

# Effect of carbon fiber on calcium phosphate bone cement<sup>①</sup>

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**Abstract:** The calcium phosphate cement ( $\alpha$ -TCP/TTCP) was reinforced with oxidation-treated carbon fibers. The effect of aspect ratio and content of carbon fiber on the compression strength and bending strength of the hardened body was discussed. The results show that the reinforcing effect is optimal as the aspect ratio is 375 and the additive amount is 0.3% (mass fraction). Under this condition, the compressive strength is increased by 55% (maximum 63.46 MPa), and the bending strength is nearly increased by 100% (maximum 11.95 MPa), respectively. However, if the additive quantity and aspect ratio are too high, the effect of the carbon fibers is limited because it can not be dispersed uniformly in the hardened body. The biological evaluation indicates that the calcium phosphate cement reinforced by carbon fibers has good biocompatibility.

**Key words:** calcium phosphate cement; oxidation treatment; carbon fiber; reinforcement; biocompatibility

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## 1 INTRODUCTION

The mechanical properties of the hardening body of calcium phosphate cement (CPC) depend on the pore distribution and porosity to a great extent, because it is a brittle porous material. During hardening, microflaws inevitably appear in the body because of the change of microstructure and volume. Hence, the flaws rapidly develop into big cracks and result in brittle fracture in the hardening body if the load reaches a certain value. The materials exhibit abrupt failure breaking under external force without any sign<sup>[1-5]</sup>. Many scholars thought that it was very difficult to overcome the shortcoming of cement itself. In order to overcome the disadvantages such as low strength and high brittleness, Ishikawa used two methods to decrease the porosity and improve the strength of the CPC hardened body by increasing the solid-liquid ratio and pressing (173 MPa) the CPC in a mould during the process hardening. The results showed that the porosity was only decreased by 26% - 28% and the flexural strength increased by at most 150%. Furthermore, the advantage of shaping the CPC at random would be lost in clinic application<sup>[6,7]</sup>. In the point of view of fracture mechanics, the methods of overcoming brittleness and improving strength are the following: reducing the stress concentration of crack tips and improving the capability of resisting crack growth, having energy consuming

mechanism to absorb the energy of external load and avoid cracks further extending, or setting obstacles in the matrix to prevent cracks from extending. Therefore, using carbon fibers to reinforce cement is one of the most effective methods<sup>[8-11]</sup>. Carbon fibers can decrease the number of microcracks, which result from the shrinkage of the cement matrix and reduce the size, prevent the microcrack growth in the hardened body at the initial stage of enduring load and ultimately become the main loader of external load. In addition, carbon fiber (CF) reinforced calcium phosphate cement shows high tensile strength and modulus of elasticity in tension, light mass and bearing abrasion, good electric and heat conductivity, excellent biostability, favorable blood compatibility, and biocompatibility<sup>[12-15]</sup>. Cement materials reinforced by CF also have higher toughness and ductility, good abrasion performance, dimension stability and can improve the flexural strength and prevent cracks forming during dry shrinking. Therefore both the physical and chemical properties as well as the biological performance of CF are fit to reinforce biological cement. This paper discussed  $\alpha$ -TCP/TTCP composite cement reinforced by oxidation-treated CF.

## 2 MATERIALS AND METHODS

### 2.1 Preparation of CPC powder

The  $\alpha$ -tricalcium phosphate ( $\alpha$ -TCP) was synthesized at 1 250 °C from a mixture of analytical

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grade dicalcium phosphate dihydrate ( $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ) and calcium carbonate ( $\text{CaCO}_3$ ) with molar ratio of 2: 1. The tetracalcium phosphate (TTCP) was prepared by heating an equimolar mixture of  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{CaCO}_3$  at 1 500 °C for 6 h and quenching at room temperature.  $\alpha$ -TCP and TTCP were combined in an appropriate ratio and milled together down to the appropriate particle size ( $< 16 \mu\text{m}$ ) in an agate ball mill to prepare calcium phosphate cement (CPC,  $\alpha$ -TCP/TTCP) powder.

## 2.2 Pretreatment of CF

The carbon fibers with a diameter of 12  $\mu\text{m}$ , tensile strength of 80–120 mm and elastic modulus of  $(4.9 - 9.8) \times 10^4$  MPa were supplied by Shanghai Carbon Factory. The carbon fibers were cleaned with deionized water to remove any contamination, dried in air, and exposed for 2 h in 0%, 2%, 4%, 6%, 8%, 10% (mass fraction) NaOH solution at 80 °C. The surface modified fibers were washed again in deionized water, subsequently dried in an oven at 150 °C, and cut into different length samples.

## 2.3 Preparation of samples

The different aspect ratio carbon fibers, which were treated with different concentrations of NaOH solution, were fully mixed with CPC cement according to different mass fraction. The CPC powder was respectively stirred up with the liquid (the solution contains three carboxyl acid groups) at the required solid-liquid ratio. The mixed paste was poured into split moulds of 30 mm  $\times$  10 mm  $\times$  10 mm and 10 mm  $\times$  10 mm  $\times$  10 mm, and then put in an incubator kept at 37 °C and 100% relative humidity for 24 h. Finally, the samples were used to test the compressive and bending strength.

## 2.4 Testing

### 2.4.1 X-ray photoelectron spectrum

The surface modification of the chopped and strand fibers was analyzed using X-ray photoelectron spectrometer (ESCALAB MK II, Britain) with a magnesium  $K_{\alpha}$  X-ray source, operated at a constant power of 200 W (10 kV, 20 mA).

### 2.4.2 Compressive and bending strength

The strength was determined on electro-hydraulic servo controlled testing system (INSTRON 1341, Instron Ltd., Britain) with a crosshead speed of 0.5 mm/min and 1.3 mm/min, respectively. The compressive strength value and the setting time represented the average values obtained from at least five samples.

### 2.4.3 Microstructure

The cement hydration products were observed by scanning electron microscope (SEM, SX-40, Akashi Seisakusho Ltd., Japan).

## 2.5 Biocompatibility experiments

The hardened powder or body containing 0.3% (mass fraction) CF (treated by 8.0% NaOH solution) was used to conduct acute and subacute toxicity tests as well as muscle stimulation, heat source, haemolysis, cruor and implantation experiments on health rats and normal person's blood to determine the biocompatibility of CPC.

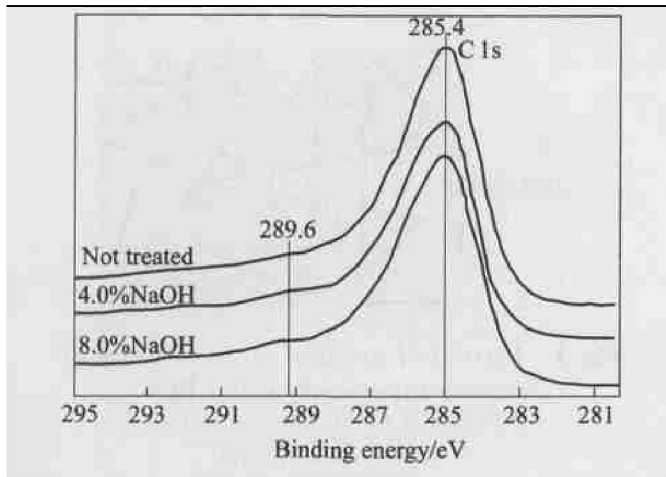
## 3 RESULTS AND DISCUSSION

### 3.1 Pretreatment of CF

The surface of the carbon fibers is apolar and hydrophobic. However, the particles of CPC are polar and hydrophilic. Therefore, the dispersion effect of untreated CF was not ideal and the interfacial adhesion between CF and cement matrix, especially the shear strength was low. In order to enhance the reinforcing effect of CF within the cement matrix, a liquid phase oxidation method was utilized to treat the CF surface. Fig. 1 shows the high-resolution spectra of  $C_{1s}$  core level for the untreated and treated carbon fiber surfaces. The  $C_{1s}$  major peak is at 285.4 eV (the carbon of graphite) and several weak peaks appear at higher binding energies between 288.0 eV and 291.0 eV (Carboxyl  $\text{C}=\text{O}$ , hydroxyl  $-\text{OH}$ , carboxyl  $-\text{COOH}$ ). After being treated with NaOH solution, the major peak of the carbon fibers is widened, the weak peaks appear and moved toward higher binding energies. The higher the concentration of NaOH, the stronger the peak at 289.60 eV. This indicates that the fiber surfaces oxidized by high concentrated NaOH solution contain a certain amount of carboxylic acid groups ( $-\text{COOH}$ ). Increasing the concentration of NaOH, the Na concentration also increases and some carboxylic acid, which incorporates into the fiber surface, may be converted into a Na-labeled carboxyl group ( $-\text{COO}^{-1}\text{Na}^{+}$ ) yielded by a neutralization reaction between  $-\text{COOH}$  and NaOH. The flexural strength and pull-out load of the treated CF are shown in Table 1. The data clearly indicate that the oxygen content of the fiber surfaces is increased and the flexural strength and pull-out load are improved at enhanced oxidization. The flexure strength strongly depends on the oxygen concentration incorporated into the fiber surfaces. The O/C ratio, flexural strength, and pull-out load of the carbon fibers are all increased by about 100% after being treated with 8.0% NaOH solution.

**Table 1** Structure performance of carbon fiber

$w(\text{NaOH})/\%$	O/C ratio	Flexural strength/MPa	Pull out load/N
0	0.079	7.21	24.73
4.0	0.108	11.95	46.84
8.0	0.117	13.34	56.62



**Fig. 1**  $C_{1s}$  spectra of fiber surfaces after being treated by NaOH solution

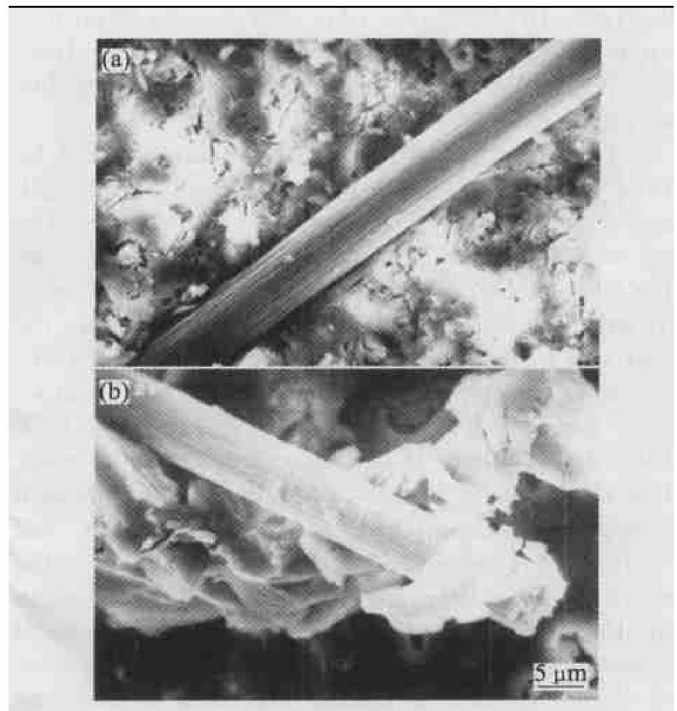
### 3.2 Effect of aspect ratio and CF content on compressive and bending strength

The carbon fibers with an aspect ratio (L/D) of 375 were modified by 0, 2%, 4%, 6%, 8%, 10% NaOH solution respectively, then uniformly mixed with CPC powder in 0.3% additive, and stirred up with solidified liquid to obtain the hardened bodies. The compressive strength is shown in Table 2. The results show that the compressive strength of the hardened bodies reinforced by CF is increased at higher concentration of NaOH and the degree of oxidation improves. As shown in Fig. 2, the surface morphology of the untreated fibers does not change and is smooth. The fibers are clearly separated from the matrix and completely exposed during the pulling process, which corresponds to the typical carbon fiber pull-out characteristics. Most of the fiber surfaces seem to be free of hydration products, suggesting that the interfacial bond between the untreated fibers and the CPC matrices is weak. In contrast, a good interfacial bond can be observed on the treated fibers, which contain flocculation hydration products that adhere irregularly to the surface. However, the rough-

ness and morphology of the treated (no matrix substance adhered) and untreated CF surfaces are almost the same. Therefore, the surface oxidation treatment of CF only increases the oxygenic groups and the improvement of flexural strength and pull-out load is related to the increase of oxygen content. Thus, a highly oxidized surface interacts more favorably with the cement matrix.

**Table 2** Reinforcing effect of carbon fiber treated with different concentration of NaOH

$w(\text{NaOH})/\%$	0	2	4	6	8	10
Compression strength/MPa	48.45	56.87	58.72	61.51	63.46	60.37



**Fig. 2** SEM photos of fracture of CF/ $\alpha$ -TCP-TTCP composite material

- (a) —Reinforced by unoxidized CF;  
(b) —Reinforced by 8.0% NaOH-oxidized CF

**Table 3** Effect of aspect ratio and content of carbon fiber on strength of  $\alpha$ -TCP/TTCP bone cement

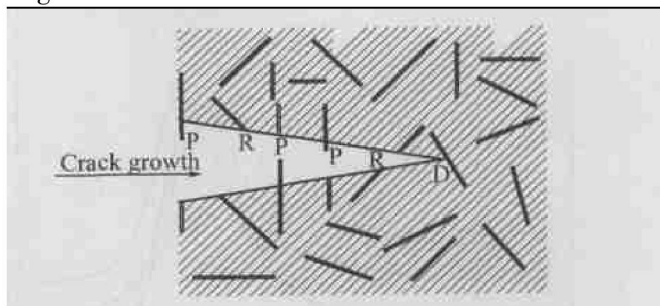
CF content/ %	Aspect ratio									
	125		250		375		500		650	
	C. S/MPa	B. S/MPa	C. S/MPa	B. S/MPa	C. S/MPa	B. S/MPa	C. S/MPa	B. S/MPa	C. S/MPa	B. S/MPa
0.05	42.11	7.82	44.28	8.04	46.76	8.31	45.01	8.26	43.07	8.05
0.1	46.98	8.35	50.03	8.82	54.05	8.93	52.42	8.54	49.44	8.12
0.2	48.49	8.78	53.26	9.15	58.13	9.82	54.98	9.12	51.26	8.23
0.3	52.30	9.24	58.01	10.22	63.46	11.95	55.27	9.87	51.98	7.99
0.4	50.04	8.93	54.78	9.31	58.20	11.08	50.88	9.93	48.32	7.87

C. S: Compression strength; B. S: Bending strength

As shown in Table 3, the strength of the composite material is improved by increasing the CF length in the CPC until a CF aspect ratio of 375. The cracks of loaded cement composite body are initiated and developed from microcracks or other defects in the matrix. The formation of cracks causes the stress concentration. As soon as the tensile load in stress concentration zones exceeds the tensile strength, the matrix is destroyed. The addition of CF in CPC increases the quantity of the interface, which can absorb some energy and prevent crack propagation. Furthermore, CF can absorb external energy in composite material, relieve the stress concentration in the crack tips and prevent crack extension. In addition, fibers with high modulus of elasticity can also share a great amount of stress. In short, the fiber that acts as reinforcer can prevent crack from expanding, conduct fracture energy to the matrix and obtain higher strength.

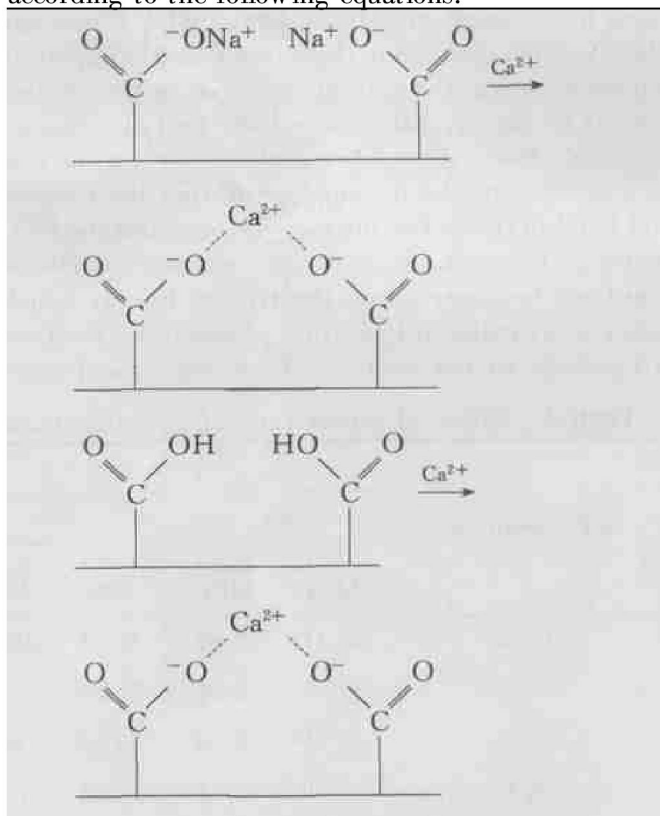
The length of the CF can be characterized by three parameters: the insertion length (length from crack surface to fiber tip), pull-out length, and critical length. As shown in Fig. 3, the fiber that is perpendicular to crack can hold back crack growth most effectively. Under this condition, the fiber can bridge the gap of the crack. The extension and fracture energy absorption of the fiber cause the destruction of the chemical bonds of both sides of the crack. If the insertion length is lower than the pull-out length, the chemical bonds will be destroyed completely and simultaneously and the fiber will be pulled out from the matrix. If the insertion length is greater than the pull-out length but lower than the critical length, the chemical bonds will be destroyed gradually toward the fiber tip until the fiber is pulled out. If the insertion length is greater than the critical length, the bonds will be destroyed at the beginning and the fiber will break. Both the fiber pull-out and fracture can absorb the energy conducted from the crack tips. At a certain amount of fracture energy, no CF pull-out or fracture occurs and only some bonds are destroyed, because most of the energy of applied load is absorbed by the CFs. Therefore, the fracture of the material is reduced and the strength is improved. If the length of the fibers is too short, the effect of stress conduction from the matrix to the fibers is not obvious and the capacity of inhibiting crack growth is weak. Moreover, the pulling out of short fibers from matrix is not an appropriate energy absorbing mechanism, so that the reinforcing effect is not ideal. At higher fiber length, the strength of the composite material is im-

proved. However, if the fibers are too long, they are difficult to uniformly disperse in the CPC matrix. Thus, the strength is decreased when the aspect ratio is greater than 375.



**Fig. 3** Pattern of invalidation mechanism of carbon fiber reinforcing CPC  
(P—Pull out CF; R—Break out CF; D—Destruction of bond)

The interface binding force between the CF and the matrix consists of mechanical, physical (van der Waals forces and hydrogen bond) and chemical adhesion. Because the untreated CF can not react with the CPC, the interfacial adhesion between the cement and the CF is mainly caused by mechanical interlocking and weak physical forces. If the interfacial adhesion is not strong enough to bear the destruction force conducted from matrix, a large amount of CF will be pulled out. Thus, the reinforcing effect of the untreated fibers is weak. The surface of the treated fibers contains  $-\text{COO}^- \text{Na}^+$  and  $-\text{COOH}$ , which can react with  $\text{Ca}^{2+}$  in CPC and produce calcium salts according to the following equations:



The monobasic  $\text{Na}^+$ , which is bound to only one

COO<sup>-</sup> group, can be replaced by Ca<sup>2+</sup> and two adjacent monobasic groups bound with one Ca<sup>2+</sup>. The remaining carboxylic acid groups without a Na labeled can also link up with the Ca<sup>2+</sup>. The substitution of Na<sup>+</sup> by Ca<sup>2+</sup> and the subsequent binding of Ca<sup>2+</sup> to two adjacent monobasic groups can promote the precipitation of hydroxyapatite hydration products, which provides the chemical interfacial adhesion and thereby improving the mechanical properties of CF-reinforced CPC composites.

Thus, it can be seen that the adhesion between the CFs and the matrix is caused by the formation of chemical bands. Besides those chemical bands, there are many other kinds of adhesion forces between the treated CFs and the CPC matrix that improve the reinforcement function of the CFs. Moreover, the formation of chemical bonds is the main reason that the flexural strength and pull out load are improved after surface modification.

As shown in Table 3, the increase of the fiber content up to 0.3% is correlated to the improvement of the CPC strength, because the CFs relieve the stress concentration zones and participate in the pull out function. The higher content of CFs can more effectively prevent crack growth. As soon as the additive amount of the CFs is higher than 0.3%, the compressive strength begins to decrease. The reason may be a large amount of air that is introduced into the compound body at increased fiber contents and forms a large amount of micro-bubble in the composite after hardening. And the existence of bubble will result in the decline of the compressive strength. Besides that, more CFs are difficult to disperse and the conglomeration and non-uniform structure lower the material performance. This shows that the CF aspect ratio and additive amount are essential for the material strength. In these experiments, the highest compressive strength is 63.46 MPa and the maximum bending strength is 11.95 MPa at an aspect ratio of 375

and an additive amount of 0.3% (mass fraction). If the additive amount and aspect ratio are too high, the function of carbon fibers is limited because of the non-uniform distribution.

The higher the oxidation degree, the more the chemical bonds are formed and the interfacial adhesion improved. Even in case of fiber breakage at the weakest point, the rest of the fiber can still bear load. As a result, the improvement of the interfacial adhesion and bonding force strength between CF and CPC matrix will lead macroscopically to a higher material composite strength. The initiation of the crack usually takes place at the interface between the fiber and the matrix. Thus, due to the increase of the oxidation degree and the interfacial adhesion, the initiation of cracks hardly takes place and the cracks hardly grow in the interface, and so less energy is absorbed and the strength of material is increased. However, Table 2 shows that the compressive strength is reduced as soon as the concentration of NaOH solution is higher than 8%. The reason is assumed that the higher the NaOH concentration, the more the COO<sup>-</sup> group appears on the CF surface. Hence, the reaction rate is increased between CPC and CFs. The quick reaction results in a great amount of porous hydration products precipitating on the fiber. Furthermore, the Ca-rich porous hydrate layers is formed and the compression strength is decreased.

### 3.3 Biocompatibility

All experimental animals moved freely and had a normal appetite. None of them died during the tests or showed bad response such as convulsion or dyspnea. The results of seven different biocompatibility tests are shown in Table 4. The  $\alpha$ -TCP/TTCP bone cement reinforced by 8% NaOH oxidation treated CFs showed innocuity and non-stimulation to tissue, did not contain heat resource substance or cause any kind of general or local toxicity

**Table 4** Result of biological tests

Test items	Results
Acute toxicity experiments	No cacoethic response such as death, convulsion and coma
Sub-acute toxicity experiments	No remarkable difference for blood routine and hematoblast whether injecting materials or not ( $P > 0.05$ ), no cells denaturalization or necrosis in slice of heart, liver and kidney.
Muscle stimulation experiments	No remarkable difference compared with contrast group, no denaturalization or necrosis, no effusion or inflammatory cell infiltrating around peripheral muscle of implanted materials. No erythrocyte fracture or agglutination.
Heat source experiments	All tests of limulus polyphemus were negative, containing no heat source substance.
Hemolysis experiments	Hemolysis ratio ( $3.2 \pm 0.8$ )%, no hemolysis response.
Cruor experiments	Four indexes of PT, APT.T, TT and albuminofibrin being in normal range and no influence to cruor function.
In vivo implantation test experiments	After 8 months, material being substituted for bony tissue and both merged for a whole organization

response as well as muscle stimulation, hemolysis, cruor, inflammation or repulsion response. Hence, the investigated CPC shows good biocompatibility.

#### 4 CONCLUSIONS

The results of improving the strength of calcium phosphate cement (CPC) by reinforcing with oxidation treated carbon fiber (CF) were described. As the fracture energy is partially absorbed by the CFs, the macroscopical strength of the composite material can be improved. In order to further increase the material composite strength, which corresponds to the interfacial adhesion between the CFs and the CPC matrix, the CFs were oxidation treated with NaOH solution. Due to the oxidation treatment, the chemical bonds are formed between the CFs and the matrix, so as to the flexural strength and pull-out load of the CFs within the CPC matrix can be improved. The reinforcing effect is optimal using a 8% NaOH solution, an aspect ratio of 375, and an additive amount of 0.3%. Under these conditions, the compressive strength is increased by 55% (the highest strength is 63.46 MPa) and the bending strength is nearly increased by 100% (the highest strength is 11.95 MPa). However, if the additive amount and the aspect ratio are too high, the function of the carbon fibers is limited because of a non-uniform distribution within the CPC matrix. The biological evaluation indicates that CPC reinforced by carbon fibers shows good biocompatibility.

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