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Development and properties of polycaprolactone/hydroxyapatite composite biomaterials

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Polycaprolactone/hydroxyapatite (PCL/HA) composites were prepared by two different procedures. The first one consists of a conventional blending of the polymer and the reinforcement material in an extruder. The second method consists of grafting of PCL on the surface of HA particles. This was achieved by a ring opening polymerization of caprolactone in the presence of HA, where its OH groups act as initiators. By this method, it was possible to obtain, in one step, a composite of PCL and surface modified HA. In both methods different percentages of filler were used to obtain several composites. These composites were characterized with respect to their mechanical properties, in the dry and wet state, by means of tensile tests on compression molded samples. The polymer/filler interface was analyzed by scanning electron microscopy. Water uptake and weight loss degradation experiments were also performed.

An increase in the modulus for higher amounts of filler was, as expected, observed in the composites obtained by both processes. Furthermore, the mechanical properties of the materials in the wet state are considerably lower than those in the dry state. However, this difference is more significant for the composites obtained by conventional blending than for composites obtained by the grafting procedure, indicating that the later procedure can be an adequate route to reduce water susceptibility of PCL/HA composites.

1. Introduction

Composites comprising biodegradable polymeric matrix and bioactive ceramic fillers may find many applications in the substitution of bone tissue and in many other orthopaedic applications [1–6].

Several polymer/ceramic combinations can be used to confer to the composites different characteristics and for controlling properties such as biocompatibility, water-uptake, rate of degradability and mechanical properties, making the materials suitable for use in a wide range of biomedical applications. However, often poor adhesion between the polymeric matrix and the ceramic particles results in early failure at the interface and in a too fast degradation of the composite mechanical properties. This phenomenon is even more significant if composites are placed in a physiological environment [7]. The filler/matrix interface is, in fact, a major determinant for the mechanical behavior of composites.

The aim of this work was to obtain polycaprolactone/hydroxyapatite (PCL/HA) composites with enhanced interfacial interaction between the polymer and the reinforcement material. Polycaprolactone is a biodegradable and non-cytotoxic polymer, currently used as biomaterial [2, 8–11]. Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) is the main mineral component of bone and because of its high bioactivity and biocompatibility is commonly used as filler in polymer-based bone substitutes [12–14]. The use of coupling agents, such as silane, polyacids, zirconyl salts and organic isocyanates, are examples of ways that have been developed to improve the polymer/filler interface [7, 15–22]. However, the use of these materials can induce a cytotoxic behavior to the composites.

In this work, two different methods were tested for preparing the composites. One consists on conventional blending of both materials in an extruder and the second one consists on grafting of PCL on the surface of the HA particles.

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In order to evaluate the effect of the surface modification, composites obtained by both methods were characterized with respect to their mechanical properties, both in the dry and wet state. Water uptake and weight loss degradation experiments were also performed.

2. Experimental

2.1. Materials and methods

2.1.1. Method I

Method I consists on a conventional blending of the biodegradable polymer, polycaprolactone, and the reinforcement material, hydroxyapatite, in an extruder.

Polycaprolactone (capa 680, Solvay Interox Ltd, UK) of MW = 80 000 and sintered hydroxyapatite (particle size 38–53 μm, Plasma Biotal, UK) were blended in an extruder at $T = 130\,^{\circ}\mathrm{C}$. Hydroxyapatite was dried under vacuum at $T = 200\,^{\circ}\mathrm{C}$, for 2 days before use. The blend was allowed to stay in the extruder for 30 min to assure a good blending. Composites with 10%, 20% and 30% (w/w) of HA were prepared.

2.1.2. Method II

In this method, a surface modification of the HA particles was performed in order to try to improve the polymer/ceramic interface. This method consists on grafting of PCL on the surface of HA particles. This was achieved by a ring opening polymerization of caprolactone (CL) in the presence of HA, where the OH groups of the hydroxyapatite act as initiators (Fig. 1).

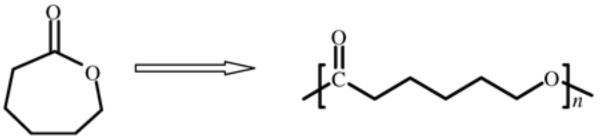

Figure 1 Schematic representation of the ring opening polymerization of caprolactone.

By this method, it was possible to obtain, in one step, a composite of PCL and surface modified HA (Fig. 2). The polymer chains chemically bound to the HA surface would create more entanglements with the polymer chains of the matrix. An improvement of the interface matrix/filler would then be expected and differences on the properties of the composite would be observed.

Caprolactone was dried with calcium hydride (CaH_2, Aldrich) overnight and distilled under Argon flow and under reduced pressure before use. Hydroxyapatite was dried under vacuum at $T = 200\,^{\circ}\mathrm{C}$, for 2 days before use. The ring opening polymerization of caprolactone (Merck, Germany) in the presence of HA was performed at $T = 130\,^{\circ}\mathrm{C}$ for 3 days in a silanized glass vial, sealed under vacuum. Stannous Octoate, $SnOct_2$ (Sigma, USA) was used as catalyst. Several filler percentages were used to obtain composites with different content of HA.

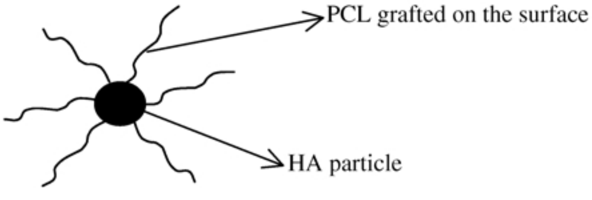

Figure 2 Cartoon showing the research approach followed for obtaining modified HA particles.

2.2. Analysis

2.2.1. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed in a Perkin Elmer TGA apparatus and used to determine the real HA content present on the composites obtained after processing by both methods.

2.2.2. Mechanical properties

Tensile tests were performed on a Zwick Z020 machine, with a 500 N load cell, using a cross-head speed of 50 mm/min until 0.3% strain. The cross-head speed was then increased to 500 mm/min until fracture. An extensometer was used in order to obtain more accurate results. Dumb-bell shaped tensile specimens (0.5 × 4 mm) of cross section) were cut from compression molded films ($T = 140\,^{\circ}\mathrm{C}$) and used for the tensile tests. The mechanical properties were determined in the dry state and in the wet state, after immersion in distilled water at 37 °C for 3 days. Both the modulus at 0.3% strain ($E_{0.3\%}$) and the ultimate tensile strength (UTS) have been determined.

2.2.3. Scanning electron microscopy

The interface between the polymer and the filler was analyzed by scanning electron microscopy (SEM) in a Leica Cambridge S360 microscope. Samples were sputter coated with gold.

2.2.4. Degradation tests

In order to simulate physiological fluids a 0.154 M NaCl aqueous isotonic saline solution with pH = 7.4 was used. Samples were cut from the compression molded films, immersed in the NaCl solution and kept in a shaking (60 rpm) water bath for periods of 3, 7 and 16 days.

The water uptake and weight loss of the samples were calculated according to the following equations:

$$\%S = (m_w - m_i)/m_i \times 100$$
$$\%W = (m_i - m_d)/m_i \times 100$$

where

$\%S$ is the water uptake degree, $\%W$ is the percentage of weight loss, m_w is the weight of the wet sample after immersion in the NaCl solution, m_i is the initial weight of the sample and m_d is the weight of the sample at the end of the experiment, after drying to constant weight.

3. Results and discussion

3.1. TGA

Thermogravimetric analysis was used to determine the real amount of HA in the composites. It showed that the real HA content present on the composites obtained after processing by both methods was in the range of 10%, 20% and 30% with an error of 2%.

3.2. Mechanical properties

In both methods, the values of $E_{0.3\%}$ increased, as expected, with increasing amounts of filler (Fig. 3).

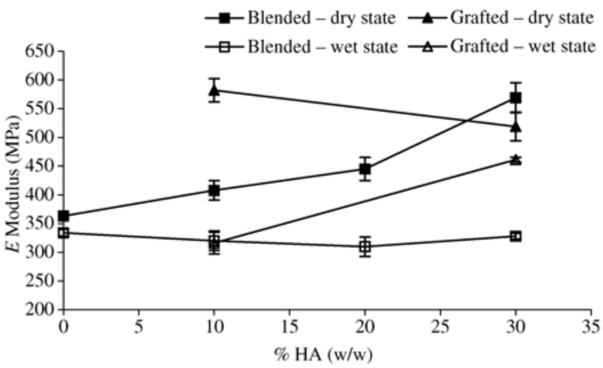

Figure 3 $E_{0.3\%}$ as function of HA amount (wt %).

The lower values obtained in the wet state can be explained by the swelling of the samples, the weakening of the interface and the plasticization effect due to the presence of water. The decrease of the values in the grafting method (method II) is smaller than in the blending method (method I), especially for higher amounts of HA. This can be explained considering that in method II the surface of the HA particles should be covered with PCL chains and consequently the effect of the water uptake would not be so significant.

It was possible to observe a decrease in UTS with increasing amounts of HA in both methods. This is typical on particle filled composites especially if the polymer/particles interface is not optimized. It results from a higher effect of stress concentration induced by the presence of the particles that becomes more relevant, for increasing concentrations, than the reinforcement effect.

Because of a better filler/matrix interaction, higher UTS values in the grafted samples could be expected. Fig. 4 shows similar values for both composites, which may indicate that the grafting was not effective enough to produce significant differences from a mechanical point of view.

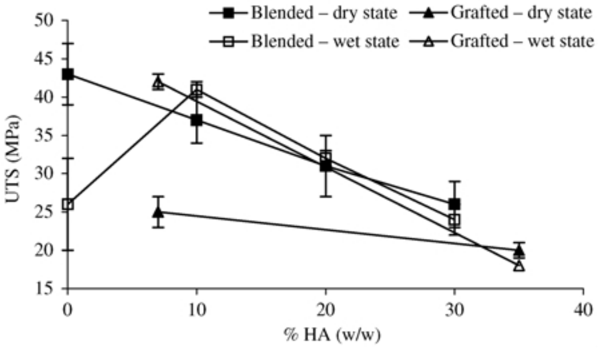

Figure 4 Ultimate tensile strength (UTS) as function of HA amount (wt %).

3.3. SEM

A SEM micrograph of the matrix material is shown in Fig. 5.

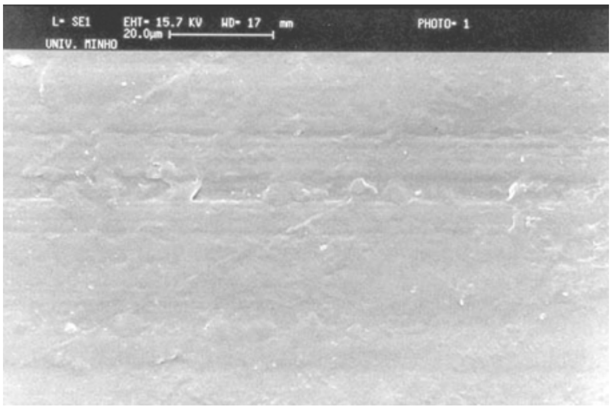

Figure 5 SEM micrograph of the surface of a compression molded sample of the selected matrix material – PCL680.

In the composites obtained by method I (Fig. 6(a) and (b)) a poor interaction between the polymer and the filler is visualized.

In the composites obtained by method II (Figs. 6(c), 7(a) and (b)), the HA particles were covered with polymer, which is an indication of a good filler/matrix interface. The results seem to indicate that there is a chemical bound between the PCL chains and the HA particles. On the other hand, some HA agglomerates could be observed which might be an evidence that the HA particles were not homogeneously dispersed in the composite and so the UTS values would not be as high as expected. This could explain why there is no significant difference in UTS values obtained in both methods.

3.4. Degradation tests

Figs. 8 and 9 present respectively the water-uptake and the weight loss vs. time for composites obtained by both methods. PCL is a polymer with low values of water uptake and degradation rate. Only short-term data is shown but the observation of the curves allows us to conclude that grafted composites have less susceptibility for water-uptake and degrade slower than the blended composites. These results prove again that the grafting of PCL on HA particles leads to a better polymer/ceramic interface and consequently to more hydrolytically stable composites. The degradation rate is, as expected, growing faster for higher amounts of water absorbed and for greater content of HA due to a preferential attack at the polymer/ceramic interface. This effect has been observed previously [5] for starch based polymers reinforced with HA.

4. Conclusions

For the composites obtained by both methods, an increase in the modulus for higher amounts of filler was observed.

Furthermore, the modulus ($E_{0.3\%}$) of the materials in the wet state is considerably lower than those in the dry state. However, this difference is more significant for the

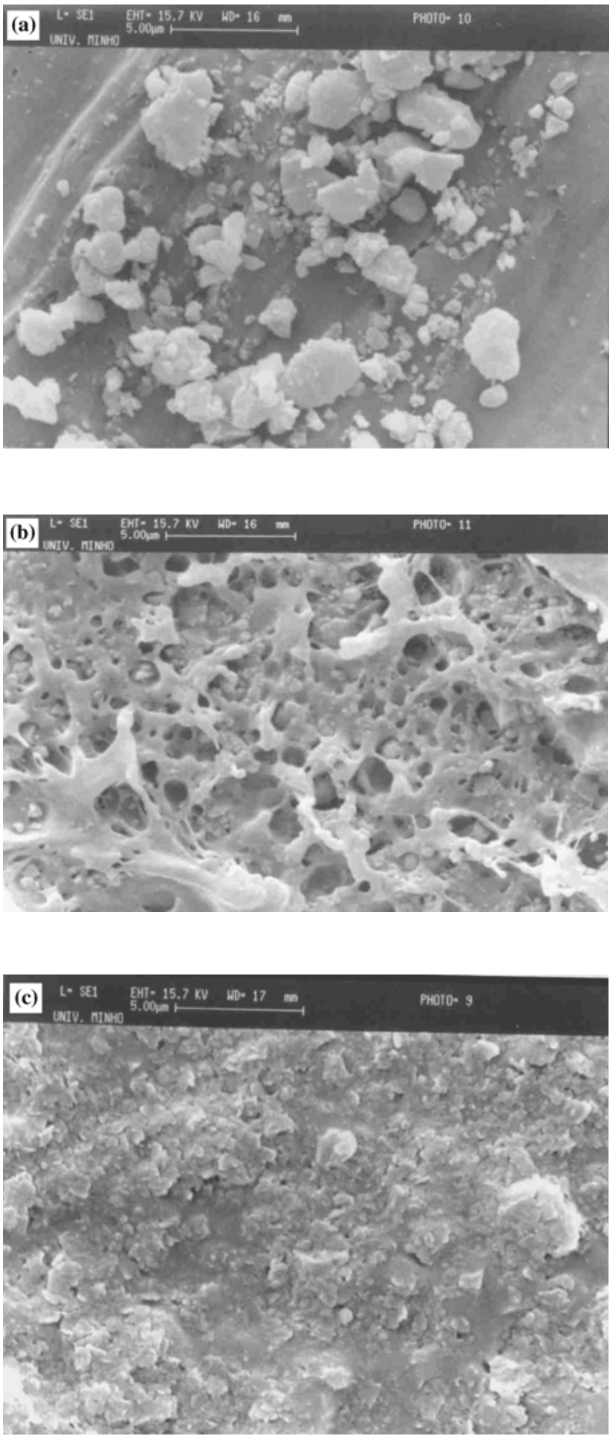

Figure 6 SEM micrograph of the surface of a compression molded sample of a 30% composite obtained by (a) and (b) method I, (c) method II. It is visible a better interaction on (c).

composites obtained by conventional blending than for composites obtained by the grafting procedure. Degradation results are in line with this observation, as the grafted composites uptake less water and degrade at a slower rate.

Although method II needs to be optimized and further experiments are needed to better characterize the grafting of PCL on the surface of the HA particles, it is possible to say that both methods, in particular, the one where a surface modification of the HA particles was performed, can be very promising routes for obtaining composites with enhanced properties to be used in orthopaedics.

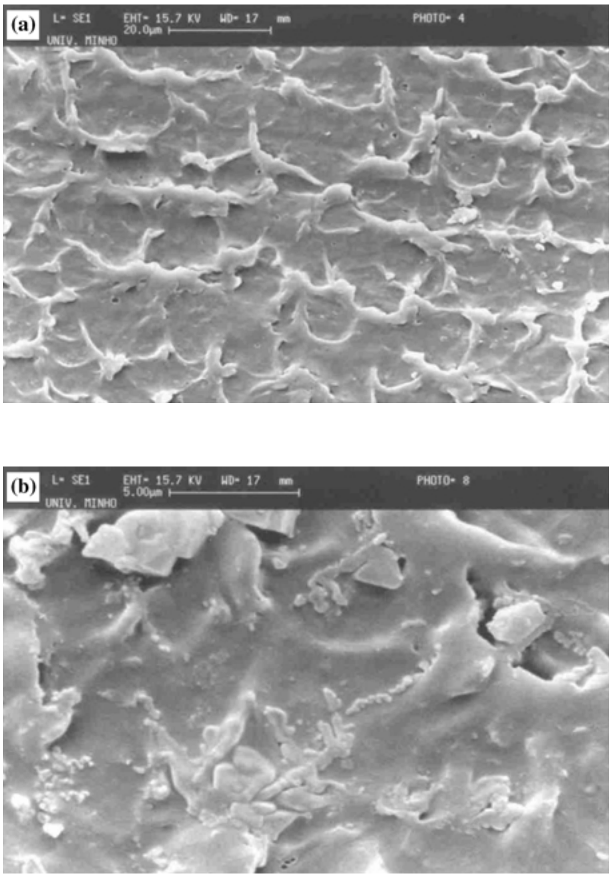

Figure 7 (a) SEM micrograph of the surface of a compression molded sample of a composite (10%) obtained by the grafting method. Again, a better polymer/ceramic interaction is clear; (b) Magnification of (a) showing the polymer covering the HA particles.

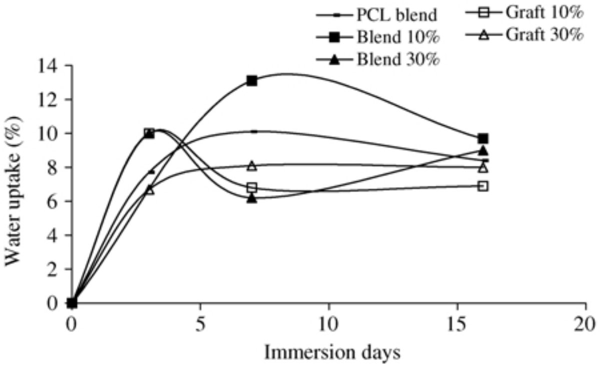

Figure 8 Water up-take vs. immersion time for PCL blend, 10% HA – method I, 30% HA – method I, 10% HA – method II, 30% HA – method II.

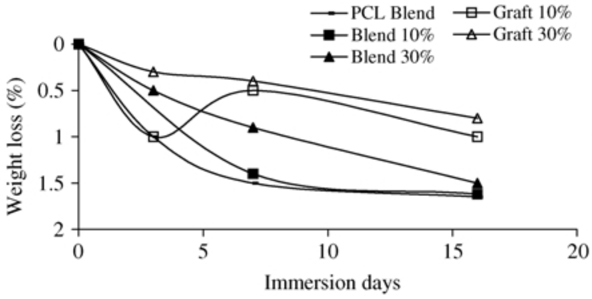

Figure 9 Weight loss vs. immersion time for PCL blend, 10%HA – method I, 30% HA – method I, 10%HA – method II, 30% HA – method II.

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