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SciVerse ScienceDirect

J. Mater. Sci. Technol., 2013, 29(6), 573−581

JMST

www.JMST.org

Thermo-mechanical, Wear and Fracture Behavior of High-density Polyethylene/Hydroxyapatite Nano Composite for Biomedical Applications: Effect of Accelerated Ageing

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[Manuscript received December 22, 2012, in revised form January 15, 2013, Available online 21 March 2013]

The objective of this work is to demonstrate how the viscoelastic, thermal, rheological, hardness, wear resistance and fracture behavior of bioinert high-density polyethylene (HDPE) can be changed by the addition of hydroxyapatite (HAP) nano particles. Also the effects of accelerated thermal ageing on the composite properties have been investigated. Different weight fractions of HAP nano particles up to 30 wt% have been incorporated in HDPE matrix by using melt blending in co-rotating intermeshing twin screw extruder. The fracture toughness results showed a remarkable decrease in proportion to the HAP content. The differential scanning calorimetry results indicated that the melting temperature and crystallinity were affected by the addition of HAP nano particles into the matrix. The complex viscosity increased as the percentage of HAP increased due to the restriction of the molecular mobility. The dynamic mechanical analysis results revealed that higher storage modulus (8.3×10^{11} Pa) could be obtained in the developed HDPE/HAP in 30 wt% compared to neat HDPE (5.1×10^{11} Pa). Finally, the hardness and wear resistance of HDPE were improved significantly due to the addition of HAP nano particles. The changes in the HDPE and its nano composite properties due to ageing showed that the HDPE and its nano composites crystallinity increased while the fracture toughness, hardness, wear resistance, storage and loss modulus decreased.

KEY WORDS: **High-density polyethylene (HDPE); Hydroxyapatite (HAP); Hardness; Accelerated ageing; Dynamic mechanical analysis (DMA); Differential scanning calorimetry (DSC); Fracture**

1. Introduction

The concept of fabricating bioactive composites for bone replacements by reinforcing a high-density polyethylene (HDPE) matrix with a bioactive hydroxyapatite (HAP) was introduced in early 1980s[1]. The mechanical coupling of the reinforcement and the matrix is resulting from the shrinkage of HDPE matrix and HAP particles during the composite processing[2]. The HAP increases the stiffness of the composite and provides bioactivity, while HDPE provides toughness but bioinert. Therefore, the mechanical and biological properties of HDPE/HAP composite can be tailored to meet specific clinical requirements. The closer modulus of HDPE/HAP composite to natural bone shows promise in solving the problem of bone resorption that has been encountered with the use of implants made up of other conventional materials[3−6]. The implants made of HDPE/HAP composite encouraged bone apposition rather than the fibrous encapsulation which was encountered with other implant materials. Tanner et al.[2] have reported successful clinical applications of this composite as orbital implants to treat problems such as post-enucleation socket syndrome and orbital floor fractures. Also the HDPE/HAP composite can be used successfully as middle ear implant.

It has been reported that the elastic modulus of HAP (in the micro scale)/polyethylene (PE) composite can reach the lower range of human cortical bone modulus[7]. This can be attributed to the low dissolubility and degradation of relatively large size of HAP[8]. Recently, the nano-scale HAP has been developed and an HDPE/HAP nano composite with acceptable properties can be easily processed. The nano HAP particles have high surface area and its size is similar to the mineral found in human hard

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http://dx.doi.org/10.1016/j.jmst.2013.03.020

tissues[8]. Also the nano HAP takes the advantage of homogenous distribution in the polymer matrix.

The mechanical and rheological properties of HDPE/HAP composite have been extensively studied[9−14]. Wang et al.[15] studied the effect of HAP particle size on the HDPE/HAP composite properties. The results showed that the composites with smaller HAP particles had higher torsional, tensile modulus and tensile strength, but had lower fracture strain. Joseph et al.[6] studied the effects of surface and morphology of HAP on the rheology and processability of an injection molding grade HDPE/HAP composite. Eniwumide et al.[16] investigated the effects of HAP morphology and PE molecular weight on the fracture toughness of PE/HAP composite.

It is well known that PE and its composites have a viscoelastic behavior even under normal loading conditions. Their overall mechanical properties change over time due to ageing either on shelf or *in vivo*. The ageing of PE and its composites causes subsurface oxidative degradation (between 1 and 2 mm) under the polymer surface[17]. This oxidative degradation causes embrittlement of the polymer and loss of its overall mechanical properties. The characterization of ageing effects on the behavior of PE and its composites that are used as bone substitutes will help in understanding and predicting the *in vivo* behavior of these composites with time. Because oxidation of PE (due to natural ageing) takes months or years to reach an appreciable level at ambient or body temperature, thermal ageing techniques have been developed to accelerate the oxidation of PE with the expectation that the material behavior after accelerated ageing will be comparable to naturally aged ones. Based on this assumption, accelerated thermal ageing has been widely used by many researchers to investigate the resistance of PE to ageing[18−21]. Using this ageing technique, from 5 to 10 years of shelf ageing can be simulated within a time period of few weeks.

To the best of our knowledge, the effects of *in vivo/in vitro* ageing on the properties of HDPE/HAP nano composite have not been investigated. Also, it is remarked that there is a lack of data on the viscoelastic and bioactive behavior of HAP/PE nano composite. Therefore, the present study is a part of research project that is intended to study the effects of accelerated ageing on thermal, mechanical, viscoelastic and fracture behavior of HDPE/HAP nano composites. Also, in this project, the effect of nano HAP ratio on the nano composite bioactivity will be investigated. The main objectives of this part of the project are: (1) fabricating of HDPE/HAP nano composite by using melt blending in a co-rotating intermeshing twin screw extruder, (2) studying the effects of HAP nano particles percentage and artificial ageing on the thermal, rheological, viscoelastic, fracture toughness, hardness and wear behavior of the HDPE nano composite.

2. Experimental

2.1. Material

The polymer used in the present work is an injection molding grade of HDPE which is referred as HDPE. The manufacturer (SABIC Company SA) indicated that this HDPE has melt flow index of about 30 g/10 min and density of about 0.94 g/cm^3. The estimated average molecular weight was about 700,000 g/mol (calculated from the melt viscosity). The hydroxyapatite (HAP) nano particles were obtained from Fluidinova, Engenharia de Fluidos, SA, Portugal. According to the manufacturer data, the typical nano-crystal size is less than 100 nm and the average aggregate size is 2.5 μm with specific surface area of 100 m^2/g.

2.2. Preparation of specimens

Weight ratios of 0, 10, 20 and 30 wt% of the HAP nano particles were pre-mixed with neat HDPE pellets to get the required nano composite pre-blend. The pre-blend was compounded in Farrell co-rotating intermeshing twin screw extruder. The twin screw extruder has a diameter of 26 mm and length/diameter (L/D) = 35. The screw speed was kept constant at 12 r/min. The temperature profile used (from feed to die) was 180, 230, 235, 240, 240, 235, and 240 °C. The extrudates from the extruder were cooled in a water bath at about 12 °C, air dried, then palletized into granules. The granules were further dried and conditioned in the lab environment for 40 h. An injection molding machine (Asian Plastic Machinery, Double Toggle I Machine, Super Master Series SM 120) was used to get a set of standard ASTM D638 type-I tensile specimens[22]. Specimens were conditioned in a standard lab environment for 40 h before further testing. ASTM D638 standard was used as our guide. Although the standard recommends testing of at least 5 specimens, ASTM standard allows testing fewer specimens if so mentioned in the report. In the present study all the experimental tests were performed with 3 specimens. All the results presented here are the median of the three measurements.

2.3. Ageing procedure

The accelerated ageing of HDPE/HAP nano composite specimens is performed in saline solution at temperature of 80 °C for 4 weeks that equals around 6 years of natural ageing[21]. In the present study, it is assumed that the ageing procedures used will result in ageing mechanism comparable to the real *in vivo* ageing mechanism[23].

2.4. Characterization methods

The morphological studies of HDPE/HAP nano composites cryo-fracture surface and single edge notched (SEN) fractured samples were examined by scanning electron microscopy (SEM, Joel, USA) at 15 kV. Prior to SEM examination, the nano composite specimens were coated with a thin layer of gold to dissipate the build-up of heat and electrical charges.

Infrared radiation (IR) was performed in the attenuated total reflection (ATR) mode by using a Bruker Spectrum Tensor 27 system equipped with an ATR cell with a diamond reflection element. This machine was used for measuring and scanning the IR absorption spectra of HDPE/HAP aged and non-aged nano composite. Samples were applied directly onto the surface of ATR crystal. Spectra result from the accumulation of 16 scans at 4 cm^{-1} resolution. The wavenumber range was 4000−400 cm^{-1}.

The single edge notched (SEN) specimens for the fracture toughness measurements were prepared by inducing a pre-crack to one side of the ASTM tensile sample (type-III) with a sharp thin razor blade. The pre-crack length was fixed at 10% (a/D). Different SEN specimens were prepared as described and tested for their fracture toughness. All of the reported measurements for all of the tests in this research represent the median of 3 experiments. The tensile tests were performed at 50 mm/s. The fracture toughness (K_I) of the neat HDPE and its nano composite