Surface modification of activated carbon cloth with calcium silicate and hydroxyapatite: bioactive composite material

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ABSTRACT

In this study new compounds consisting of activated carbon cloths (ACC) modified with calcium silicate (CaSiO3) were prepared for hydroxyapatite (HAP) generation. ACC samples were oxidized with 8 M HNO3 at different times (15 min and 2 h), to increase oxygenated functional groups. The CaSiO3 fine powders were prepared by chemical coprecipitation using Ca(NO3)2·4H2O and Si(OCH3)4, and 5 M NaOH was used as precipitant. The resulting powders were mixed with ethanol by ultrasound stirring and the previously oxidized carbon fibers were placed leaving under stirring for 30 min to allow particle dispersion. Once the formed compounds were dried, the samples were immersed in a simulated body fluid (SBF) solution for 21 days in conical tubes at 36.5 °C to allow the HAP formation on the ACC/CaSiO3 composite surface. The results indicated that the increase in oxidation time improves HAP formation on the surface from ACC/CaSiO3 compounds and this bioactive composite may be a potential material for bone regeneration.

1. Introduction

In recent years, medical treatments cost for traumatisms, infections and tumors related to bone tissue, has increased since there is a growing need for repair or replacement of damaged tissues for healthy ones [1, 2, 3]. Bone is composed by a calcified osseous matrix, cells, and bioactive compounds. The matrix mass contents around 69 % of mineral materials, 22 % of organic compounds and 9 % of water [4]. Hydroxyapatite (HAP), Ca10(PO4)6(OH)2, is the principal mineral inorganic phase [5, 6] with a Ca/P ratio less than 1.67 [7,8]. It is considered the most adequate bio-

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adsorption capacity for low concentration of adsorbate than other adsorbent materials [27]. These characteristics make suitable ACC to be used for several applications like in medicine, because of the biocompatibility of the material [28, 29]. Lopez Peñalver et al. demonstrated that ACC is a good support for MSC, reducing their growth time and improving their proliferation and differentiation [30]. Ruiz de Almodóvar et al. patented a new biomaterial that allows bone tissue and artificial bone regeneration by stem cells from umbilical cord previously differentiated on a ACC matrix [31].

In the present work, a methodology to obtain an ACC/CaSiO3/HAP composite is presented. ACC samples were oxidized with HNO3 varying time. Also, CaSiO3 was added to improve the HAP formation on the composite surface using simulated body fluid (SBF).

2. Methods

2.1. Activated carbon cloth (ACC) oxidation

Activated carbon cloth FM10 (Flexzorb™ ACC) was provided by Calgon Carbon Corporation. ACC modification was performed using HNO3 as an oxidizing agent, as reported by Rangel-Mendez and Streut [32]. In a ball mill, 50 mL of HNO3 in an 8 M concentration was heated at 85 °C. Once the temperature was constant, a 3 cm² ACC piece was added to the flask, varying the oxidation time in 15 min (CC15m) and 2 h (CC2h). The time was assigned with a low and high contact time with the oxidizing agent, by preliminary tests. A piece without oxidation process was used as control (CCSOx). After the oxidation time was concluded, the flask was submerged in cold water in order to stop the reaction. Finally, samples were washed with sufficient deionized water and dried at room temperature for 48 h.

2.2. Calcium silicate (CaSiO3) synthesis and dispersion on ACC

Calcium silicate powders were prepared by coprecipitation method using Ca(NO3)2.4H2O (Fermont) and TEOS (Sigma-Aldrich) as raw materials. The compounds were dissolved separately in ethanol. When dissolved, both solutions were mixed and the concentration was adjusted to 0.2 mol L⁻¹, according to the method reported by Hazar [33]. The solution was mixed by magnetic stirring for 30 min. Precipitation was performed adding a NaOH 5 M solution. The precipitate obtained was filtered (Whatmann® filter paper No. 42) and dried at 100 °C for 12 h and finally the product was calcined at 800 °C during 2 h.

CaSiO3 powders were dispersed on the ACC, using an ultrasonic bath. CCSOx, CC15m and CC2h were submerged separately in a Petri dish with 20 mL of ethanol, and 0.1 g of CaSiO3 powders were dropped in the solution and mixed in an ultrasonic bath for 30 min at room temperature, for a dispersion on the ACC surface. All samples were shaken to remove excess of calcium silicate powder. The dispersion carried out was stable for a dispersion on the ACC surface. All samples were shaken to remove excess of calcium silicate powder. The dispersion carried out was stable for a dispersion on the ACC surface.

2.3. Hydroxyapatite (HAP) generation with simulated body fluid (SBF)

HAP formation on the ACC/CaSiO3 samples (CCSOx, CC15m, CC2h) surface was performed using SBF according to the method proposed by Kokubo and Takadama [34]. The solution was prepared according to the body ions concentration (Table 1) [33,35]. Once the solution was prepared, 20 mL were added to a conical tube bottle and the ACC/CaSiO3 samples were added separately. Conical tubes were sealed and put in an incubator (LabTech LSI-3016A) at 36.5 °C for 21 days. Finally, the samples were washed with deionized water and dried at room temperature.

2.4. Materials characterization

In order to verify HAP growth, the products obtained were characterized by Field Emission Scanning Electron Microscopy with EDS (JEOL JSM-7200F) without previous preparation since the samples were conductive, Infrared spectroscopy with ATR module and KBr preparation (PerkinElmer Nicolet 47), X-ray Photoelectron Spectroscopy (Thermofisher Scientific K-Alpha), Thermogravimetric Analysis with and oxidizing air atmosphere (TA Instruments TGA 550) and N2 physisorption at 77 K (BEL BELSORP-miniX). Boehm titrations were carried out according to Schönher et al [36]. XRD measurements were made on Bruker D8 Advance equipment (CuKα: 1.54 Å, 40 mA and 40 kV).

3. Results and discussion

3.1. ACC/CaSiO3/HAP thermal, texture, and morphological properties

3.1.1. Thermal properties

Thermogravimetric analysis was carried out to determine ACC decomposition temperature and oxidation degree. Figure 1 shows the TGA curves at 10 °C min⁻¹ heating rate for CCSOx, CC15m and CC2h samples, which showed a similar behavior. The first drop observed was at 80 °C for all the samples, attributed to moisture loss from ACC surface.

Moreover, the difference in degradation temperatures in the next thermal decomposition observed was of 90 % loss due to carbon

Table 1. Ion concentrations of simulated body fluid and human blood plasma.

| Ion     | Ion concentration (mM) |
|---------|------------------------|
| Na⁺     | 142                    |
| K⁺      | 5                      |
| Ca²⁺    | 2.5                    |
| Mg²⁺    | 1.5                    |
| HCO₃⁻   | 4.2                    |
| Cl⁻     | 103                    |
| HPO₄⁻   | 1                      |
| SO₄²⁻   | 0.5                    |

Figure 1. TGA of modified ACC with CaSiO3 after 21 days of immersion in SBF.
oxidation and oxygen loss. The degradation temperature for CCSOx was 510 °C, 461 °C for CC15m and 422 °C for CC2h. The difference in the samples is the time in contact with the oxidizing agent and can be inferred that when the oxidation degree increases the degradation temperature decreases due to the presence of more oxygenated groups, which has been reported that improves the combustion process [37]. Furthermore, the remaining 10 % in the samples, increasing with oxidation time 7.83% for CCSOx, 8.91% for CC15m and for CC2h 9.19%, that was attributed to the presence of inorganic materials, such as HAP, CaSiO3 and a minimum amount of ashes (<5 %) [38]. The results demonstrated the presence of an inorganic materials with a higher amount increasing the oxidation time.

3.1.2. Morphology properties

Surface morphology of the samples was evaluated by scanning electron microscopy technique. Figure 2 shows the micrographs of the analyzed samples. Commercial ACC is shown in Figures 2a and 2b, where an arrangement in the fabric fibers is clearly observed. In addition, each fiber is formed by several filaments of the original precursor material (rayon). ACCs modified with CaSiO3 and immersed in SBF for 21 days showed different surface structures; in CCSOx (Figures 2c and 2d) and in CC15m (Figures 2e and 2f) the formation of small distributed particles can be observed, which is attributed to the formation of HAP after immersion in SBF. Figures 2g and 2h shows the CC2h, in which in contrast to the previous samples, a greater HAP growth can be observed on a large part of the fibers. As described above, it can be inferred that CC2h presents higher bioactivity since the HAP formation on the surface of the material is clearly observed (Figure 2h) indicating that, the increase in oxidation time improves the HAP formation.

3.1.3. Texture properties

The texture measurements were made with the N2 physisorption 77 K technique, in BEL BELSORP-mini-X equipment. CC2h texture properties

| Sample   | A_{\text{sup}} (m^2 g^{-1}) | V_{\text{pore}} (cm^3 g^{-1}) | D_{\text{pore}} (nm) |
|----------|-----------------------------|-------------------------------|----------------------|
| Commercial ACC [43] | 1300 | 0.439 | 0.22 |
| CCSOx    | 809  | 0.401 | 2.43 |
| CC15m    | 741  | 0.398 | 2.65 |
| CC2h     | 1012 | 0.491 | 1.94 |

Figure 3. XRD patterns for the incubated samples with SBF and CaSiO3.

Figure 4. FTIR spectra for modified ACC with CaSiO3 after 21 days in SBF.
are summarized in Table 2. The surface area of the conventional ACC and CC2h are 1300 and 1012 m² g⁻¹ and the pore volumes are 0.439 and 0.491 cm³ g⁻¹, respectively. The results show that the oxidation caused a decrease in the surface area. This behavior can be attributed to the destruction or combustion of the pore walls, and to the narrow pore blockage caused by the products formed during the oxidation or by the introduction of oxygenated groups on the surface [39]. A slight increase in the pore volume of the CC2h sample is observed, which may be due to the presence of CaSiO₃ and HAP which are porous particles [40]. The average pore diameter for conventional ACC was 0.22 nm and for CC2h was 1.94 nm, which shows that there was a small increase because acid oxidation slightly enlarges the pores [32]. The porous structure consists mainly of micropores because the average diameter is less than 2 nm [41, 42]. The presence of the SBF ions that begin to form the hydroxyapatite particles seems to clog the pores, so that a decrease in their surface area and pore volume values is observed in the samples CCSOx and CC15m.

Figure 3 shows the XRD patterns for the obtained samples. The results demonstrated the presence of HAP on ACC surface observed in the signals around 32°, and 66° for CC2h and CC15m samples corresponding to JCPDS 96-901-1095 and also signals at 24°, 28°, 36° and 56° corresponding to CaSiO₃ were observed in all the samples (JCPDS 96-901-1095). For CCSOx any signal was observed for HAp. The typical amorphous graphite surface was observed on signals between 20°–30° and 40°–50°. The intensity of the signals depends on the amount of the ceramic materials, and only 5% of the composite were of these.

### Table 3. Oxygenated functional groups quantification (meq g⁻¹) on the samples surface obtained by titrations.

| Sample   | Carboxyl | Lactones | Phenols |
|----------|----------|----------|---------|
| ACC      | 0.075    | 0.124    | N/D     |
| CCSOx    | 0.071    | 0.119    | N/D     |
| ACC15m   | 0.242    | 0.299    | 0.043   |
| CC15m    | 0.225    | 0.288    | 0.041   |
| ACC2h    | 0.398    | 0.376    | 0.108   |
| CC2h     | 0.371    | 0.365    | 0.101   |

*ND: Not detectable.

3.1.4. ACC/CaSiO₃/HAP chemical properties

To determine the bonds formed after ACC modification, infrared spectroscopy tests were performed. Figure 4 shows the infrared spectra for CCSOx, CC15m, and for CC2h. All the samples analyzed revealed very similar spectra, where the most significant double signal is located between 2800 and 3000 cm⁻¹ and corresponds to the C–H stretch. The band at 1715 cm⁻¹ is attributable to the C=O stretch of the carbonyl group, and the band at 1456 cm⁻¹ corresponds to methyl group (-CH2) bending vibrations. These bands are characteristic for carbon materials, and although there is no clear difference between the studied samples, it has been proven in previous studies that by contacting an activated carbon with an oxidizing agent such as nitric acid, the amount of oxygenated groups concentration increases [44]. Also, small signals in 1116 and 1085 cm⁻¹ corresponds to the phosphate ion present on the HAp structure [45]. The typical signals of wollastonite were not observed since all the particles were coated with hydroxyapatite, and is important to note, that since the activated carbon cloth is the 95% content of the material, the functional groups of hydroxyapatite are less intense than the ones of ACC.

Figure 5. XPS analysis of CC2h after 21 days of immersion in SBF.

Figure 6. XPS spectra of CC2h: (a) C1s; (b) O1s; (c) Ca2p; (d) P2p.
To demonstrate the successful activation of the surface, titrations were carried out and the results are shown in Table 3, in comparison with the oxidized materials, ACC (without oxidation) ACC15m (15 min oxidation) and ACC2h (2 h oxidation). The commercial ACC showed the presence of carboxyl (0.075 meq g⁻¹) and lactones (0.124 meq g⁻¹) groups, due to the carbonization and activation process. When the commercial ACC was added to the oxidizing agent (HNO₃) varying time, the oxygenated functional groups were increased on the surface of the samples [44]. For the incubated samples with CaSiO₃ after 21 days in SBF, the oxygenated functional groups were increased on the surface of the samples [44]. For the incubated samples with CaSiO₃ after 21 days in SBF, the oxygenated functional groups decreased. The results demonstrate that oxygenated groups are a determining factor in the formation and growth of hydroxyapatite on the surface, results observed also in XRD patterns. In addition, TCA2h lost more than 90 % of their weight at a temperature of 422 °C and around 5 % weight corresponds to HAP and CaSiO₃. Oxidation causes a slight decrease in surface area and a large part of the porous structure consists mainly of micropores (<2 nm). The bioactivity tests showed that the compounds (ACC/CCSiO₃) improve the HAP growth on the ACC surface with a higher oxidation degree. This compound may be a potential material for bone regeneration, however tight adhesion and the mechanical properties of the samples need to be measured.

4. Conclusions

As observed in SEM images, CC2h (oxidized for 2 h) has a higher HAP content when immersed in SBF for 21 days. The EDS analysis showed a mass of 17.85 % for Ca and 8.68 % for P in CC2h, which indicates a 1.59 ratio for Ca/P. These results agree with the EDS analysis, showing Ca2p and P2p signals, corresponding to the HAP presence on the analyzed surface, results observed also in XRD patterns. In addition, TCA2h lost more than 90 % of their weight at a temperature of 422 °C and around 5 % weight corresponds to HAP and CaSiO₃. Oxidation causes a slight decrease in surface area and a large part of the porous structure consists mainly of micropores (<2 nm). The bioactivity tests showed that the compounds (ACC/CCSiO₃) improve the HAP growth on the ACC surface with a higher oxidation degree. This compound may be a potential material for bone regeneration, however tight adhesion and the mechanical properties of the samples need to be measured.

Declarations

Author contribution statement

Yohana Y. García-Guel: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.
Elia M. Múzquiz-Ramos: Conceived and designed the experiments; Analyzed and interpreted the data.
Jorge C. Ríos-Hurtado: Conceived and designed the experiments; Performed the experiments.
Sergio E. Flores-Villaseñor: Analyzed and interpreted the data.
Griselda B. Escalante-Ibarra: Contributed reagents, materials, analysis tools or data.

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Data availability statement

Data included in article/supplementary material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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