days of immersion.

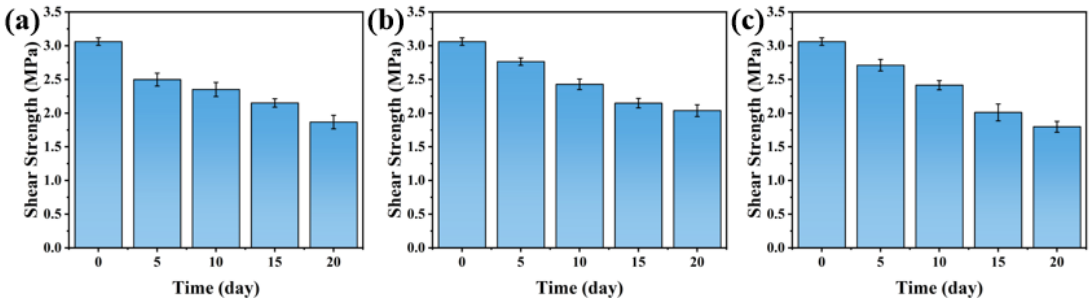


Figure 5. Evolution of the shear strength of PHAP3 adhesive under different ageing conditions: (**a**) water immersion, (**b**) UV irradiation, (**c**) humid heat ageing.

The UV resistance of PHAP3 was evaluated using a UV ageing chamber maintained at 60 °C with an irradiation intensity of 1.55 W/m². The specimens were exposed for up to 20 days and periodically removed to examine changes in surface morphology and bonding performance. SEM micrographs (Figure 6c,d) show that the surface remained largely unaffected during the first five days; thereafter, microcracks gradually nucleated and

propagated, attributed to bond breakage and the generation of internal stresses induced by UV photons [31]. XRD analysis (Figure 6a) indicates that, as the duration of UV irradiation increased, the intensity of the $Al(H_2PO_4)_3$ diffraction peaks gradually increased and the peak shapes became sharper, suggesting an increase in crystallinity. This phenomenon may be attributed to UV-induced local thermal effects or the removal of water molecules, which promoted the rearrangement and crystallisation of aluminium dihydrogen phosphate. In the FTIR spectrum (Figure 6b), the water absorption peaks at 3420 cm^{-1} and 1640 cm^{-1} may be related to moisture absorption during the sample preparation process; characteristic peaks at 1121 cm^{-1} (P-O), 913 cm^{-1} (P-O-H), 718 cm^{-1} (Al-O) and 513 cm^{-1} (P-O) did not exhibit significant shifts or intensity decay following irradiation, indicating that the main aluminium phosphate framework had not undergone significant degradation. A comprehensive analysis of morphological and spectroscopic data reveals that the primary effect of UV irradiation on the hybrid aluminium phosphate binder is the initiation and propagation of surface cracks, primarily caused by physical shrinkage and local bond breakage, whilst the chemical composition and short-range ordered structure of the binder remained relatively stable over the 20-day irradiation period. These results indicate that PVA hybrid modification confers excellent UV ageing resistance to the aluminium phosphate binder, providing a structural foundation for its outdoor applications.

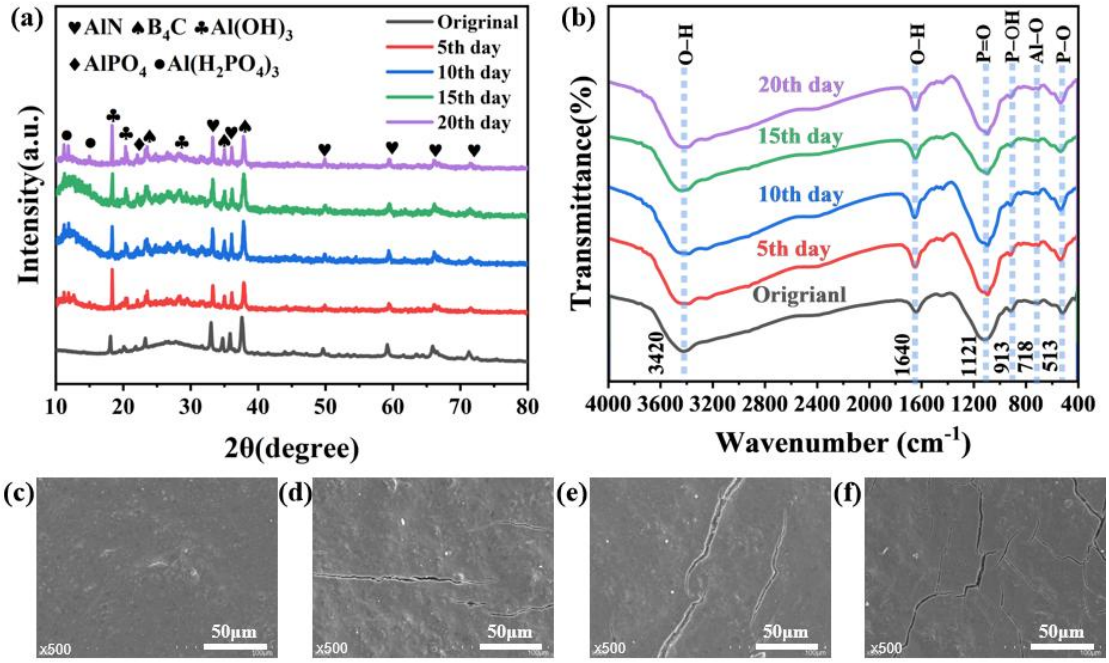


Figure 6. Morphological and structural evolution of the PHAP3 binder following exposure to UV light for varying durations: (**a**) XRD pattern, (**b**) FTIR spectrum, (**c**–**f**) SEM images after 5, 10, 15 and 20 days of exposure.

Despite the appearance of surface cracking, FTIR and XRD analyses suggest that the main phosphate-related structural features remained relatively stable during irradiation. The shear strength of PHAP3 decreased from an initial value of 3.05 MPa to 2.05 MPa after 20 days, representing a retention rate of 67.2%. The decrease in strength may be associated with UV-induced changes in the PVA-containing organic phase. UV exposure can induce radical-mediated photo-oxidative reactions and chain scission in polymer chains, potentially weakening the cohesive structure of the organic phase and affecting the mechanical

properties of the hybrid binder [32]. In addition, changes at the organic–inorganic interface may influence interfacial load transfer and contribute to the reduction in bonding strength. The loss of strength was primarily concentrated in the first 10 days, after which the rate of decline slowed, suggesting that the degradation process became less pronounced during the subsequent irradiation period. Although PVA incorporation did not completely prevent UV-induced deterioration, PHAP3 maintained a shear-strength retention rate of 67.2% after 20 days of exposure. These results indicate the potential of the hybrid binder for applications involving UV exposure, although its long-term outdoor durability requires further consideration. The introduction of UV absorbers or radical scavengers may provide an additional approach to improving its weathering resistance.

The structural evolution of the hybrid aluminium phosphate binder under humid–heat conditions (55 °C and 90% RH) was investigated through SEM, XRD and FTIR analyses. The initial surface was dense and smooth, as shown in Figure 7c,d. It remained relatively flat after 5 days, whereas deep and interconnected grooves appeared after 20 days. This morphological deterioration may be associated with moisture-assisted hydration and hydrolysis of susceptible phosphate species, together with the dissolution and leaching of water-soluble components. Previous studies have demonstrated that the structural evolution of aluminium phosphate hydrates is influenced by temperature and water vapour pressure [33].

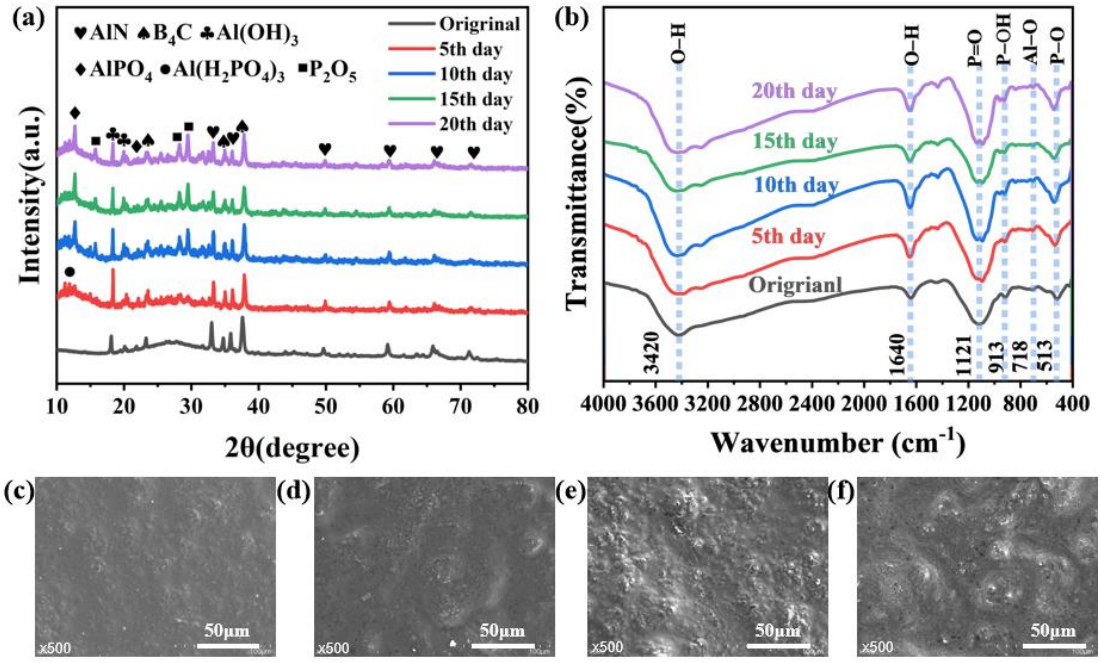


Figure 7. Morphological and structural evolution of the PHAP3 binder under humid and hot conditions: (**a**) XRD pattern, (**b**) FTIR spectrum, (**c**–**f**) SEM images after 5, 10, 15 and 20 days of storage.

XRD analysis (Figure 7a) shows that an $Al(H_2PO_4)_3$-related diffraction peak appears after 5 days of ageing, while diffraction peaks assigned to P_2O_5 become evident after 10 days. These changes indicate progressive evolution of the phosphate phase composition during humid–heat exposure, accompanied by changes in the local phosphate structures. The phase composition of aluminium phosphate binders has also been reported to depend on their chemical composition and thermal treatment conditions [34].

FTIR analysis (Figure 7b) reveals that the O-H-related absorption bands at 3420 and 1640 cm^{-1} gradually increase in intensity, suggesting increased water-associated vibrations during humid–heat ageing. Changes in the phosphate-related bands at 1121 and 913 cm^{-1}, together with the attenuation of the Al-O-related bands at 718 and 513 cm^{-1}, indicate

variations in the local chemical environments of the phosphate and aluminium-containing structures. Multiscale analysis indicates that although PVA modification improves moisture resistance, the binder still undergoes progressive structural deterioration under prolonged humid–heat exposure. Overall, the combined XRD, FTIR and SEM results suggest that humid–heat exposure induces changes in the phosphate phase composition and local chemical environments, accompanied by progressive surface deterioration. These changes, together with the possible dissolution and leaching of soluble phosphate species, may contribute to the reduction in bonding performance during prolonged exposure.

Figure 5c illustrates the variation in shear strength of the hybrid aluminium phosphate binder PHAP3 over time under constant temperature and humidity conditions. The initial shear strength was 3.06 MPa; after 5 days in a humid–heat environment, it decreased to 2.71 MPa; after 10 days, it further decreased to 2.41 MPa; and after 15 and 20 days, the strengths were 2.01 MPa and 1.80 MPa, respectively. Overall, a continuous decline is observed, with a relatively rapid rate of decrease during the first 10 days, followed by a slight slowdown. This deterioration in performance can be attributed to the progressive destruction of the binder's chemical structure caused by the coupled action of heat and moisture. Water molecules penetrate the cross-linked network, triggering the hydrolysis of the aluminium phosphate backbone to form intermediate products such as $Al(H_2PO_4)_3$, which subsequently decompose into P_2O_5, leading to a reduction in effective cross-linking density; simultaneously, the leaching of soluble oligomers forms microcracks and voids, weakening the interfacial bonding with the aluminium substrate [35]. Compared with UV ageing, the damp-heat environment causes more significant damage to strength, indicating that the erosion caused by water molecules is more severe than photochemical degradation.

The performance of the PVA/AlN-modified aluminium phosphate binder is associated with the respective functions of the inorganic and organic components. AlN was incorporated into the phosphate matrix as an inorganic modification component, providing the basis for the previously established improvement in curing behaviour and mechanical integrity. On this basis, PVA was introduced to further regulate the microstructure and bonding characteristics of the binder. The interaction between PVA chains and phosphate species, together with the film-forming characteristics of the polymer, contributes to the formation of a more continuous binder structure. The flexible PVA chains also influence the arrangement of the inorganic phosphate network and help accommodate local deformation [36]. Meanwhile, the incorporation of AlN contributes to the structural characteristics of the inorganic matrix. The resulting PVA-containing AlN-modified binder exhibits composition-dependent mechanical and environmental ageing behaviour, with 3 wt% PVA providing the most favourable overall performance among the investigated formulations.

4. Conclusions

In this study, PVA was incorporated into a previously developed AlN-modified aluminium phosphate binder to investigate the effects of polymer content on its structural characteristics, mechanical properties, and environmental durability. The results demonstrate that PVA incorporation influences the film-forming characteristics and microstructure of the binder, leading to composition-dependent changes in bonding performance. Among the investigated formulations, PHAP3 exhibits the highest room-temperature shear strength of 3.06 MPa, representing an increase of 14.6% compared with the PVA-free AlN-modified reference PHAP0. Furthermore, PHAP3 exhibits improved strength retention following water immersion, UV irradiation, and humid–heat ageing. These findings demonstrate that appropriate PVA incorporation is an effective approach to further improving the performance of AlN-modified aluminium phosphate binders.

https://doi.org/10.3390/met16111259

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/met16111259/s1, Figure S1: Microscopic morphology of the aluminium phosphate binder (a) 0%Wt AIN; (b) 10%Wt AIN(PPA0), Figure S2: Morphology of ANAP2 modified aluminum phosphate adhesive at different temperatures (a) 300 ℃; (b) 500 ℃, Figure S3: FT-IR spectra of ANAP2 adhesive after heat treatment at different temperatures, Figure S4: Figure 4-7 AlN modified aluminum phosphate adhesive (a) TG curve; (b) DTG curve; (c) DSC curve, Figure S5: Variations in phase composition, shear strength and micromorphology of the PHAP0 adhesive after water immersion (a) XRD patterns, (b) shear strength, (c-f) SEM micrographs after 5, 10, 15 and 20 days of immersion, Figure S6: Variations in phase composition, shear strength and micromorphology of the PHAP0 adhesive after ultraviolet exposure for different durations (a) XRD patterns, (b) shear strength, (c-f) SEM images after 5, 10, 15 and 20 days of exposure, Figure S7: Variations in phase composition, shear strength and micromorphology of the PHAP0 adhesive under humid-heat conditions: (a) XRD patterns, (b) shear strength, (c-f) SEM micrographs after 5, 10, 15 and 20 days of exposure.

Author Contributions: Conceptualization, Y.R. and F.W.; methodology, J.Y., Q.M. and W.W.; software, Q.M.; validation, T.Z., J.Y. and F.W.; formal analysis, Y.R., T.Z. and Q.M.; investigation, Y.R. and X.W.; resources, F.W., Y.S. and W.W.; data curation, X.W.; writing−original draft preparation, X.W. and J.Y.; writing−review and editing, J.Q.; visualization, X.W.; supervision, Q.M. and W.W.; project administration, Y.S. and J.Q.; funding acquisition, T.Z. and Y.S. All authors have read and agreed to the published version of the manuscript.

Funding: This work was financially supported by the National Natural Science Foundation of China (No. 52574176) and the Jiangsu Provincial Special Fund Project for Carbon Peaking and Carbon Neutrality (No. BT2025025).

Data Availability Statement: The original contributions presented in this study are included in the article/Supplementary Material. Further inquiries can be directed to the corresponding author(s).

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Wang, M.; Liu, J.; Du, H.; Hou, F.; Guo, A.; Zhao, Y.; Zhang, J. A new practical inorganic phosphate adhesive applied under both air and argon atmosphere. *J. Alloys Compd.* **2014**, *617*, 219–221.
2. Wang, Q.; Jia, D.; Duan, W.; Yang, H.; Ma, S.; He, P.; Colombo, P.; Zhou, Y. Effect of P/Al ratio on an acid aluminum phosphate solution: Thermal evolution and hygroscopic behavior. *J. Alloys Compd.* **2023**, *966*, 171487.
3. Wang, M.; Zhang, J.; Wei, T.; Zhou, Q.; Li, Z. Effect of Al:P ratio on bonding performance of high-temperature resistant aluminum phosphate adhesive. *Int. J. Adhes. Adhes.* **2020**, *100*, 102627.
4. Huo, S.; Dong, Z.; Li, X.; Liu, P.; Chen, P.; Zhu, B. Preparation of a modified multi-component phosphate adhesive for connection of 316L stainless steel and its reinforcement mechanism. *Int. J. Adhes. Adhes.* **2023**, *125*, 103437.
5. Li, J.; Liu, J.; Zhang, Y.; Wan, Y.; Liu, J.; Cai, G.; Tao, X.; Jing, W.; Wang, M. Preparation and properties of high-temperature resistant inorganic phosphate-based adhesive for connecting quartz glass at elevated temperatures. *Ceram. Int.* **2024**, *50*, 16.
6. Liu, J.; Wan, Y.; Xiao, B.; Li, J.; Hu, Z.; Zhang, R.; Hu, X.; Liu, J.; Cai, G.; Liu, H.; et al. The preparation and performance analysis of zirconium-modified aluminum phosphate-based high-temperature(RT-1500 °C)resistant adhesive for joining alumina in extreme environment. *J. Adv. Ceram.* **2024**, *13*, 911–932.
7. Wang, Y.; Yang, J.; Chen, Z.; Wang, J.; Wang, C.; Yang, J.; Gu, J.; Li, Q. Preparation and performance analysis of an inorganic adhesive for alumina ceramic joining with a wide operating temperature range. *Ceram. Int.* **2025**, *51*, 21274–21286.
8. Xie, L.; Li, Y.; Hu, W.; Fang, S.; Chen, X.-Q. A novel inorganic phosphate-based adhesive for bonding archaeological pottery: A preliminary exploration. *Herit. Sci.* **2024**, *12*, 164.
9. Aladejana, J.T.; Wu, Z.; Li, D.; Guelifack, K.; Wei, W.; Wang, X.A.; Xie, Y. Facile approach for glutaraldehyde cross-linking of PVA/aluminophosphate adhesives for wood-based panels. *ACS Sustain. Chem. Eng.* **2019**, *7*, 18524–18533.
10. Wu, Z.; Chen, T.; Aladejana, J.T.; Zhang, Z.; Liang, S.; Xiao, Y.; Lin, J.; Wang, X.; Xie, Y. Eco-benign PVA/aluminum phosphate as an alternative to formaldehyde-based adhesives in wood-based panels. *RSC Adv.* **2021**, *11*, 34416–34423.

11. Mohamed Saat, A.; Johan, M.R. The surface structure and thermal properties of novel polymer composite films based on partially phosphorylated poly(vinyl alcohol) with aluminum phosphate. *Sci. World J.* **2014**, *2014*, 439839.
12. Mohamed Saat, A.; Kamil, M.S.; Hamizi, N.A.; Badruddin, I.A.; Ghazali, N.; Sagadevan, S.; Kamangar, S.; Khan, T.M.Y.; Johan, M.R. Influence of reaction pH towards the physicochemical characteristics of phosphorylated polyvinyl alcohol-aluminum phosphate nanocomposite. *Coatings* **2021**, *11*, 1105.
13. Song, H.G.; Han, J. Hybrid organic-inorganic coating with enhanced oxygen- and UV-barrier performance: Polyelectrolyte complex based on sodium alginate, poly(vinyl alcohol), and reconstructed layered double hydroxide. *Int. J. Biol. Macromol.* **2024**, *260*, 129335.
14. Liu, B.; Zhang, J.; Guo, H. Research Progress of Polyvinyl Alcohol Water-Resistant Film Materials. *Membranes* **2022**, *12*, 347.
15. Suleiman, G.S.A.; Zeng, X.; Chakma, R.; Wakai, I.Y.; Feng, Y. Recent advances and challenges in thermal stability of PVA-based film: A review. *Polym. Adv. Technol.* **2024**, *35*, e6327.
16. Ma, C.; Chen, H.; Wang, C.; Zhang, J.; Qi, H.; Zhou, L. Effects of Nano-Aluminum Nitride on the Performance of an Ultrahigh-Temperature Inorganic Phosphate Adhesive Cured at Room Temperature. *Materials* **2017**, *10*, 1266.
17. Wu, G.; Liu, G.; Li, X.; Peng, Z.; Zhou, Q.; Qi, T. Enhanced phosphate removal with fine activated alumina synthesized from a sodium aluminate solution: Performance and mechanism. *RSC Adv.* **2022**, *12*, 4562–4571.
18. Goj, P.; Handke, B.; Stoch, P. Vibrational characteristics of aluminum-phosphate compounds by an experimental and theoretical approach. *Sci. Rep.* **2022**, *12*, 17495.
19. Wu, Y.; Fu, H.; Zhang, L.; Lin, Y.; Kizilkaya, O.; Xu, J. Toward a Rapid-Fabricated Triboelectric Device with a 1,3-Phosphorylated Poly(vinyl alcohol) Polymer for Water Turbulence Energy Harvesting. *ACS Omega* **2018**, *3*, 8421–8428.
20. Li, M.; Gao, X.; Li, T. Performance characterization and coating mechanism of polyvinyl-alcohol-coated Nanoaluminium powder. *J. Saudi Chem. Soc.* **2025**, *29*, 29.
21. Greczynski, G.; Hultman, L. Binding energy referencing in X-ray photoelectron spectroscopy. *Nat. Rev. Mater.* **2025**, *10*, 62–78.
22. Tsioptsias, C.; Fardis, D.; Ntampou, X.; Tsivintzelis, I.; Panayiotou, C. Thermal Behavior of Poly(vinyl alcohol) in the Form of Physically Crosslinked Film. *Polymers* **2023**, *15*, 1843.
23. Alhulaybi, Z.A.; Dubdub, I. Kinetics Study of PVA Polymer by Model-Free and Model-Fitting Methods Using TGA. *Polymers* **2024**, *16*, 629.
24. Chen, T.; Wu, Z.; Wang, X.A.; Wang, W.; Huang, D.; Wei, Q.; Wu, B.; Xie, Y. Hierarchical lamellar aluminophosphate materials with porosity as ecofriendly inorganic adhesive for wood-based boards. *ACS Sustain. Chem. Eng.* **2018**, *6*, 6273–6280.
25. Chen, D.; He, L.; Shang, S. Study on aluminum phosphate binder and related Al_2O_3-SiC ceramic coating. *Mater. Sci. Eng. A* **2003**, *348*, 29–35.
26. Wang, J.; Shan, H.; Wu, Y.; Song, L.; Xue, J.; Wang, B.; Wang, C. Room-temperature curing high-strength, water-resistant, flame-retardant adhesive based on aluminum dihydrogen phosphate and gelatinized starch cross-linking. *Int. J. Biol. Macromol.* **2025**, *306*, 141441.
27. Wang, J.; Wu, M.; Miao, X.; Wang, Y.; Bian, D.; Zhao, Y. Organic-inorganic in-situ hybrid aluminum dihydrogen phosphate binder for enhancing tribocorrosion resistance of ceramic coatings. *Colloids Surf. A Physicochem. Eng. Asp.* **2023**, 658, 130765.
28. Adediwura, S.C.; Wied, J.K.; Litterscheid, C.; der Günne, J.S.A. Stability, structure, dynamics and thermal properties of C-type aluminium tris-dihydrogen phosphate. *Dalton Trans.* **2025**, *54*, 16727–16736.
29. Min, J.; Zhang, X.; Zhao, Y.; Li, S.; Lv, F.; Wan, H. Molecular-level understanding of the strength degradation of aluminum-adhesive bonding interface under water immersion. *Surf. Interfaces* **2025**, 56, 105521.
30. Chomiak, M.; Sałaciński, M.; Gołębiowski, F.; Broda, P. Durability and Corrosion Resistance Test of Adhesive Joints Using Two Adherence Promoters for the Connection of Aerospace Aluminum Alloys. *Materials* **2022**, *15*, 8733.
31. Aprilia, N.S.S.; Hps, A.K.; Olaiya, N.; Amin, A.; Abdullah, C.; Kamarazaman, S.; Zuhra, Z.; Rahmah, K.; Fitriani, F.; A Gopakumar, D. Ultraviolet light exposure degradation effect on the properties of nanocrystalline cellulose-reinforced polyvinyl alcohol composite film. *Prog. Rubber Plast. Recycl. Technol.* **2021**, *38*, 21–37.
32. Duga, A.; Bajer, D.; Kaczmarek, H. Photochemical and Thermal Stability of Bionanocellulose/Poly(Vinyl Alcohol) Blends. *Polymers* **2022**, *14*, *4364.*
33. Tanaka, Y.; Takano, S.; Miyayama, M. Stability and proton conductivity of $AlH_2P_3O_{10} \cdot nH_2O$ under various water vapor pressures. *J. Ceram. Soc. Jpn.* **2003**, *111*, 323–326.
34. Tricot, G.; Hu, H.; Beaussart, A.; Fernandes, I.; Perrot, C. Effect of the P/Al Molar Ratio and Heating Rate on the Composi-Tion of Alumino-Phosphate Binders. *Materials* **2022**, *15*, 2337.

35. Wang, Q.; Duan, W.; Jia, D.; Ma, S.; Yang, H.; He, P.; Zhou, Y. Reaction mechanism, hygroscopic behavior, and properties of aluminum phosphate adhesive. *Ceramics International* **2024**, 50, 27889–27909
36. Lu, X.; Zeng, Y.; Yang, Y.; Yang, X.; Wei, E.; Cui, C.; Xie, J.; Qin, Y.; Qian, Z. PVA/PA/H_3PO_4 Hydrogel Films with Ultrawide Pressure and Strain Sensing Range via Facile Fabrication Method. *Adv. Mater. Technol.* **2023**, *8*, 2202123.

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.