PRODUCTION AND CHARACTERIZATION OF TRACHEOBRONCHIAL STENTS PRODUCED WITH POLYDIMETHYLSILOXANE/CALCIUM PHOSPHATE

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Abstract:
A composite of polydimethylsiloxane/calcium phosphate (PDMS/CP) has been developed by using biomimetic technique. This process involved the precipitation of calcium phosphate nanoparticles within the PDMS matrix during the composite mixing. The stents used in trachea were cross-linked in a steel matrix at specific temperature and time.

Scanning electron microscopy (SEM) micrographs of the PDMS/CP composite exhibited calcium phosphates particles from the elastomeric matrix at the fracture surface. The phases measured by x-ray diffraction (XRD) shows hydroxyapatite (HA) and calcium phosphate anidrous (DCPA). Hardness measurements found was higher than pure PDMS because of the presence of nanoparticles, as expected.

Keywords: polydimethylsiloxane, calcium phosphate, hydroxyapatite, stents, composite.

Introduction
For a long time polydimethylsiloxane (PDMS) have been used in biomedical applications. The properties of PDMS promise a great convenience in clinical applications because it presents good biocompatibility, low toxicity, physiological inertness and blood compatibility. Some devices based on PDMS are drainage implants in glaucoma, blood pumps, mammary prostheses, cardiac pacemaker leads, medical adhesives, denture liners and others [1]. In chemical application, PDMS presents a high degree of thermal stability, oxidation resistance, chemical inertness and good mechanical properties (tensile strength higher than 1 MPa and ductility higher than 500%) [2].

For this reason many studies have focused on improving physicochemical and biological properties of polymers such as PDMS through incorporation of bioactive inorganic substances (calcium phosphates or, specifically, hydroxyapatite) [2].

In general, bioceramics exhibit excellent biological performance that can promote new bone formation by self-degradation under the microenvironment of the organism to produce a pore-like structure, facilitating adherence in tissues and tissue ingrowth. For this reason, hydroxyapatite (HA, Ca₁₀(PO₄)₆(OH)₂) is preferred than other calcium phosphates because it is similar to primary constituent of bone. Hydroxyapatite can form a bonding with bone tissues and it possesses excellent biocompatibility. However, in contrast to PDMS, hydroxyapatite demonstrates poor processing properties because it is brittle. At present, hydroxyapatite or PDMS can be utilized as plastic surgical material, but it is not ideal. Naturally, it would be interesting to combine the advantages of hydroxyapatite and PDMS and to form a new material system [2-4].

An important use of the polydimethylsiloxane in the field of biomaterials has been to develop stents, especially for tracheobronchial applications. In this case, the purpose of the use of these stents is to provide a better quality of life, thus allowing the passage of air and food to the patient. One approach to improving the bioactivity in this case is a mixture of biologically active silicone and nanosized-hydroxyapatite (n-HA).

In order to produce the stents with PDMS through incorporation of bioactive inorganic substances (calcium phosphates, specially, hydroxyapatite), a new method was developed. In this process the formation of calcium phosphate occurs in situ facilitating the production and incorporation of calcium phosphates.

Materials e Methods
In order to produce the PDMS/CP composite, 20 wt.% of Ca(OH)₂ was mixed to medical grade PDMS (MED-4735, Nusil Technology) in an open two-roll mixer until its homogenization. A suitable quantity of H₃PO₄ was added in order to promote a Ca/P molar ratio of 1/1 and the mixture was homogenized again.

The material was placed in metallic molds and pressed in order to obtain around 3 mm of thickness samples for tests and in a steel matrix to obtain the implantable stents. The composite was cross-linked at 185 °C for 45 minutes.

Scanning electron microscopy (SEM) analyses were
carried out in order to identify the presence of hydroxyapatite in the fractured surfaces. The phase composition of the composite was analyzed by x-ray diffraction (XRD) (Philips X’Pert MPD, Κα = 1.5418 Å) under operating conditions of 40 kV and 40 mA. Shore A hardness was measured in a Mitutoyo ID-S1012M durometer according to ASTM D2240 in five samples with 6 mm of thickness.

**Results and Discussion**

The method to produce PDMS/CP consists in obtaining the calcium phosphate in situ during the production of PDMS tracheobronchial stents. The reaction occurs by mixing Ca(OH)\(_2\) and H\(_3\)PO\(_4\) in the PDMS and it can be represented by equation 1.

\[
\text{Ca(OH)}_2(\text{sol}) + \text{H}_3\text{PO}_4(\text{liq}) \rightarrow \text{CaHPO}_4\cdot2\text{H}_2\text{O}_{(\text{sol})} (\text{DCPD}) + \text{Ca(OH)}_2'_{(\text{sol})}
\]

According to literature, dibasic calcium phosphate dihydrate (DCPD) can be transformed into dibasic calcium phosphate anhydrate (DCPA) at temperatures around 80 °C [5]. Therefore, after cross-linking reaction at 185 °C, DCPD suffered dehydration to form DCPA. The second reaction can be described by equation 2.

\[
\text{CaHPO}_4\cdot2\text{H}_2\text{O}_{(\text{sol})} (\text{DCPD}) + \text{Ca(OH)}_2'_{(\text{sol})} \Delta \rightarrow \text{CaHPO}_4\cdot4\text{H}_2\text{O}_{(\text{sol})} (\text{DPCA}) + 2\text{H}_2\text{O}_{(\text{gas})}
\]

The figure 01 shows XRD spectrum of PDMS/CP that presents DCPA and hydroxyapatite as filler phases in the composite.

![XRD spectrum of PDMS/CP composite.](image)

**Figure 01: X-ray patterns of PDMS/CP composite.**

The pH found in the composite is around 7.12. The material reached the necessary pH value to precipitate hydroxyapatite, in which DCPA is transformed into hydroxyapatite during the production of the composite because of favorable conditions. As described by [6], the pH value found is recommended range for implantable materials [6].

Table 01 shows Shore A hardness of PDMS and PDMS/CP. The composite presents higher hardness value in comparison to PDMS. As expected, it occurs due to presence of filler phases (HA and DCPA) into the material.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hardness</th>
</tr>
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<tbody>
<tr>
<td>PDMS</td>
<td>30.50 ± 0.75</td>
</tr>
<tr>
<td>PDMS/CP</td>
<td>42.00 ± 0.52</td>
</tr>
</tbody>
</table>

It is known that introducing ceramic filler phases in the PDMS, the hardness increases comparing to pure PDMS. The results of hardness are shown in the table 01.

Figure 02 presents SEM micrographs showing the fracture surface morphology of the composite.

![SEM fracture surface of PDMS with calcium phosphate.](image)

**Figure 02: SEM fracture surface of PDMS with calcium phosphate.**

Micrographs of the PDMS/CP composites exhibited calcium phosphate particles from the elastomeric matrix at the fracture surface. On the other hand, calcium phosphates particles remained well attached to the matrix in the PDMS/CP composite and pH on water was maintained at physiological values.

**Conclusion**

The composite presented the presence of HA and DCPA in the composite after cross-linking reaction. The hardness shows higher values for PDMS/CP, in the other words, the introduction of filler phases in PDMS increased the hardness of composite. The microstructure presents calcium phosphate particles on the surface.

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References


