DEPOSITION OF THE HYDROXYAPATITE PARTICLES ON THE POLYETHER ETHER KETONE SURFACE FOR ORTHOPAEDIC APPLICATIONS

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I would like to dedicate this thesis to

My Parents

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ABSTRACT

Polyether-ether-ketone (PEEK) has a similar elastic modulus close to bone and as a result it can be a suitable alternative material to metallic implants which generally have higher moduli. However, the bio-inertness of PEEK prevents it from integrating well with the surrounding tissues. Many efforts have been made to overcome this problem including the deposition of hydroxyapatite (HA) on PEEK via plasma spraying. Current issues which have arisen with this method are low bonding strength between the substrate and the coating layer, as well as producing a non-uniform density of the coating. In this study, chemical deposition method was used to deposit HA crystalline particles on a treated PEEK substrate without any subsequent sintering process. The surface of PEEK was first sulphonated to create –SO_3H functional group. It was then immersed in suspension of HA in water where the HA particles were chemically connected to the –SO_3H functional group. The treated layer has a 3D porous property but exhibits very low mechanical properties. A compress force was applied on the coated layer for improving its mechanical properties. EDX and XRD results confirmed the existence of crystalline HA on the treated layer. FT-IR analysis was used to confirm the chemical bonding between HA and the substrate. The bioactivity of the HA treated layer was evaluated in terms of wettability. The water contact angle test showed 50% increase in wettability of the treated samples as compared to PEEK. The scratch and nano-indentation tests were carried out on the treated layer to assess its adhesion strength to the substrate and its mechanical strength respectively. The results showed that the compression caused 142% and 36.9% increment of the elasticity modulus and scratch hardness of the treated layer respectively. However, it caused 59% increase in the water contact angle. These findings indicate that the proposed new method is easy to process and does not require special equipment as compared to the Plasma Spray technique. The proposed method can be an alternative technique to change the bio-inertness of PEEK to become more bioactive PEEK which is good for polymeric implant material.

ABSTRAK

Polieter - eter – keton (PEEK) mempunyai modulus kekenyalan yang hampir sama dengan tulang dan oleh yang demikian, ia sesuai digunakan sebagai satu bahan alternatif kepada implan logam sedia ada yang secara umumnya mempunyai modulus kekenyalan yang lebih tinggi. Namun, sifat bio-lengai PEEK menghalangnya daripada menyatu dengan baik dengan tisu di sekelilingnya. Banyak usaha telah dilakukan untuk mengatasi masalah ini termasuklah melalui pemendapan hidroksiapatit (HA) ke atas PEEK dengan kaedah penyemburan plasma. Isu-isu terkini yang timbul daripada kaedah ini adalah daya ikatan yang lemah di antara substrat dan lapisan salutan serta penghasilan ketumpatan salutan yang tidak seragam. Dalam kajian ini, kaedah mendapan kimia telah digunakan untuk memendapkan zarah hablur HA ke atas substrat PEEK terawat tanpa memerlukan proses pengsinteran selepasnya. Mula-mula sekali permukaan PEEK menjalani proses pengsulfonan untuk membentuk kumpulan berfungsi $–SO_3H$. Kemudian, ia direndamkan dalam larutan HA di dalam air yang mana zarah-zarah HA tergabung secara kimia dengan kumpulan berfungsi $–SO_3H$. Lapisan yang dirawat mempunyai sifat keliangan 3 dimensi tetapi mempamerkan sifat kekuatan mekanikal yang sangat rendah. Satu daya mampatan telah dikenakan ke atas lapisan salutan tersebut untuk memperbaiki sifat mekanikalnya. Keputusan EDX dan XRD mengesahkan kewujudan HA berhablur pada lapisan salutan yang terawat. Analisa FT-IR telah digunakan untuk mengesahkan ikatan kimia di antara HA dan substrat. Keaktifan bio lapisan terawat HA dinilai dari segi sifat kebolehbasahannya. Ujian sudut sentuhan air menunjukkan peningkatan sebanyak 50% sifat kebolehbasahan bagi sampel terawat berbanding dengan sampel PEEK. Ujian calar dan ujian lekukan nano masing-masing telah dijalankan ke atas lapisan terawat untuk menilai kekuatan lekatannya kepada substrat dan juga menilai kekuatan mekanikalnya. Keputusan menunjukkan bahawa mampatan telah menyebabkan peningkatan sebanyak 142% dan 36.9% kepada modulus kekenyalan dan kekerasan calar masing-masing ke atas lapisan terawat. Walau bagaimana pun, mampatan ini juga menyebabkan peningkatan sebanyak 59% kepada sudut sentuhan air. Penemuan-penemuan ini menunjukkan kaedah baru yang dicadangkan adalah mudah untuk diproses dan tidak memerlukan peralatan khas jika dibandingkan dengan teknik semburan plasma. Kaedah yang dicadangkan ini boleh menjadi satu kaedah alternatif bagi mengubah sifat bio-lengai PEEK kepada sifat yang lebih bioaktif yang mana ia baik bagi bahan implan berasaskan polimer.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

Ac - projected contact area between the sample and indenter
ALP - Alkaline phosphatase
ANAB - Accelerated Neutral Atom Beam
ASTM - American Society for Testing and Materials
A-TiO_2 Anatase-rich titanium dioxide
BCP - Biphasic Calcium Phosphates
BIC - Bone - in- contact
BMP-2 - Bone morphogenetic protein-2
CFR-PEEK - Carbon-fiber-reinforced PEEK
CS - Calcium oxide and silicon dioxide
CT - Computed tomography
CVD - Chemical Vapour Deposition
DLC - Diamond-like carbon
DSC - Differential scanning calorimetry
E - Modulus of elasticity
ECM - Extracellular matrixes
EDX - Energy Dispersive X-ray Spectroscopy
F - Load
FDA - Food and Drug Administration of united state
FN - Fibronectin
GPa - Giga Pascal
gr - Gram
Gy - Gray (SI unit of absorbed radiation)
H - Hardness
HA - Hydroxyapatite
HBMSC - Human Bone Mesenchymal Stem Cells

hr/hrs - Hour/Hours
Hs - Scratch hardness
ISO - International Organization for Standardization
LC - Critical load
LC1 - First cohesive failure in coating layer
LC2 - Adhesive failure
min - Minute
MPa - Mega Pascal
MRI - Magnetic resonance imaging
MTS - Methoxyphenyl tetrazolium salt
NMR - Infrared spectroscopy nuclear magnetic resonance
ºC - Degree of Celsius
PAEK - Polyaryl ether ketones
PEEK - Polyether ether ketone
PEKEKK - Poly-ether-ketone-ether-ketone-ketone
PLIF - Posterior lumbar inter-body fusion cage
PLLA - Poly-L-lactic acid
PMMA - Poly (methyl methacrylate)
ppb - Part per billion
PS - Polystyrene
PVD - Plasma vapor deposition
R-TiO_2 Rutile-rich titanium dioxide
S - Stiffness
SBF - Simulated Body Fluid
SPEEK - Sulphonated Polyether ether ketone
Tg - Glass transition temperature
Ti - Titanium
TiO_2 - Titanium dioxide
UV - Ultraviolet
VPS - Vacuum plasma spraying
W - Width of the scratch
XRD - X-ray diffraction
XRD - X-ray Diffraction Spectroscopy
YSZ - Yttria-stabilized zirconia

α - Indenter face angle

βTCP - β-tricalciumphosphate

δ - Indentation depth

δc - Contact depth

ε - Geometric constant of indenter

μm - Micro meter

υ - Poisson’s ratio

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Background of the Research

One of the most costly and wide spread health problems is back pain, resulting in more lost productivity of the patient in comparison to other diseases in the United State (Birkmeyer and Weinstein, 1999; Frymoyer and Ducker, 1991). For instance, lasting back pain was increased in the patient from 3.9% to 10.2% between 1992 and 2006 in North Carolina households (Freburger *et al.*, 2009). In 2014 in the United States, over 200,000 spinal fusion surgeries were performed (Zigler, 2015). Around 25% of back pain patients will undergo spinal surgery. Spinal fusion is one of the methods which can be used in many cases to reduce problems of some segment of the spinal column. In spinal fusion surgery, two or more adjacent vertebrae (bone of spinal column) will be immobilized. The adjacent vertebrae are bonded together and the disc between the vertebrae is removed to stimulate the bone growth in between them forming one solid bone (Wu and Yarin, 2013). Many interbody fusion cages with various materials are made. Some of them are made from titanium such as the Ray, Harms, Pyramesh, Lordotic LT and InterFix cages. Some of them are made from polyether ether ketone (PEEK) such as SynCage, and some are made from Cortical Bone Dowel and carbon fiber such as Brantigan cage (Kurtz and Devine, 2007).

The high elastic modulus of titanium (~100GPa) as compared to the adjacent bone, which is implanted in, for instance cortical bone (~15GPa) can result in stress shielding which cause decline of the bone that is in contact with the titanium implant. In the case of spinal implants, in which a large percentage volume of the vertebrae consists of cancellous bone (the modulus of elasticity ~0.3GPa) the shielding problem becomes one of the main issues. In the design of spinal cage, choosing material with low modulus of elasticity is desired. Cancellous bone is a soft, cellular-structured bone, which absorbs shock in the spinal column. Metal ions release is another issue in metallic implants which can cause failure (Ramakrishna *et al.* 2001; Stadelmann *et al.* 2008). These phenomena increase motivation of research towards polymeric implants. In order to reduce the problem of titanium spinal fusion cage, polymer materials with closer modulus elasticity to the bone and high strength have been utilized (Kurtz and Devine, 2007).

Low modulus of elasticity, excellent chemical stability, resistance to radiation used in sterilization procedures, transparency to radio waves, compatibility with reinforcing agent (such as carbon fiber) which can get wide variety of mechanical strength (4~20GPa, depending on fiber volume fraction), etc. have made PEEK as an ideal choice for load bearing implants (Han *et al.*, 2010; Kurtz and Devine, 2007; Sobieraj *et al.* 2009; Toth *et al.*, 2006; Williams, 2008; Xing *et al.*, 2004). PEEK has been used for load bearing orthopaedic applications such as screws, spinal cage, and dental implant (Schwitalla and Muller, 2011; Williams *et al.* 1987).

Food and Drug Administration of the United States (FDA) have accepted carbon-fiber-reinforced PEEK (CFR-PEEK) for spinal fusion cages for human use since the 1990s. Biomaterial PEEK has twenty years of successful clinical history in spinal fusion cage (Kurtz and Devine, 2007). While titanium is still being used for manufacturing the spinal fusion cages, most of the companies have switched their focus to PEEK instead of titanium. For instance, the designers of the Wallis posterior dynamic stabilization system have changed their titanium inter-spinous component to PEEK (Senegas, 2002).

Despite these excellent properties, PEEK is still categorized as bioinert due to its very low reaction with the surrounding bone tissue, which limits its potential applications (Kurtz and Devine, 2007; Rabiei and Sandukas, 2013). To overcome this problem several methods have been proposed, in which the deposition of the hydroxyapatite is one the most attractive methods for researchers. This coating has attracted the attention of many researchers and is the only commercial method for improving the bioactivity of the PEEK implants. Crystalline HA coating is required to stabilize the layer especially for long term orthopaedic and dental implants. In the present methods, the coated HA on the implants require sintering process in order to transform amorphous structure to crystalline (Rabiei and Sandukas, 2013). Sulphonation of PEEK is one of the activation method which deposit the SO_3H functional group via immersion in sulphuric acid (Zhao *et al.,* 2013). This active surface of sulphonated PEEK (SPEEK) can be use for binding with particles.

1.2 Problem Statement

Traditional heat treatment for crystallizing of amorphous HA coating layer has been done via annealing at 600˚C or higher. This temperature is above the melting point of PEEK (340˚C). To overcome this problem, three new methods of microwave sintering (Adams *et al.*, 2006), laser-induced crystallization (P. M. Smith, Carey, and Sigmon, 1997), and hydrothermal annealing (Ozeki *et al.* 2003; Tong *et al.*, 1997; Yang *et al.* 2007) have been investigated and reported with some success. PEEK is transparent to microwave and it allows heating on HA layer. Laser method is able to provide localized heating and saturated steam is utilized in hydrothermal annealing. Although these methods can crystallize the HA coating layer without spoiling the bulk of the PEEK substrate, at the interface layer between the HA coating and the substrate is impaired (Rabiei and Sandukas, 2013). This research was guided by the following questions:

1. Can sulphonated PEEK be linked to crystalline HA?

2. What is the effect of the sulphonation time on the wettability (bioactivity) of the treated PEEK?
3. What is the effect of the compression load on the properties of the treated layer?

1.3 Objectives of the Research

The principal objective of this research was to establish a new method for depositing crystalline HA on PEEK with the intention to eliminate subsequent sintering of the HA coating. The specific objectives for this research were as follows:

1. To evaluate the linking process via sulphonation for depositing the HA particles with high percentage of crystallinity.
2. To evaluate the effect of different sulphonation process parameters on the surface wettability of the treated PEEK.
3. To compare the mechanical properties and surface morphology of the treated layer before and after applying compression load.

1.4 Scopes of the Research

The research was conducted within the following limits:

1. Polyether ether ketone (PEEK) was used as the substrate material.
2. Sulphonation process was conducted to activate the surface of the PEEK by depositing $-SO_3H$ polar functional group on the molecular chain of the PEEK. The sulphonation process time was varied between 3 to 20 minutes.

3. Fourier Transfer Infrared Spectroscopy (FTIR) was used for evaluating the chemical bonding; X-Ray Diffraction (XRD) for evaluating the crystallinity of the treated layer; Field Emission Scanning Electron Microscope (FESEM) for observing surface morphology; Energy Dispersive X-Ray Spectroscopy (EDX) for determining elements; and Atomic Force Microscope (AFM) for evaluating surface roughness.
4. Mechanical properties of the treated layer were investigated using nanoindentation and micro scratch test.
5. Wettability property of the treated layer was evaluated using water contact angle analysis.
6. Hydraulic press was employed to apply compression load of 15MPa on the treated layer.

1.5 Significance of the Research

Plasma spray is the most popular method used to deposit HA on the PEEK biomedical implant. It was followed by microwave sintering process treatment for increasing the HA crystallinity. Due to high temperature processing, this method has been reported posing problems at the interface HA - substrate layer though the process is capable to provide the required crystallinity level. The equipment used for depositing HA via plasma spray technique is also expensive and demands a secondary microwave process which adds cost and time for manufacturing an implant. In contrast, the proposed method uses a chemical deposition of crystalline HA particles on sulphonated PEEK that could eliminate these costly equipment and secondary processes to manufacture an implant. It is expected the cost will become cheaper with the new method. This encouraging technique also has a great potential to eliminate problems occurred at the interface layer due to high temperature. It is also expected that the manufactured implant via the proposed method becomes more sustainable in the long run.

1.6 Organization of the Thesis

This thesis consists of five chapters: Chapter 1 briefly discusses the background of problem, problem statement, objectives of the research, scope of the research, contribution and organization of the thesis. Chapter 2 discusses the background of biomaterials, and recent strategies for improving the bioactivity of the PEEK's implant. Chapter 3 describes the research methodology used in conducting this research. Chapter 4 presents the experimental results and discusses the findings from experimental trials. Chapter 5 provides the conclusions of the research.

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