Calcium Phosphate-Coated Carbon Fibers as Efficient Reinforcements for High-Performance Hydroxyapatite Biocomposites

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Abstract

Hydroxyapatite (HAp)-based composites reinforced with carbon fibers have attracted considerable attention for load-bearing biomedical applications because they combine the excellent bioactivity of calcium phosphate ceramics with the superior mechanical properties of high-performance fibers. In this study, β-tricalcium phosphate (β-TCP)-coated carbon fibers were incorporated into a hydroxyapatite matrix to enhance interfacial bonding and improve the overall mechanical performance of the composite. Surface modification of the fibers was characterized using X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM), while the fabricated composites were evaluated in terms of density, bending strength, and Young's modulus.

The results demonstrated that β-TCP surface modification significantly improved the structural and mechanical characteristics of the composites. Compared with the composite reinforced with untreated carbon fibers, the coated-fiber composite exhibited an increase in density from 2.3 to 2.9 g cm^{-3} and a remarkable improvement in bending strength from 36 to 82 MPa, while maintaining a slightly lower Young's modulus that may provide better mechanical compatibility with bone tissue. SEM observations revealed a denser and more homogeneous microstructure with fewer visible defects, whereas XPS analysis confirmed the introduction of oxygen-containing functional groups that enhanced the surface reactivity of the fibers and promoted stronger interactions with the hydroxyapatite matrix. The β-TCP coating acted as an effective interfacial transition layer, facilitating stress transfer and improving composite integrity.

These findings demonstrate that β-TCP-coated carbon fibers provide an efficient reinforcement strategy for hydroxyapatite-based composites and highlight the importance of interface engineering in developing mechanically reliable biomaterials for orthopedic implants and bone reconstruction applications.

Keywords: Hydroxyapatite; Carbon fibers; Calcium phosphate coating; Surface modification; Interfacial adhesion; Mechanical properties; Biomaterials.

1. Introduction

Hydroxyapatite (HAp, $Ca_{10}(PO_4)_6(OH)_2$) is one of the most important calcium phosphate bioceramics used in orthopedic and dental applications because of its excellent biocompatibility, bioactivity, and osteoconductive properties. Owing to its close chemical resemblance to the mineral phase of human bone, HAp has been extensively employed in bone regeneration and implant technologies. However, its intrinsic brittleness and relatively low fracture toughness significantly limit its application in load-bearing environments, prompting extensive research into reinforcement strategies aimed at improving its mechanical performance while preserving its biological advantages (Furko et al., 2023, Abbas Alsalami & Abbas, 2024, Chun et al., 2022).

Fiber reinforcement has emerged as an effective approach for overcoming the mechanical limitations of brittle ceramic matrices. Among the available reinforcement materials, carbon fibers have attracted considerable attention due to their high tensile strength, low density, excellent fatigue resistance, and long-term structural stability. Recent developments in high-performance fibers have further expanded their applications in advanced composites, including biomedical materials where lightweight structures and superior mechanical properties are essential (Liu et al., 2024; Raja et al., 2025, Çelebi Efe & Yenilmez, 2022).

The incorporation of carbon fibers into hydroxyapatite matrices has demonstrated promising potential for improving strength, toughness, and durability without compromising bioactivity. Recent studies have reported that carbon fiber-reinforced hydroxyapatite composites exhibit enhanced mechanical and tribological performance, making them attractive candidates for bone reconstruction and tissue engineering applications. In particular, optimization of the reinforcement architecture and interfacial characteristics has been recognized as a key factor governing the overall behavior of these composites (Munaf Aljewari et al., 2024; Demirel, 2025, Ali et al., 2023).

Despite these advantages, achieving strong interfacial bonding between carbon fibers and hydroxyapatite remains a significant challenge. The chemically inert nature and relatively low surface activity of carbon fibers often result in insufficient adhesion with ceramic matrices, reducing stress transfer efficiency and increasing the likelihood of interfacial debonding and crack propagation under mechanical loading. Consequently, considerable attention has been directed toward surface engineering techniques that modify fiber chemistry and improve compatibility with surrounding matrices (Demirci & Bahce, 2023, Al Mamari et al., 2025).

Among these approaches, calcium phosphate-based coatings have proven particularly effective because they provide a bioactive transition layer that enhances fiber–matrix interactions while maintaining chemical compatibility with hydroxyapatite((Deng & Li, 2024,Kim et al., 2023,Yoo et al., 2022).

Surface-modified carbon fibers coated with calcium phosphate or related ceramic layers have demonstrated improved adhesion, greater structural integrity, and enhanced mechanical performance compared with untreated reinforcements. Furthermore, multilayer ceramic coatings can reduce interfacial defects and facilitate more efficient load transfer across the composite structure (Zhao et al., 2022; Zhao et al., 2024; Rogala-Wielgus & Zieliński, 2024).

Based on these recent advances, the present study investigates the influence of β-tricalcium phosphate (β-TCP) coatings on the interfacial characteristics and mechanical performance of hydroxyapatite/carbon fiber composites. Surface modification of the fibers was evaluated using X-ray photoelectron spectroscopy (XPS), while scanning electron microscopy (SEM) was employed to examine the morphology of the coated fibers and fabricated composites. The effects of the coating on density, bending strength, Young's modulus, and microstructural integrity were systematically assessed to provide further insight into the development of mechanically enhanced hydroxyapatite-based composites for potential bone reconstruction applications.

2. Experimental

2.1 Materials

Polyacrylonitrile (PAN)-based carbon fibers (Lanzhou Carbon, specific surface area: 0.78 $m^2\ g^{-1}$) were used as the reinforcing phase. Analytical-grade calcium nitrate tetrahydrate [$Ca(NO_3)_2 \cdot 4H_2O$], diammonium hydrogen phosphate [$(NH_4)_2HPO_4$, 99.5%], hydrochloric acid (HCl), and ammonium hydroxide (NH_4OH) were employed for the preparation of the calcium phosphate electrolyte. The electrolyte solution was prepared with a Ca^{2+} concentration of 4 mmol L^{-1}, a Ca/P molar ratio of 1.5, and adjusted to pH 4.6.

2.2 Surface Modification and Coating of Carbon Fibers

The carbon fibers were divided into two groups. The first group (C1) was used in its as-received condition without chemical treatment, whereas the second group (C2) was chemically activated by boiling in nitric acid for 3 h. After treatment, the fibers were thoroughly rinsed with distilled water and dried at 100 °C for 24 h.

Calcium phosphate coatings were subsequently deposited onto the activated carbon fibers using an electrodeposition process. In the electrochemical cell, the carbon fibers served as the cathode and graphite acted as the anode. Electrodeposition was carried out in the prepared electrolyte at 60 °C under continuous magnetic stirring with an applied potential of 50 mV for 2 h. The coated fibers were then removed, rinsed with distilled water to eliminate residual electrolyte, and dried at 100 °C for 72 h.

2.3 Fabrication of Hydroxyapatite/Carbon Fiber Composites

Hydroxyapatite composites reinforced with untreated and coated carbon fibers were fabricated through mechanical blending using a twin-screw mill to ensure homogeneous dispersion of the reinforcement within the ceramic matrix. The blended mixtures were subsequently consolidated by compression molding and sintered under vacuum conditions to obtain dense composite specimens suitable for microstructural and mechanical characterization.

2.4 Characterization

The surface chemical characteristics of untreated and modified carbon fibers were analyzed using X-ray photoelectron spectroscopy (XPS) to evaluate the changes induced by chemical treatment and coating deposition. The morphology of the coated fibers and the microstructure of the fabricated composites were examined using scanning electron microscopy (SEM) after gold sputter coating. Mechanical performance was assessed by measuring the density, bending strength, and Young's modulus of the fabricated composites, allowing the influence of surface modification and calcium phosphate coating on the structural integrity and interfacial performance of the HAp/carbon fiber system to be systematically evaluated.

3. Results and Discussion

3.1 Mechanical Properties of Hydroxyapatite/Carbon Fiber Composites

The physical and mechanical properties of the fabricated hydroxyapatite/carbon fiber composites are presented in **Table 1**. The results clearly demonstrate that the surface modification of carbon fibers and the subsequent deposition of a β-tricalcium phosphate (β-TCP) coating substantially influenced the overall performance of the composites.

Table 1. Physical and mechanical properties of hydroxyapatite/carbon fiber composites reinforced with untreated and β-TCP-coated carbon fibers.

Composite	Reinforcement Type	Density (g/cm^3)	Bending Strength (MPa)	Young's Modulus (GPa)
I	HAp + untreated carbon fibers	2.3	36	87
II	HAp + β-TCP-coated carbon fibers	2.9	82	79

Compared with the composite reinforced with untreated carbon fibers (Composite I), the β-TCP-coated system (Composite II) exhibited a markedly higher density and bending strength. The density increased from 2.3 to 2.9 g cm^{-3}, indicating improved consolidation and reduced structural defects, while the bending strength increased from 36 to 82 MPa, corresponding to an enhancement of approximately 128%. This substantial improvement demonstrates the effectiveness of β-TCP surface modification in strengthening the interaction between the reinforcement and the hydroxyapatite matrix.

In contrast, Composite II exhibited a modest reduction in Young's modulus from 87 to 79 GPa. Although this decrease reflects slightly lower stiffness, it may be advantageous for biomedical applications because materials with elastic moduli closer to those of natural bone can reduce stress shielding and promote more favorable load transfer at the implant–bone interface. Therefore, the simultaneous increase in bending strength and moderate reduction in stiffness suggests an overall improvement in the biomechanical suitability of the coated composite.

The enhanced mechanical behavior can be attributed primarily to the improved interfacial adhesion resulting from the β-TCP coating. A stronger interface facilitates more efficient stress transfer from the hydroxyapatite matrix to the reinforcing fibers, thereby delaying crack initiation and limiting interfacial debonding during loading. In addition, the coating is expected to reduce local defects at the fiber–matrix boundary and contribute to a more integrated composite microstructure.

These findings are consistent with recent reports demonstrating that calcium phosphate-based surface modifications significantly improve the mechanical performance of carbon fiber-reinforced hydroxyapatite composites through enhanced interfacial compatibility and optimized load transfer mechanisms (Zhao et al., 2022; Demirci & Bahce, 2023; Zhao et al., 2024). Likewise, recent investigations on hybrid hydroxyapatite/carbon fiber systems have emphasized that appropriate surface engineering of reinforcing fibers is essential for achieving superior structural integrity and mechanical reliability in biomedical composites (Munaf Aljewari et al., 2024; Demirel, 2025).

Overall, the results presented in Table 1 demonstrate that β-TCP-coated carbon fibers provide an effective reinforcement strategy for hydroxyapatite-based composites, yielding materials with improved density, significantly enhanced bending strength, and mechanical characteristics that are potentially more compatible with load-bearing orthopedic applications.

3.2 Microstructural Analysis by Scanning Electron Microscopy

Scanning electron microscopy (SEM) was employed to investigate the influence of fiber surface modification on the microstructure of the fabricated hydroxyapatite composites. As illustrated in **Figure 1**, the composite reinforced with untreated carbon fibers (Composite I) exhibited a relatively porous microstructure with visible cracks and discontinuities distributed throughout the matrix. These structural imperfections are indicative of insufficient interfacial bonding between the untreated fibers and the hydroxyapatite matrix, which can adversely affect stress transfer and mechanical performance.

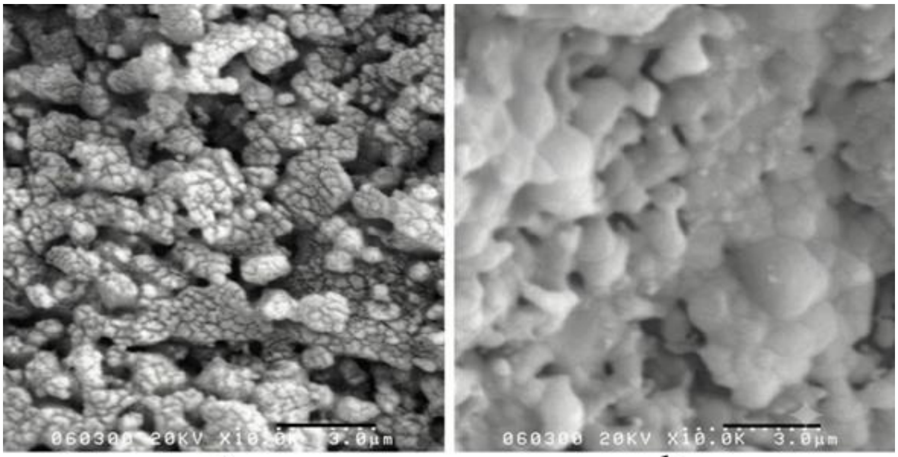

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Figure 1 SEM images illustrating the microstructural characteristics of HAp/carbon fiber composites: (a) Composite I containing untreated carbon fibers, showing a relatively porous structure with visible cracks, and (b) Composite II containing β-TCP-coated carbon fibers, exhibiting a denser and more homogeneous microstructure.

In contrast, the composite reinforced with β-TCP-coated carbon fibers (Composite II) displayed a denser and more homogeneous morphology with a noticeable reduction in microcracks and interfacial defects. The coated fibers appeared to be more effectively integrated within the ceramic matrix, suggesting improved compatibility and stronger interfacial adhesion. The enhanced microstructural integrity is consistent with the higher density and bending strength observed in the mechanical characterization.

The improved morphology can be attributed to the presence of the calcium phosphate coating, which provides a chemically compatible transition layer between the carbon fibers and the hydroxyapatite matrix. This interfacial layer promotes more uniform stress distribution during processing and mechanical loading while reducing the likelihood of crack initiation and propagation. Similar observations have been reported in recent studies, where calcium phosphate-coated carbon fibers significantly enhanced the structural cohesion and mechanical performance of hydroxyapatite-based composites (Zhao et al., 2024; Demirel, 2025).

Overall, the SEM observations confirm that surface modification of carbon fibers plays a crucial role in improving composite densification and interfacial integrity, thereby contributing directly to the superior mechanical behavior of the β-TCP-coated hydroxyapatite/carbon fiber composite.

3.3 Surface Chemical Characterization by XPS

The surface chemical composition of the untreated and chemically modified carbon fibers was investigated using X-ray photoelectron spectroscopy (XPS), and the corresponding spectra are presented in **Figure 2**. The analysis revealed noticeable changes in the surface chemistry of the fibers after nitric acid treatment and subsequent calcium phosphate deposition. In particular, the modified fibers exhibited an increased intensity of oxygen-containing functional groups, including C–O, C=O, and O–C=O species, indicating successful surface activation.

The introduction of these polar functional groups enhances the surface energy and wettability of the carbon fibers, thereby improving their affinity toward the hydroxyapatite matrix. Such chemical activation provides favorable nucleation sites for calcium phosphate deposition and promotes stronger physicochemical interactions at the fiber–matrix interface. As a consequence, the modified fibers are expected to facilitate more efficient stress transfer and reduce the likelihood of interfacial debonding under mechanical loading.

The XPS findings are consistent with the mechanical results presented in Table 1 and the SEM observations shown in Figure 1. The enhanced surface reactivity resulting from chemical treatment contributes to the formation of a more integrated composite structure, which is reflected by the higher density and significantly improved bending strength of the β-TCP-coated composite. These observations agree with recent reports demonstrating that surface functionalization of carbon fibers is an effective strategy for improving interfacial bonding and mechanical reliability in hydroxyapatite-based composites (Demirci & Bahce, 2023; Zhao et al., 2022; Zhao et al., 2024).

Therefore, XPS analysis provides direct evidence that surface chemical modification plays a fundamental role in strengthening the interaction between carbon fibers and the hydroxyapatite matrix, ultimately contributing to the enhanced structural integrity and biomechanical performance of the fabricated composites.

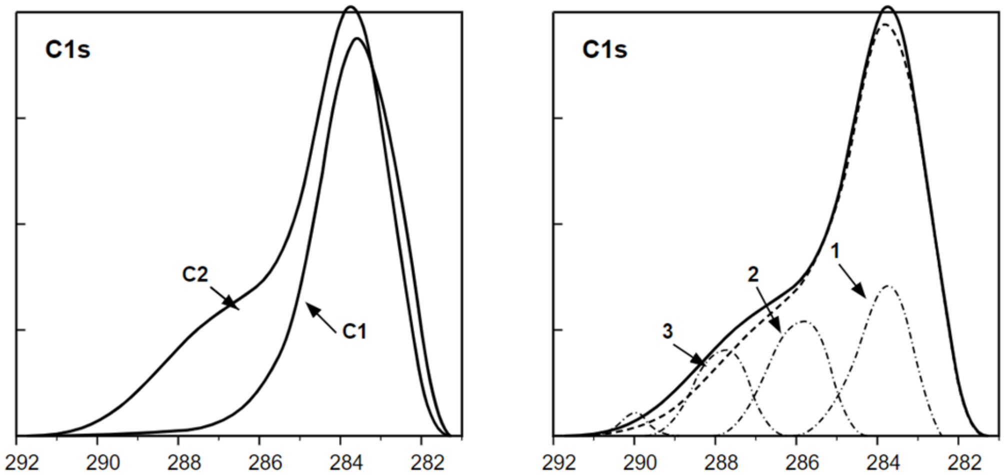

Figure 2. X-ray photoelectron spectroscopy (XPS) spectra of untreated (C1) and chemically modified (C2) carbon fibers, illustrating the increased abundance of oxygen-containing functional groups after surface treatment. The enhanced surface functionality promotes calcium phosphate deposition and improves interfacial bonding with the hydroxyapatite matrix.

3.4 Morphology of β-TCP-Coated Carbon Fibers

The morphology of the calcium phosphate-coated carbon fibers was examined by scanning electron microscopy (SEM), as presented in **Figure 3**. The micrographs reveal the successful formation of a continuous coating layer on the fiber surface, indicating that the electrodeposition process effectively modified the carbon fibers without causing apparent structural damage.

Compared with untreated fibers, the coated fibers exhibited a rougher surface texture and a more uniform coverage, features that are expected to increase the effective contact area between the reinforcement and the hydroxyapatite matrix. Such morphological changes are beneficial for promoting mechanical interlocking as well as physicochemical interactions at the interface, thereby improving stress transfer efficiency under external loading.

The presence of the β-TCP coating also provides a compatible intermediate layer between the carbon fibers and the surrounding ceramic matrix. This transition layer is expected to reduce local stress concentrations and minimize the formation of interfacial defects during composite fabrication and service. Consequently, the coated fibers contribute to improved densification and structural continuity, consistent with the higher density and bending strength observed for Composite II.

The SEM observations further support the XPS results, which demonstrated enhanced surface functionality following chemical treatment. Together, these findings indicate that both chemical activation and calcium phosphate deposition play complementary roles in improving fiber–matrix interactions and overall composite performance. Similar improvements in interfacial morphology and mechanical behavior have been reported for calcium phosphate-coated carbon fiber systems and related biomedical composites in recent studies (Demirci & Bahce, 2023; Zhao et al., 2022; Zhao et al., 2024).

Overall, the SEM analysis confirms that the electrodeposited β-TCP coating provides a homogeneous and well-adhered surface modification that enhances the compatibility between carbon fibers and the hydroxyapatite matrix, thereby contributing to the superior mechanical properties of the fabricated composites.

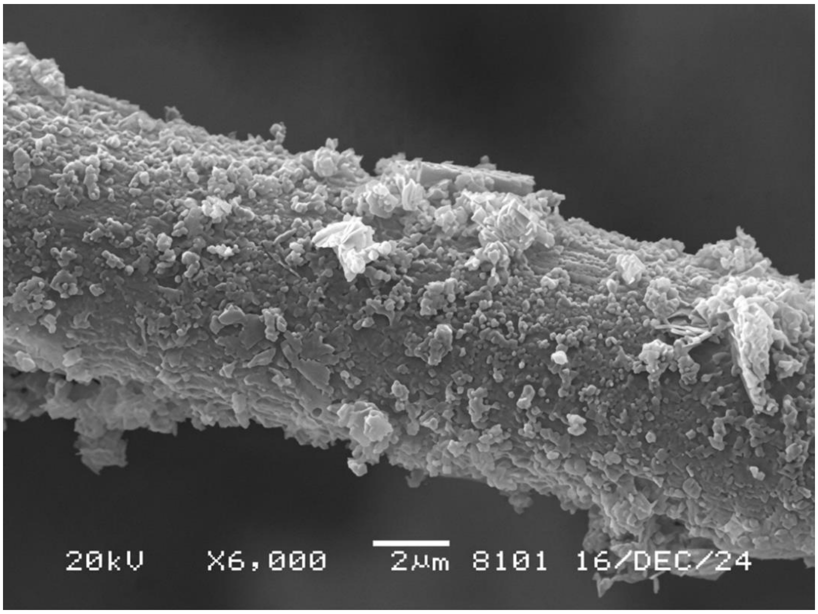

Figure 3. SEM image of β-tricalcium phosphate (β-TCP)-coated carbon fibers after electrodeposition, showing the formation of a continuous and uniformly distributed surface layer. The coating increases surface roughness and provides a favorable interface for stronger adhesion with the hydroxyapatite matrix, contributing to improved composite integrity and mechanical performance.

4. Conclusions

In this study, β-tricalcium phosphate (β-TCP)-coated carbon fibers were successfully employed as reinforcing agents for hydroxyapatite-based composites to improve their interfacial characteristics and mechanical performance. The combined results obtained from mechanical testing, X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM) demonstrated that surface modification of carbon fibers plays a crucial role in enhancing the overall quality of the composite.

The β-TCP-coated composite exhibited a significant improvement in bending strength together with an increase in density compared with the composite reinforced with untreated carbon fibers, indicating more effective load transfer and improved structural consolidation. Although a slight reduction in Young's modulus was observed, this change may provide better mechanical compatibility with natural bone and could be advantageous for load-bearing biomedical applications.

XPS analysis confirmed that chemical treatment increased the abundance of oxygen-containing functional groups on the carbon fiber surface, creating favorable sites for calcium phosphate deposition and strengthening interfacial interactions. SEM observations further revealed that the coated fibers were associated with a denser and more homogeneous composite microstructure containing fewer visible defects and microcracks, supporting the improvements observed in the mechanical properties.

Overall, the findings demonstrate that β-TCP surface coating is an effective strategy for enhancing the interfacial bonding and structural integrity of hydroxyapatite/carbon fiber composites. The proposed approach offers a promising route for the development of mechanically improved bioactive materials with potential applications in bone repair, orthopedic implants, and tissue engineering. Future studies may focus on evaluating the long-term biological performance, fracture toughness, wear resistance, and in vitro or in vivo behavior of these composites to further assess their clinical potential.

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