Preparation and characterization of bioactive composites and fibers for dental applications

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Maryam Qidwai[a], Muhammad Ali Sheraz[a], Sofia Ahmed[a], Abdulaziz Abdullah Alkhuraif[b], Ihtesham ur Rehman[a],*

[a] *Department of Materials Science and Engineering, The Kroto Research Institute, University of Sheffield, North Campus, Broad Lane, Sheffield S3 7HQ, UK*
[b] *Dental biomaterial research chair, College of applied medical science King Saud University, Saudi Arabia*

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ABSTRACT

Objectives. The present study was carried out to create composites and fibers using polyurethane (PU) with hydroxyapatite (HA) that could be used for dental applications.

Methods. Composites with varying HA concentration were prepared by solution casting technique. Similarly, PU–HA fibers with varying PU hard and soft segments and fixed HA concentration were also prepared. Various characterization techniques, such as, X-ray diffractometry, differential scanning calorimetry, scanning electron microscopy and Fourier transform infrared spectroscopy in conjunction with photo-acoustic sampling cell were employed to study the composites and fibers for changes in their physicochemical properties before and after immersion in artificial saliva at 37 °C for up to 5 days.

Results. The results indicated formation of amorphous apatite layers with maximum amorphicity in composites containing highest amount of HA with 5 days of immersion in artificial saliva. Similarly, fibers with more PU hard segment resulted in better transformation of crystalline HA to its amorphous state with increasing immersion time thus confirming the bioactive nature of the HA–PU fibers.

Significance. Concentrations of HA and PU hard segment along with the duration of immersion in artificial saliva are two major factors involved in the modification of solid-state properties of HA. The amorphous apatite layer on the surface is known to have tendency to bind with living tissues and hence the use of optimum amount of HA and PU hard segment in composites and fibers, respectively could help in the development of novel dental filling material.

1. Introduction

In the recent past, the use of polymer composites for biomedical applications has gained massive recognition. Composites are popularly used as dental filling materials for restoration of tooth caries and are much preferred over other dental restorative materials due to their user friendly properties [1,2]. Properties of the composites, such as their biological and mechanical characteristics, can be tailored by changing type

and ratio of the ingredients which may affect the interfacial adhesion at the interface where polymeric matrix comes in contact with the surrounding environment [2,3]. Therefore, it has always been of great significance to develop a correlation between in vitro and in vivo results regarding the changes in physical and chemical properties, stability, degradation, etc. of the composites.

Polyurethane (PU) polymers are widely used as biomaterials in clinical applications. Over the years, their morphology, mechanical properties, synthesis and chemical properties have managed to gain significant attention of researchers due to their excellent and easily alterable properties [2,3]. PU is comprised of different groups of polymers containing linkages of urethane within chains of each polymer. The fundamental parts of the polymer include the hard segments containing isocyanates and diols as chain extenders, and the soft segment containing polyols. All these monomers determine the properties of the resulting polymer [2]. Degradation of PU is known to be affected by pH and temperature and it is reported that the body temperature (37 °C) along with its aqueous environment is sufficient to degrade a number of polymers [2–4]. The process of hydrolysis and the rate of hydrolytic degradation for PU are related to the ester and ether linkages in the structure which are determined by the composition of hard and soft segments [2]. Some other factors involved in affecting the biostability of PU are synthesis, processing, fabrication, surface area, physiological environment, etc. [2,5].

Hydroxyapatites (HA) due to their biocompatibility have found wide variety of uses in the field of dentistry and medicine. HA can exist in both crystalline and amorphous forms and is able to transform from one form to the other during preparation [6,7]. The availability of HA in different forms has resulted in variable results in the respective fields and has caused some restrictions regarding its requirements by US Food and Drug Agency [6]. Crystalline forms of HA are known to have better bond strength and cohesive properties whereas amorphous forms of HA are known to have high dissolution [7]. The amorphous forms of HA when present on the outer surface of coating promote the growth of osseous tissue better than the crystalline form but do influence the stability of the implant or composite if present in excess or throughout the material [6,7]. It is therefore of utmost importance to evaluate a particular form before its application.

The stability of dental composites in an aqueous environment depends upon its adequate mechanical properties with non-porous and smooth surfaces because these properties are profoundly affected by the action of water [1]. It has also been reported that dissolution or degradation in surface layers may take place in materials that remain in contact with body fluids and some loss of unbound components is suspected may be along with fluid uptake into the basic structure. This fluid uptake in discrete zones of the material may exert unwanted residual pressure on the tissues thus resulting in softening, degradation or leakage of the materials [2,6,8].

The object of the present investigation is to prepare PU–HA composites and fibers with varying HA concentrations in composites and PU hard segments in fibers and study the effect of artificial saliva on their stability and solid-state properties

with respect to time. This study would help in the development of composites and fibers of PU–HA with appropriate solid-state properties that could be used in the field of dentistry as novel obturating materials.

2. Materials and methods

2.1. Materials

Biomedical grade PU (Z3A1) was obtained from Biomer Technology Limited (Runcorn, UK), HA (sintered powder, Captal® S) from Plasma Biotal Limited (Buxton, UK) and tetrahydrofuran (THF) (99.99%) from Fisher Scientific Inc. (Loughborough, UK). Versalink® P-650 (oligomericdiamine) was procured from Air products and Chemicals, Inc. (Allentown, USA), methylene diphenyl diisocyanate from Biesterfeld (Hamburg, Germany) and Cil Release® (1812 E) spray from Chemical Innovations Limited (Preston, UK). Artificial saliva (Saliveze™, Wyvern Medical Limited, UK) was purchased from a local pharmacy.

2.2. Preparation of PU stock solution

A stock solution of 5% PU was prepared in THF. The solution was stirred on a magnetic stirrer for 24 h at room temperature, protected from light.

2.3. Preparation of PU–HA composites by solution casting method

PU–HA composites were prepared in different ratios of 1:2, 1:4, 1:6, 1:8 and 1:10 by solution casting technique. From the stock solution, 10 ml of PU was taken out in a 25 ml conical flask and further stirred for 30 min. HA is insoluble in THF and forms a suspension when mixed with PU in THF solution. Therefore, each time HA powder was gradually added to the conical flask containing PU solution during stirring in order to obtain uniform dispersion. After adding all the HA powder of the desired ratio, the solution was further stirred for 30 min and then immediately poured in an aluminum mold. Before pouring of the suspension, the molds were sprayed with a mold releasing agent (Cil release®) in order to remove the composites easily from the mold. Slow evaporation of the solvent was achieved by covering the molds with a glass slide. Each set of composites was prepared in triplicate.

2.4. Preparation of PU–HA fibers by solution casting method

The composition of each type of fiber is given in Table 1. The fibers with varying amount of PU were prepared by thoroughly mixing Versalink® P-650 (PU-soft segment) and methylene diphenyl diisocyanate (MDI) (PU-hard segment) with HA powder to form a homogenous mixture before casting into a custom made aluminum mold. The mold was sprayed in the similar manner as described above to easily obtain the longitudinal fibers. Each set of fibers was prepared in triplicate.