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Article

Synthesis of Hierarchical Alumina Microspheres with Enhanced Interfacial Properties for High-Performance Polymer Composites

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Abstract: Alumina (Al_2O_3) has been widely used as a ceramic filler for polymer composites due to its excellent thermal stability, high hardness, and good electrical insulation. However, conventional alumina particles with smooth surfaces and limited surface areas exhibit poor interfacial compatibility with polymer matrices, leading to suboptimal mechanical reinforcement. In this work, we designed and fabricated hierarchical alumina microspheres (H-Al_2O_3) via a facile hydrothermal self-assembly route combined with surfactant-assisted morphology control, followed by calcination. Compared to pristine alumina particles (P-Al_2O_3), the obtained H-Al_2O_3 microspheres are composed of self-assembled nanosheets, exhibiting a rough, porous surface and significantly enlarged specific surface area. Structural characterizations by scanning electron microscopy (SEM), X-ray diffraction (XRD), and Brunauer–Emmett–Teller (BET) analyses confirmed the α-Al_2O_3 phase and a BET surface area nearly three times higher than P-Al_2O_3. When incorporated into an epoxy resin matrix at 10 wt% loading, the H-Al_2O_3-reinforced composites showed markedly improved tensile strength, fracture toughness, and dynamic mechanical properties relative to P-Al_2O_3-filled counterparts. The superior performance is attributed to the hierarchical microstructure enabling enhanced physical interlocking and better interfacial adhesion with the polymer matrix. The proposed design strategy opens a new avenue for engineering high-performance ceramic fillers via microstructural control.

Keywords: alumina microspheres; hierarchical structure; polymer composites; interfacial properties; hydrothermal synthesis

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1. Introduction

Alumina (Al_2O_3) is among the most widely utilized ceramic materials, prized for its exceptionally high melting point, outstanding chemical stability, and remarkable hardness. These intrinsic properties, combined with its availability and cost-effectiveness, have positioned alumina as a key functional additive across a broad spectrum of engineering applications. Within polymer matrix composites, alumina is frequently incorporated as a filler to improve not only mechanical strength and stiffness but also thermal conductivity, dimensional stability, and wear resistance [1]. Such enhancements make alumina-filled composites highly attractive for demanding service environments, including electronic packaging materials requiring efficient heat dissipation, wear-resistant coatings subjected to severe frictional loads, and structural components designed for high-performance engineering systems. Furthermore, the versatility of alumina enables its integration into both thermosetting and thermoplastic matrices, allowing for tailored composite designs that address diverse industrial requirements.

Despite these advantages, conventional alumina particles exhibit smooth surfaces with low specific surface areas (typically below $5\ m^2 \cdot g^{-1}$ for α-Al_2O_3), leading to inadequate interfacial bonding with organic matrices. Weak filler–matrix adhesion often results in stress concentrations and poor stress transfer efficiency, limiting the overall reinforcement effect.

Recent studies suggest that tailoring the particle morphology and constructing multiscale hierarchical structures—wherein nano- or microscale features coexist—could substantially boost the filler–matrix interfacial area, improve wettability, and introduce mechanical interlocking mechanisms [2]. Hierarchical structures also help to increase the surface energy and create more active sites for physical or chemical interactions.

Motivated by such findings, this work reports a facile synthesis route for producing hierarchical alumina microspheres (H-Al_2O_3) and evaluates their potential as high-performance fillers for polymer composites.

2. Research Hypotheses

In this study, we put forward the central hypothesis that tailoring the microstructure of ceramic fillers, specifically alumina particles, from conventional smooth-surfaced morphologies to hierarchical microspheres composed of self-assembled nanosheets, can markedly improve the interfacial bonding between the filler and a polymer matrix. This improvement in interfacial strength is expected to occur through two complementary mechanisms: the physical interlocking effect afforded by the high surface roughness of the hierarchical structure, and the increased number of potential contact sites enabled by its enlarged specific surface area. Together, these microstructural features should enhance stress transfer efficiency and delay crack initiation and propagation at the filler–matrix boundary.

Furthermore, we hypothesize that the hierarchical structuring of alumina will significantly increase its accessible surface area compared with pristine α-Al_2O_3 particles of similar size, owing to the introduction of mesopores and protruding nanosheets [3]. Such an increase in surface area is anticipated to amplify van der Waals forces and potential secondary bonding interactions with the surrounding polymer chains, thereby reducing interfacial voids and improving wetting during composite fabrication. This effect is likely to be more pronounced in thermosetting polymer matrices, such as epoxy resins, which can more effectively infiltrate the porous shell of the hierarchical microspheres during curing.

Finally, we anticipate that the improvement in interfacial properties resulting from the adoption of hierarchical alumina morphologies will manifest in measurable enhancements in mechanical performance metrics at relatively low filler loadings. Specifically, composites incorporating H-Al_2O_3 are expected to display higher tensile strength, greater fracture toughness, and elevated storage modulus relative to those filled with conventional smooth-surfaced alumina. These property improvements would validate the concept of structural morphology design as an accessible and efficient strategy for developing high-performance polymer composites through filler engineering.

3. Research Design

The research was designed to explore the influence of filler microstructure on the interfacial performance of polymer composites by synthesizing and characterizing two distinct forms of alumina [4,5]. The first type, denoted as pristine alumina (P-Al_2O_3), was prepared using a conventional hydrothermal precipitation route in which aluminum nitrate nonahydrate served as the aluminum source and aqueous ammonia acted as the precipitating agent. The resulting aluminum hydroxide precursor was subjected to hydrothermal treatment at 180 °C for 12 h, followed by thorough washing and drying. To obtain the desired α-Al_2O_3 phase, the dried precursor was calcined at 1200 °C for four hours in air. This method yields submicron to micron-sized particles with relatively smooth surfaces, providing a baseline morphology against which the hierarchical structure could be compared.

In contrast, the hierarchical alumina microspheres (H-Al_2O_3) were synthesized via a modified hydrothermal process designed to induce nanosheet self-assembly on spherical frameworks. The modification involved introducing urea as a slow-releasing precipitant and morphology regulator, along with sodium dodecyl sulfate (SDS) as a surfactant template. Urea decomposition during hydrothermal treatment gradually increased the pH, allowing controlled precipitation and growth of plate-like alumina hydrates, while SDS adsorbed selectively to promote anisotropic growth and nanosheet formation [6]. The hydrothermal reaction was maintained at 180 °C for 24 h to facilitate complete self-assembly into spherical aggregates composed of radially oriented nanosheets. Following filtration, washing, and drying, the resulting microspheres were calcined at 1200 °C for four hours to convert the hydrated phases into α-Al_2O_3 while retaining their hierarchical architecture.

To evaluate the structure and surface characteristics of P-Al_2O_3 and H-Al_2O_3, X-ray diffractometer (XRD, Bruker D8 Advance) and scanning electron microscopy (SEM, F-6000, Wellrun Technology Co., Ltd.) were adopted. Brunor-Emmett-Teller (BET, Micromeritics ASAP 2460) surface area analysis was conducted. SEM (acceleration voltage 5 kV, working distance 8 mm) was used to observe the particle morphology and surface roughness, while XRD (Cu Kα radiation, λ=1.5406 A, scanning rate 2°/min) confirmed the crystal phase and ensured that the morphology modification would not change the basic α-Al_2O_3 phase. BET measurement based on nitrogen adsorption-desorption isotherms (degassing conditions: 200°C, 6 h) was used to quantitatively compare the specific surface areas of two types of alumina, thereby establishing the correlation between microstructure and surface area enhancement.

For evaluation of the practical benefits of the hierarchical morphology, both types of alumina were incorporated as fillers into an epoxy resin matrix at a loading level of 10 wt% using mechanical mixing and vacuum-assisted degassing before curing [7]. The resulting composites were subjected to mechanical property testing, including uniaxial tensile tests to determine tensile strength, fracture toughness measurements via the single edge notch bending (SENB) method, and dynamic mechanical analysis (DMA) to assess viscoelastic performance. These tests provided direct evidence of the relationship between the hierarchical structural features of the filler and the macroscopic performance of the composites.

4. Empirical Analysis

The morphological characteristics of the synthesized alumina samples were first investigated in detail using scanning electron microscopy (SEM), which provided direct visual evidence of the distinct structural features formed under different synthesis conditions. As shown in the micrographs, a pronounced contrast emerges between the pristine alumina (P-Al_2O_3, Figure 1(a1–a2)) and the hierarchically structured alumina (H-Al_2O_3, Figure 1(b1–b2)). The P-Al_2O_3 sample is composed primarily of relatively dense, compact particles with smooth and featureless surfaces, displaying minimal textural irregularities. These particles possess an average size within the range of approximately 1–3 μm, suggesting a relatively low specific surface area and limited interfacial roughness [8]. In stark contrast, the H-Al_2O_3 sample exhibits a highly distinctive morphology characterized by well-defined microspheres with diameters of roughly 2–4 μm. Each microsphere is constructed from a dense assembly of radially oriented nanosheets, each with an average thickness of about 50 nm [9]. This nanosheet arrangement imparts a unique flower-like architecture with an abundance of open channels and void spaces, yielding a markedly porous structure. Such hierarchical organization not only enhances the visual complexity of the particles but also dramatically increases the total accessible surface area. The pronounced three-dimensional roughness and interconnected porosity of the H-Al_2O_3 are anticipated to facilitate deeper polymer chain infiltration into the filler surface and promote mechanical interlocking at the filler–matrix interface, thereby potentially improving load transfer efficiency and interfacial adhesion in composite applications.

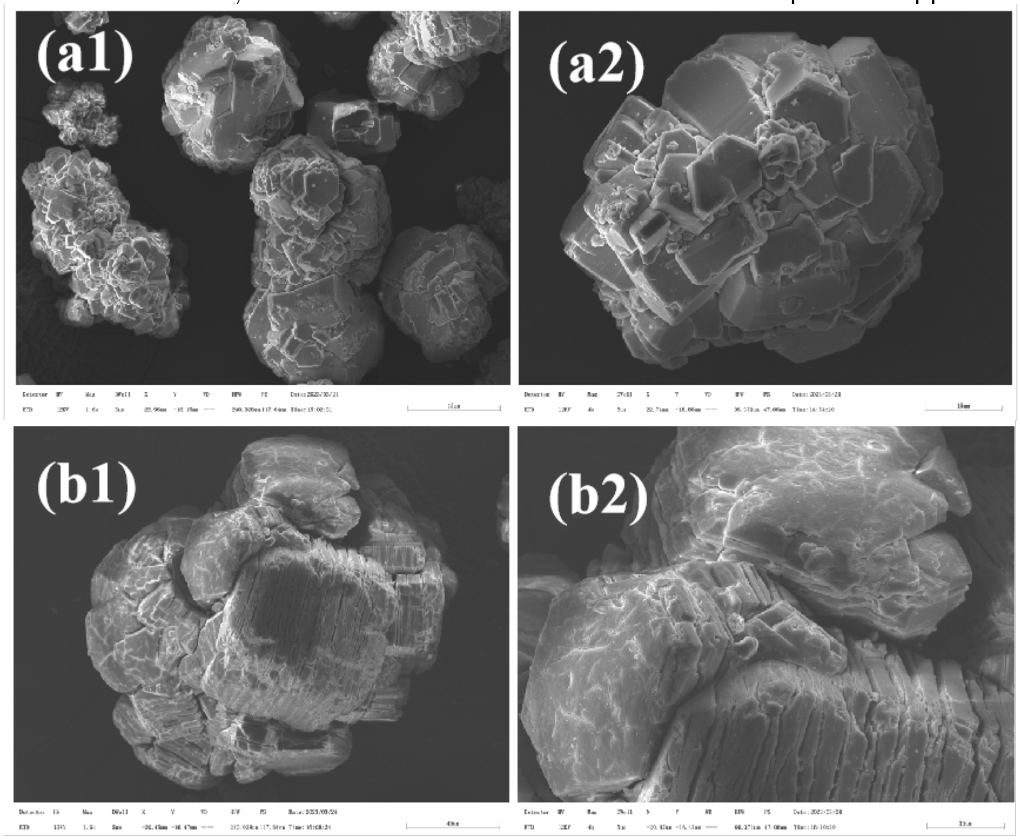

Figure 1. (A) SEM image of the original alumina particles (P-Al_2O_3, a1-a2), showing a smooth and relatively dense morphology, and (b1-b2) hierarchical alumina microspheres (H-Al_2O_3), which are composed of nanosheets arranged radially.

X-ray diffraction (XRD) analysis was carried out to assess the crystalline phases of the two alumina types. The diffraction patterns of both P-Al_2O_3 (Figure 2(a)) and H-Al_2O_3 (Figure 2(b)) exhibit sharp, well-defined peaks at 2θ values corresponding to the (012), (104), (113), (024), and (116) planes of α-Al_2O_3, in agreement with the standard JCPDS No. 10-0173 [10]. The absence of any secondary phases or shift in peak positions indicates that the morphological modulation introduced in the synthesis of H-Al_2O_3 does not alter its fundamental crystal structure. This confirms that the structural hierarchy is purely a morphological feature arising from controlled self-assembly, rather than from a change in chemical composition or lattice type.

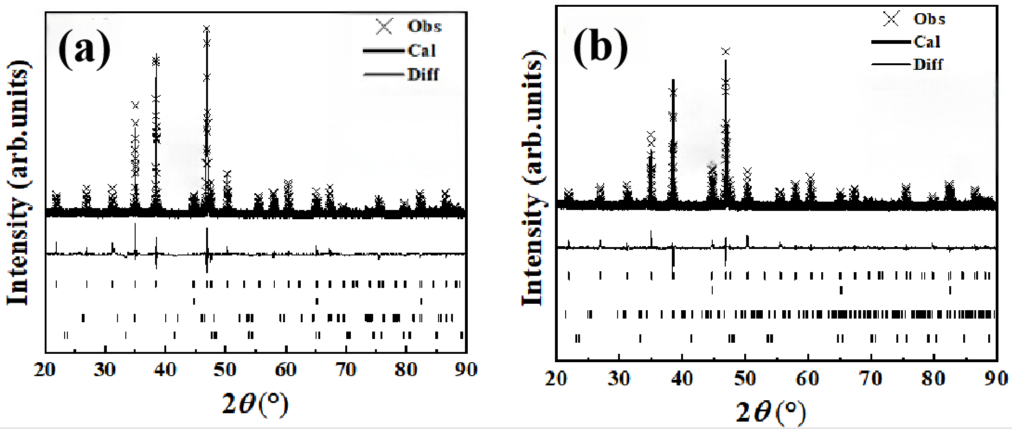

Figure 2. XRD patterns of P-Al_2O_3 (a) and H-Al_2O_3 (b) both show characteristic peaks corresponding to α-Al_2O_3.

Nitrogen adsorption–desorption analysis following the Brunauer–Emmett–Teller (BET) method was used to demonstrate a notable difference in specific surface area between the two samples [11]. P-Al_2O_3 exhibits a modest surface area of 4.8 $m^2{\cdot}g^{-1}$, typical for α-phase alumina with smooth morphology. In sharp contrast, H-Al_2O_3 achieves a surface area of 15.6 $m^2{\cdot}g^{-1}$, representing more than a threefold increase. The N_2 adsorption–desorption isotherm of H-Al_2O_3 displays a clear type IV profile with a pronounced hysteresis loop, indicating the presence of mesoporous features. This substantial enhancement in surface area is directly attributable to the nanosheet network and interstitial voids within the microsphere surface, enabling significantly greater contact with surrounding polymer chains in composite materials (Figure 3).

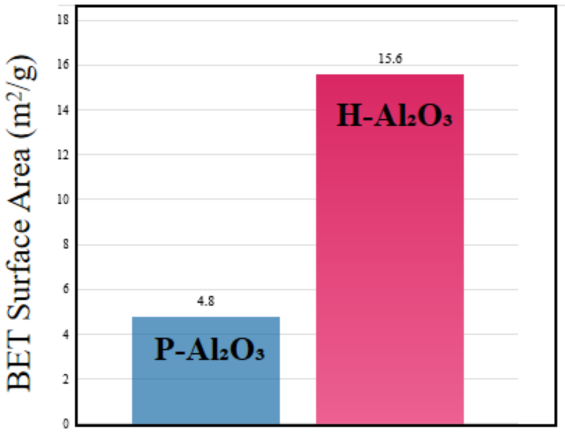

Figure 3. Comparison of the specific surface area values of P-Al_2O_3 and H-Al_2O_3 obtained through BET analysis.

The influence of these morphological differences on composite performance was evaluated using tensile testing, fracture toughness measurement, and dynamic mechanical analysis (DMA) of epoxy-based composites containing 10 wt% of each filler type. The composite incorporating P-Al_2O_3 registered a tensile strength of 78 MPa and a fracture toughness of 1.20 $MPa{\cdot}m^{1/2}$. By contrast, the H-Al_2O_3-filled composite exhibited tensile strength elevated to 91 MPa and fracture toughness increased to 1.48 $MPa{\cdot}m^{1/2}$, representing improvements of approximately 16.7% and 23.3%, respectively. The DMA results further confirm these trends, with the storage modulus at 25 °C rising from 2.1 GPa for the P-Al_2O_3 composite to 2.5 GPa for the H-Al_2O_3 composite, highlighting enhanced stiffness and elastic energy storage capacity (not shown). These results strongly support the premise that the increased surface roughness and porosity of H-Al_2O_3 facilitate superior stress transfer and delay crack propagation, thereby markedly improving overall mechanical performance.

Taken together, the combined findings from SEM, XRD, BET surface area analysis, and mechanical performance testing provide strong validation of the initial hypothesis that deliberate microstructural control of alumina fillers can markedly enhance the interfacial interactions between ceramic particulates and polymer matrices. The hierarchically engineered surface architecture of H-Al_2O_3 not only delivers a substantially higher specific surface area, as revealed by BET measurements, but also presents a multi-scale topography that facilitates more efficient polymer chain entanglement and mechanical interlocking at the filler–matrix boundary. XRD results confirm the preservation of crystalline integrity during morphological modification, while SEM imaging highlights the presence of radially aligned nanosheet assemblies that generate extensive porosity and three-dimensional surface roughness. This synergistic combination of structural features translates directly into measurable gains in composite performance, as evidenced by improvements in tensile strength, fracture toughness, and viscoelastic response. Collectively, these results underscore the potential of H-Al_2O_3 as a robust and versatile filler material, capable of enabling the development of next-generation high-performance polymer composites with enhanced durability and functional reliability.

5. Conclusion

In this work, we have successfully developed a facile and effective strategy for synthesizing hierarchically structured alumina microspheres (H-Al_2O_3) using a urea/SDS-assisted hydrothermal self-assembly route followed by high-temperature calcination. Compared with pristine alumina particles (P-Al_2O_3) obtained via a conventional hydrothermal method, the H-Al_2O_3 microspheres exhibit a markedly different morphology characterized by a spherical framework assembled from thin, radially oriented nanosheets. This architecture results in a rough, mesoporous surface with significantly higher specific surface area, without altering the α-Al_2O_3 crystalline phase. The morphology transformation is thus achieved purely by microstructural design, confirming the effectiveness of the combined templating and controlled precipitation approach.

Comprehensive characterization by SEM, XRD, and BET analyses provided direct evidence of the enhanced surface complexity and increased porosity of H-Al_2O_3. The BET surface area was increased by more than threefold relative to that of P-Al_2O_3, demonstrating the substantial impact of the hierarchical morphology on accessible surface sites. This increased surface exposure is critical in determining the extent and quality of interactions at the filler–matrix interface in polymer composite systems. The hierarchical structure inherently promotes better wetting, increased van der Waals interactions, and mechanical interlocking with the polymer chains, thereby improving load transfer efficiency within the composite.

The beneficial effects of introducing H-Al_2O_3 as a filler were further verified through mechanical performance testing of epoxy composites containing 10 wt% alumina. The composites reinforced with H-Al_2O_3 achieved higher tensile strength, greater fracture toughness, and an increase in storage modulus compared to those reinforced with smooth-surfaced P-Al_2O_3. These enhancements can be directly correlated to the unique three-dimensional nanosheet architecture of the H-Al_2O_3 microspheres, which maximizes filler–matrix contact and retards crack initiation and growth under mechanical loading.

Overall, the findings of this study provide compelling evidence that the deliberate engineering of hierarchical filler morphologies represents a highly effective and practical strategy for enhancing interfacial bonding and, consequently, overall composite performance. The synthesis methodology demonstrated here, while tailored to alumina, is inherently adaptable and can be extended to a broad range of ceramic systems and polymer matrices, making it a versatile framework for designing next-generation functional fillers. By integrating precise microstructural control into otherwise conventional material systems, it becomes possible to achieve significant performance gains—such as improved mechanical strength, fracture resistance, and durability—without necessitating major alterations to composite formulation or processing protocols. This approach not only offers a cost-effective pathway to performance optimization but also paves the way for the wider adoption of hierarchical ceramic fillers in advanced structural and multifunctional materials, spanning sectors from aerospace and automotive engineering to energy storage and protective coatings.

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