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ORIGINAL ARTICLE

A kinetic analysis of the melting HA/Y-PSZ/HDPE nano bio composite for hard tissue materials

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Abstract Melting characteristics of high-density polyethylene (HDPE) mixed with nano-size ceramic fillers (hydroxyl apatite and yttria stabilised zirconia) was analysed using the isochronal heating rate between 10 °C min^{-1} and 80 °C min^{-1}. In this investigation, the kinetics of melting of HDPE-ceramic composites was analysed using the Avrami equation and the Kissinger model, applied to the Avrami formalism. The magnitude of the apparent energy barrier for the melting of HDPE falls within a range of 12 kJ mol^{-1} and 22 kJ mol^{-1}, with a tendency for heterogeneous melting which was determined by characterising the value of Avrami exponent, *n* found to vary between 1 and 2. The heterogeneous nature of melting was also confirmed using the scanning electron microscopy, from which the evidences for both nano- and micro-scale interactions of HDPE with ceramic fillers (HA and yttria stabilised zirconia) were confirmed on a microscopic scale.

1. Introduction

Hydroxyapatite (HA: $Ca_{10}(PO_4)_6(OH)_2$) is one of the main constituents of bones and is the only inorganic part of mammalian bone structure. At present there is an urgent need for using the grafts for replacing damaged bone, which might be achieved via any of either endogenous or exogenous materials: auto graft, allograft or a xenograft. Both auto grafts and allografts are proving difficult to access for medical reasons and due to the shortage of supply, which is why the popular alternative is to have a xenograft, which must be biocompatible. For xenografts, hydroxyapatite HA is widely used for research (Wang, 2003) and in commercial products, however this mineral is intrinsically weak and has to be used with another load-bearing material for making a structure which is comparable with natural bone (Wang et al., 1998).

Amongst a range of implant and bone analogue materials, since 80 s, the HA reinforced with high-density polyethylene (HDPE) is the commercial brand (HAPEX™), which has been quite well proven for its biocompatibility (Yari Sadi et al., 2006). This is because the HA mimics natural bone, and when processed with micro- and macro porous scaffolds, the osteoinduction commences well by absorbing bone morphogenic proteins, growth factors, and progenitor stem cells.

Abbreviations: HA, hydroxyapatite; Y-PSZ, yttria partial stabilised zirconia.

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Once osteoconduction commences in the composite structure, the process of osseointegration takes over locally by allowing the formation of collagen (Weiner and Wagner, 1998).

Bone, as a composite, has a complex microstructural feature which has been a major challenge in mimicking its load-bearing performance, when designing with HA based composite. In order to overcome the poor strength and elastic modulus of HA, the polymer-based bio-composite as materials engineering approach has been developed (Evans et al., 1990) for bone graft and suitable implant materials (Tripathi et al., 2010). The review (Tripathi et al., 2010) presents a comparison of mechanical properties including the coefficient of friction and wear rates against ceramic and metal surfaces. The role of HDPE in the artificial bone composite is to provide the intermediate functions of collagen, which is essential for bone function, as it is anisotropic in its load-bearing properties (Bonefield, 2006; Kong et al., 1999; Yari Sadi et al., 2004). The incorporation of HDPE with ceramic fillers therefore provides the much needed mechanical compatibility, which otherwise is difficult to engineer in synthetic composites. Most importantly, HDPE is biocompatible and does not produce any toxins (Evans et al., 1990; Kong et al. 1999; Tripathi et al., 2010) which hinder osteogenesis and osseointegration.

In brief, the literature so far strongly suggests that the interaction of ceramic particulates with HDPE determines the tensile strength and fracture behaviour of the HDPE-HA composites, which has formed the basis for selecting the nano particles of HA and zirconia for bio-composite materials engineering (Huang et al., 2009; Wang and Bonefield, 2001; Zhuang and Aizawa, 2013).

Recently, nano-scale HA (10–100 nm) has received much attention owing to its superior functional properties (Zhu et al., 2004), compared with the micrometre-scale HA materials. The nano-sized HA structure is also known for promoting pre osteoblast adhesion, differentiation and proliferation, and setting up the transport of calcium ions for osteoconduction (Silvio et al., 2002). Relevant osteogenic processes occur in nano-HA structure at a much faster rate than that reported for the micro- and macro-HA (Yari Sadi et al., 2008; Wang and Bonefield, 2001). In HA, the addition of zirconia increases strength and elastic modulus (Bonefield, 2006, Tripathi et al., 2010).

The main aim of this article is to characterise the kinetics of melting of HDPE in the presence of nano-scale HA and Y_2O_3-partial stabilised zirconia (Y-PSZ). Since the HDPE is a low melting (130 °C) material, implying that in the composite structure, the creep flow and viscous properties might be governed by the nano-scale interaction with the high melting point ceramic phases, which we aim to analyse using DSC. To the best of our knowledge, the kinetics of melting of HDPE in the presence of nano-scale (10–100 nm) particulates, especially of HA and zirconia are not reported.

The effect of different types of ceramic fillers on the rheological and thermal properties of polymer matrix were investigated previously (Chafidz et al., 2011; Joseph et al., 2002; Khasraghi et al., 2011), however in this study our focus is on the role of nano sized fillers on the melting kinetics for HDPE composite, as an approach to understanding the nano particulate filler-polymer matrix interaction which is also examined, in light of the potential use of such materials as implant or graft. The viability of osteoblasts are known to be dependent on the materials structure, especially surface properties which in such composites might be dependent on the structural relaxation, e.g. flow behaviour during fabrication. On the melting of HDPE with different ceramic filler phases the literature is limited (Alothman et al., 2014; Chen et al., 2013; Cupta et al., 1994). More specifically no report on the influence of nano-particulates of HA and Y-PSZ with HDPE on thermal behaviour and kinetics of melting are known, correlating with the microstructural changes.

2. Experimental

2.1. Preparation of nano-composite materials

HDPE powder with average particle size of 5 μm and the powder density 0.959 g cm^{-3} was used as a matrix material for the fabrication of bio-composite material for bone grafting.

Two different types of ceramic filler materials were used: (a) 99% pure HA having 20 nm average particle size and a particle density of 3.140 g cm^{-3}, and (b) partially-stabilised zirconia (ZrO_2-PSZ) which was doped with 3 mol% of yttria (Y_2O_3). The Y-PSZ nano powder was 99.9% pure and had an average particle size of 40 nm and density of 5.91 g cm^{-3}. Powders were dry mixed in a ball mill and then hot pressed at 140 °C, using 140 MPa compression pressure, after which the disc shape test samples with 15 mm diameter and height varying between 7 and 10 mm were obtained.

2.2. Differential scanning calorimetric (DSC) measurements

For the characterisation of melting properties of the bio-composites, the Perkin–Elmer DSC-8000 Thermal Analyzer was used.

The sample size for each scan varied in the range of 10–12 mg. Two different scanning conditions were applied: (a) several isochronal rates (10, 15, 20, 25, 30, 35, 40, and 80 °C min^{-1}) of scanning for heating ramp and a fixed cooling rate of 150 °C min^{-1} were adopted. (b) in the second type of scan the rates for heating and cooling were maintained at 5, 10, 20, 30, 40 and 80 °C min^{-1}.

2.3. Determination of kinetics parameters

For determining the kinetics of melting, we adopted the technique used for measuring the rate of devitrification of a glass (Jordan and Jha, 1994; Sandler et al., 2003), which is based on the Kissinger method for the analysis of Avrami model for phase transformation kinetics (Avrami, 1941; Chen, 1978; Kissinger, 1957). The reason for choosing this method is quite apparent due to the similarity in the thermal behaviour during heating and cooling cycle of an HDPE and a glass. In a multicomponent system, the melting rate is dependent on the rate of heating which is why it is essential to use the single-scan differential scanning plots for melting at different rates for the characterisation of rate of melting in the nano-composite ceramic mixed HDPE. As an example, a single scan non-isothermal DSC plot is shown in Fig. 1, from which the onset of melting T_o, peak of melting T_p, and the heat of fusion data are obtained. In this figure, the values of T_o and T_p were calculated from the intersection of the extrapolated linear section of the falling peak edge with the baseline and from the

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