Materials Science and Engineering C 48 (2015) 642–650

Contents lists available at ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

The influence of silanisation on the mechanical and degradation behaviour of PLGA/HA composites

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ARTICLE INFO

Article history:
Received 20 November 2013
Received in revised form 6 October 2014
Accepted 17 December 2014
Available online 18 December 2014

Keywords:
Hydroxyapatite
Trialkoxysilanes
Poly(D L lactide-co-glycolide (50:50)) (PLGA)
Silanisation
In-vitro degradation
Plastic mechanical properties

ABSTRACT

This study investigates the influence of silanisation on the mechanical and degradation behaviour of PLGA/HA composites. Three different silanes (mercaptopropyl trimethoxy silane (MPTMS), aminopropyl trimethoxy silane (APTMS) and aminopropyltriethoxy silane (APTES)) were applied to HA substrates in order to study the effect of head group (which binds to the polymer) and tail group (which binds to the surface hydroxyl groups in HA). A composite of hydroxyapatite (HA) and poly(D,L lactide-co-glycolide (50:50)) (PLGA) was investigated.
The influence of concentration, the reaction time, drying temperature and substrate surface on silanisation was examined. TGA was used to detect the degree of silanisation.
HA with MPTMS (1 wt.% MPTMS with reaction time of 1 h) was used as filler in PLGA-30 wt.% HA composites for an in-vitro degradation study carried out in PBS. In addition, the mechanical properties of the composites were studied.
Silanisation affects the properties of the composite by improving the bonding at the interface and hence it was found to influence the plastic mechanical properties rather than the elastic mechanical properties or the degradation profile of the composite.

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1. Introduction

Poly(α-hydroxy acids) are biodegradable, biocompatible and bioresorbable polymers. PLGA is a copolymer of Polylactic Acid (PLA) and Polyglycolic Acid (PGA) [18]. Poly(α-hydroxy acids) can be used as the matrix phase in composites. Hydroxyapatite (HA) resembles the mineral component of bone [22] and has been used as filler in polymer composites [3,35]. Composites produced to mimic bone [9,12,27] have resulted in the values (for the mechanical properties tested) being either too high [9] or too low [29,35]. The properties of the composite can be influenced by altering the bonding between the filler and the matrix phase at the interface [10]. Trialkoxysilanes are used in this study as no toxic by-product is produced when using these silanes. Recent studies have shown that silanization lowers crystallinity of treated HA when compared to untreated HA [2]. Modifying the surface of filler using compounds such as organosilanes can affect the bonding at the interface of the composites. Organosilanes are organic compounds that bind at the interface of the composite and can be used to improve the properties of HA composites [10]. More recently, Lopez-Aranguren et al. [16] reported that silanisation results in weakly hydrogen bonded silane as well as chemically bonded silane.

In a study where HA was used as the substrate the pH was acidic for the hydrolysis of the silane prior to the addition of HA and it was increased to a basic pH after the addition of HA [8,19]. The pH was altered in order to encourage the condensation and formation of silanols on the surface of HA. This has been further validated in a recent study using APTES [24].

The time allowed for hydrolysis also varies greatly and it could range from 15 to 50 min for methoxy silanes with various functional groups (pH of 3.5) [8] to 24 h (pH not monitored) for MPS [7].

In many cases the reaction is carried out at room temperature when HA is used as the substrate [6,10,32]. However, as was reported in a study using MPS and hydroxyapatite as substrate the reaction temperature can be increased above room temperature [23]. The reaction was carried out at room temperature in the present study.

Tham et al. [31] reported the silanisation of HA with 2–8 wt.% MPS in PMMA/HA composites. No significant differences were observed in the flexural strength or tensile modulus with change in the weight fraction. Increasing the concentration higher than 2.0 wt.% results in formation of oligomeric or polymeric siloxane networks that are detrimental to the overall strength of the composite [28].

Apart from the Si–O–Si linkages and the Si–OH linkages produced in a silanisation reaction, silanes also form dimers, siloxane chains or three dimensional networks and these three dimensional networks have no

Abbreviations: HA, hydroxyapatite; MPTMS, mercaptopropyl trimethoxy silane; APTMS, aminopropyl trimethoxy silane; APTES, aminopropyl triethoxy silane; PBS, phosphate buffered saline; ICP-AES, inductively coupled plasma-atomic emission spectroscopy

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http://dx.doi.org/10.1016/j.msec.2014.12.056
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free Si–OH reactive moieties in the structure. This means that there is no chemical bond formed between the silane and the substrate [25].

The method commonly used to detect the silanisation of a substrate is the Fourier Transform Infrared Spectroscopy (FTIR) [4,16]. However, TGA has been used to determine the silanisation of various substrates including HA [14,17,31].

Literature has reported two peaks observed for silanised samples one associated with physisorbed (unreacted) silane and the other due to chemisorbed (reacted) silane. [34] reported that flash vaporisation to 250°C removed any trace of physisorbed silane. The vaporisation of physisorbed and hydrogen-bonded silanol molecules (chemisorbed) was reported to occur in the temperature range of 150–375 °C [16].

The effect of silanisation on the degradation of polymer composites has not been studied in great detail. Previous studies have focussed on the effect of silanes on the solvent sorption characteristics of composites [5,13,30].

The amount of water absorbed has been reported to increase with increasing filler content for composites with unmodified or silanised HA as filler which was attributed to an increase in the water-soluble impurities with increase in filler content [5]. It has also been reported that the presence of silanised filler may result in an increase of water absorption due to a coating of silanol groups (Si–OH) that adsorbs more water onto its surface than unsilanised material [26].

It has been reported in the literature that silanisation of filler reduces the rate of loss of material during in-vitro degradation and was attributed to the hydrophobicity of silane molecules [20].

In the study presented in this paper three different silanes (mercaptopropyl trimethoxy silane (MPTMS), aminopropyl trimethoxy silane (APTMS) and aminopropyltriethoxy silane (APTES)) were applied to HA substrates in order to study the effect of head group (which binds to the polymer) and tail group (which binds to the surface hydroxyl groups in HA).

The influence of various parameters such as concentration, reaction time, and surface area on the reaction was studied. In addition, the effect of physisorbed and chemisorbed silane on the mechanical properties and degradation profile of the composite was investigated.

2. Materials and methods

2.1. Materials

The materials were used as received unless mentioned. Calcium hydroxide (Ca(OH)2, 99 + %) was purchased from Fisher Scientific, UK and orthophosphoric acid (H3PO4, 85%) was purchased from Acros Organics, UK. PLGA (50:50) was purchased from Surmodics Pharmaceuticals, USA. The three silanes used were MPTMS, APTMS and APTES from Sigma Aldrich, UK. PBS (0.01 M) powder was purchased from Sigma Aldrich, UK. Standard solutions used for the detection of calcium concentration were purchased from Fisher Scientific, UK.

2.2. HA synthesis

HA was synthesised at room temperature using an aqueous precipitation reaction between 0.5 M Ca(OH)2 (Fisher Scientific, UK) and 0.3 M H3PO4 (Acros Organics, UK). The pH was maintained above 10.5 with the addition of ammonia. The HA thus synthesised was ground, milled and sieved using a 180 μm sieve. The powder produced using this method will be referred to as "uncalcined HA." In addition some of the powder was calcined at 800 °C for 4 h in an air atmosphere and will be referred to as "HA calcined in air".

2.3. Silanisation

Silanisation was carried out using 90% ethanol as a solvent and HA as substrate in the ratio of 1:2 (w/w, HA:ethanol). APTES, APTMS and MPTMS were added in concentrations of 0.1–2 wt.% of HA (as-synthesised) to the ethanol and allowed to stir for 1 h prior to adding the HA to activate silanol groups in the solution [10]. 2 g of substrate was used for each reaction. The sample was dried in vacuum at 120 °C for 48 h. Using this method the silane may be bound to the surface of the HA. Silanisation was carried out without the use of the solvent so as to prevent a reaction between silane and HA. The desired concentration of silane was added directly to the HA powder and left to stir for the duration of the reaction times studied. The powders silanised using this method were not dried and were used as produced. This means that the silane was not bound to the surface of HA.

2.3.1. Factors affecting silanisation

The concentration of the silanes was varied between 0.1 and 2-wt.%. Four different reaction times (1, 2, 3 and 24 h) were used. The rate of hydrolysis of silane is dependent on the concentration of silane and so occurs slower for low concentration of silanes [1]. These time points were chosen in order to identify the optimum reaction time.

The tail group of the silane is bonded to the HA and to compare the effect of different tail groups 2-wt.% APTES, APTMS and MPTMS at 1,2, 3 and 24 h were analysed.

The effect of calcination and hence the surface area of the substrate on the degree of silanisation was analysed by comparing the silanisation of uncalcined HA with HA calcined in air. The silanisation was carried out using 1-wt.% MPTMS and a reaction time of 1 h.

2.4. Characterisation of silanised powders

2.4.1. Surface area measurement

The BET (Brunauer–Emmett–Teller) method was used to calculate the surface area (Table 1) of the different powders synthesised. A Tristar3000 from Micromeritics was used.

2.4.2. TGA

A Q500 TGA (TA instruments, USA) was used to carry out the analysis. The reaction was carried out in an air atmosphere with approximately 10–12 mg of sample used. The temperature was increased at a rate of 10 °C/min from room temperature to 600 °C.

2.5. Composite production

A two-step process produced the composites; the first involved the mixing of the polymer and filler in acetone; the second, injection moulding of the mixture.

2.5.1. Mixing

PLGA and 30-wt.% HA (1.0 wt.% MPTMS, 1 h) were mixed in a Polytetrafluoroethylene (PTFE) container with acetone as solvent for 1 h using an overhead magnetic stirrer. The mix was then allowed to stand for a further hour before drying in a vacuum oven at 40 °C overnight.

2.5.2. Injection moulding

The mixture of PLGA and HA was processed into dumbbell shaped specimens (to be used for studying elastic mechanical properties), and cylindrical specimens (for the degradation study and to study plastic deformation) using a 12 cm^3 DSM Xplore mini injection moulder. A mould temperature of 35 °C and melt temperature of 140 °C was used. The injection pressure was 5.0 bar whereas the filling pressure and the holding pressure were 2.0 bar. The holding time for the uncalcined

Table 1
Specific surface area for HA powders obtained from the BET.

Type of HA	Specific surface area
Uncalcined HA	87.2 m^2/g
Calcined in air HA	23.3 m^2/g

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