

**PREPARATION AND CHARACTERIZATION OF
HYBRID FILLER REINFORCED UHMWPE
COMPOSITES FOR ARTIFICIAL JOINT
REPLACEMENT**

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UNIVERSITI MALAYSIA PERLIS

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**Preparation and Characterization of Hybrid Filler
Reinforced UHMWPE Composites for Artificial Joint
Replacement**

by

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A thesis submitted in fulfillment of the requirements for the degree of
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LIST OF ABBREVIATIONS

3-APTES	3-Aminopropyl Triethyloxysilane
Al ₂ O ₃	Aluminium Oxide/Alumina
ASTM	American Society for Testing and Materials
CNT	Carbon nanotube
CS	Chitosan
DSC	Differential Scanning Calorimetry
E _B	Elongation at Break
FTIR	Fourier Transform Infrared
GO	Graphene Oxide
HA	Hydroxyapatite
HDPE	High-density polyethylene
LDPE	Low-density Polyethylene
PMMA	Polymethyl Methacrylate
SEM	Scanning Electron Microscope
SiO ₂	Silicon Dioxide
TGA	Thermogravimetry Analysis
TiO ₂	Titanium Dioxide
tZnO	Treated (3-APTES) Zinc Oxide
UHMWPE	Ultra-High Molecular Weight Polyethylene
wt. %	Weight percentage
ZnO	Zinc Oxide

Penyediaan dan Pencirian Komposit UHMWPE Diperkukuh Pengisi Hibrid bagi Penggantian Sendi Buatan

ABSTRAK

Ini merupakan satu kajian mengenai UHMWPE diisi pelbagai kandungan Zink Oksida (ZnO) (3, 7, 12, 18 and 25 wt.%) dan penghibridan melalui penambahan kitosan (CS). Kajian lanjutan dilakukan dengan menjalankan rawatan permukaan 3-APTES terhadap partikel dengan 3-APTES sebagai ejen gandingan. Kesemua spesimen komposit dicampur menggunakan teknik penghancuran bebola kering dan komposit disediakan menggunakan pengacuan mampatan panas. Penambahan ZnO terhadap UHMWPE menghasilkan kenaikan dalam kekuatan tegangan sebanyak 28.99% berbanding UHMWPE tidak terisi pada kandungan 12wt.% ZnO. Penambahan ZnO sehingga kadar optimum (12 wt.%) telah menaikkan rintangan terhadap kehausan, selaras dengan pengurangan berat paling minimal. Kekuatan lenturan dan modulus lenturan dengan penambahan ZnO sehingga 25 wt.% apabila dibandingkan dengan UHMWPE tulen. Walaubagaimanapun, penambahan CS (1, 2, 3 wt%) terhadap komposit UHMWPE/ZnO dengan kandungan ZnO optimum (12 wt.%) telah menurunkan rintangan terhadap kehausan komposit hibrid tersebut dimana terdapat penurunan dalam kekuatan dan modulus lenturan tetapi masih tinggi berbanding UHMWPE tulen. Penambahan ZnO ke dalam UHMWPE telah menurunkan takat lebur (T_m) komposit itu tetapi melambatkan takat degradasi komposit tersebut. Penyiasatan lanjutan melalui penambahan kitosan telah menurunkan peratusan penghabluran, X_c UHMWPE. Nilai kekerasan telah meningkat dengan penambahan kandungan ZnO namun penambahan CS telah menurunkan nilai kekerasan. Kesan rawatan keatas ZnO terhadap sifat komposit UHMWPE mengakibatkan penambahbaikan dalam kesemua aspek komposit UHMWPE dan komposit hibrid. Nilai perubahan terbesar merupakan dalam kekuatan regangan dan rintangan terhadap kelusuan pada 12 wt.% kandungan ZnO dirawat ($tZnO$). Namun, kekuatan dan modulus kelenturan telah dicapai melalui penambahan 2 wt.% CS terhadap komposit hibrid UHMWPE. Penstabilan haba juga telah tercapai dengan lebih kandungan $tZnO$ bilamana degradasi melalui haba UHMWPE telah terhalang sebanyak 7% untuk nilai $T_{10\%}$. Akhirnya, adalah terbukti secara eksperimental bahawa komposit hibrid CS— $tZnO$ sebagai pengisi telah mencapai keputusan terbaik dalam aspek bio-keserasian melalui teknik Alamar Blue (AB) assay.

Preparation and Characterization of Hybrid Filler Reinforced UHMWPE Composites for Artificial Joint Replacement

ABSTRACT

This is a study of ultra-high molecular weight polyethylene (UHMWPE) reinforced with zinc oxide (ZnO) under various filler loadings (3, 7, 12, 18 and 25 wt.%) and hybridized with incorporation of chitosan (CS). Further development of the UHMWPE composite was via 3-APTES treatment of the ZnO particulates with silane as a coupling agent. All composite specimens were mixed via dry ball milling and prepared using hot compression molding. Additions of ZnO towards UHMWPE resulted in an increase of 28.99% in the ultimate tensile strength compared to unfilled UHMWPE with the optimum percentage (12 wt%) of ZnO. The addition of 12 wt.% ZnO also has significantly increase the wear resistance of tested composites, in accordance with the minimal weight loss. The flexural strength and modulus had a notably high improvement through ZnO addition up to 25 wt% as compared to pure UHMWPE. However, the incorporation of CS (1, 2, 3 wt%) in the optimum percentage (12 wt%) of UHMWPE/ZnO composites has slightly changed the properties of the hybrid composites where the addition of CS had resulted in lower flexural strength and wear resistance than that of 12 wt% ZnO UHMWPE composite but still higher than that of pure UHMWPE. The addition of ZnO to the UHMWPE matrix had lowered the melting temperature (T_m) of the composite but delaying the degradation temperature of the composite. Further investigation of dual filler incorporation was done by addition of CS to the UHMWPE/ZnO composite and resulted in reduction of the degree of crystallization, X_c , of UHMWPE. Chemical resistance was improved with higher ZnO content with a slight reduction of mass change after incorporation of CS. The hardness value increased with ZnO addition but higher incorporation of CS had lowered the hardness value. Effect of treatment on ZnO towards the properties of UHMWPE composite and hybrid resulted in a significant improvement compared to UHMWPE filled untreated ZnO on all properties on both UHMWPE composite and hybrid composites. The highest magnitude of change was seen in the tensile strength and wear resistance was at 12 wt.% of treated ZnO (tZnO) content. However, the flexural properties achieved highest point with incorporation of 2 wt.% CS towards UHMWPE/tZnO. Thermal stability was also achieved with more tZnO addition where the thermal degradation of UHMWPE was hindered around 7% for the $T_{10\%}$ value. Ultimately, it was experimentally proven that the UHMWPE hybrid composite with CS—tZnO as fillers had best out in the terms of biocompatibility via Alamar Blue (AB) assay.

CHAPTER 1

INTRODUCTION

1.1 Introduction

The use of UHMWPE in the arthroplasty fields begun approximately about 20 years after the first arthroplasty by Philip Wiles in the late 1930s (Reynolds et al., 2007). Back then, the components were fully metal or metal-on-metal (MOM) for both femoral and acetabular component which stainless steel was used (Klapperich et al., 1999). In 1950, an effort to fabricate a new material for arthroplasty was carried out by using cast cobalt chrome molybdenum (CoCrMo) alloy. These first generation MOM designs encountered several critical issues with design tolerance, biocompatibility and metallic hypersensitivity. In the 1950s, Sir John Charnley tested the frictional properties of natural joints and concluded that they perform well because of their low coefficient of friction (COF). This was due to the unique properties of the cartilage tissue that expels synovial fluid between the contacted surfaces. These fluids then became separated by thin liquid film (hydrodynamic lubrication), while artificial joint fabricated from synthetic materials must operate with (almost) no liquid between the contact surfaces (boundary lubrication) (Ludema, 1996). UHMWPE was used as artificial joint parts since its early appearance on November 1962 and even until today UHMWPE still maintained as gold standard bearing material for total joint replacements (Kurtz, 2004). It has been chosen over other polymers because of its excellent wear resistance, suitable

mechanical properties and biocompatibility in the physiological environment (Liu et al., 2013).

In current practice, there are about 1 million total joint replacement surgeries yearly worldwide (Ingham et al., 2005). According to a study which was funded by the U.S. National Institutes of Health's National Institute of Arthritis and Musculoskeletal and Skin Diseases in 2012, there are currently 4.5 million individuals are living with at least one Total Knee Replacement (TKR) in the United States alone (Weinstein et al., 2012). Knee replacement was the 14th most common inpatient procedure in 2009. Over 650 thousand knee replacement taken place in the 2010. From 1997 until 2009 there was an increase of 84% of the case has been occurred that is from 120, 000 to 220, 000 respectively. From these procedures only 80% knee replacement lasts 20 years and 1.8% had postoperative infection (Fawzi et al., 2011). This poses a higher drive for further development for the UHMWPE surface in TKR as problems such as wear, internal infection and post-surgery swelling would occur more in number.

1.2 Problem Statement

Material properties in the aspect of its mechanical, thermal, physical and bioactivity scope are vital in developing a biomedical device. UHMWPE is an excellent candidate to serve as the joint surface in TKR. However, the device wear resistance is a concern and biomedical properties such as biocompatibility, antimicrobial or cytotoxicity have yet to be developed as UHMWPE was known as a bio-inert material. Enhancements of UHMWPE are focused on the prevention of infection, material properties (mechanical properties, thermal and tribology) of the components and methods of fixation. Previous researchers have participated in enhancing the wear

resistance of UHMWPE by addition of particulates (Moreno, 2013) and fiber reinforcement (Holloway et al., 2013). The use of UHMWPE as a composite matrix has been studied with numerous types of fillers, such as carbons (i.e. carbon black (Chan et al., 1997), carbon fiber (Thongruang et al., 2002), graphite and carbon nanotube (Ruan et al., 2003), ceramics (i.e. kaolin (Wu et al., 2001), wollastonite (Tong et al., 2003), quartz (Xie. et al., 2003), zirconium (Plumlee et al., 2009) and zeolite (Chang, 2013a), natural particles (i.e. natural coral (Ge et al., 2009)) or metals (Anderson et al., 2002). Wear debris also poses a risk of osteolysis (Ingham et al., 2005), a condition where the bone would demineralized and become weak. Since most biomaterials are focused on bio-inert materials, this also promotes osteolysis. A bioactive material would produce an environment compatible with osteogenesis (bone growth), with the mineralizing interface developing as a natural bonding connection between living and non-living materials (Cao et al., 1996). Addition of zinc oxide can boost the antibacterial properties as well as reinforcement for UHMWPE (Chang, et al., 2013d). Plus, incorporation of a biocompatible material such as chitosan would increase the bioactivity of the composite. Agglomeration of particulate fillers are also a challenge among researchers, thus surface treatment was proposed to counter this problem. Further study of hybridization of UHMWPE reinforced composite also have been lacking amongst researchers, thus, this study was focused on the enhancement of mechanical, wear and bioactivity properties for UHMWPE reinforced composites through different additions of potential hybrid fillers that are Zinc Oxide (ZnO) and Chitosan.

1.3 Scope of study

This is a study of ultra-high molecular weight polyethylene (UHMWPE) reinforced with zinc oxide (ZnO) under various filler ranging from 3 to 25 wt.%. The optimum ZnO content was based on its mechanical properties, specifically the tensile strength value above all else. After the selection of the optimum ZnO content, the UHMWPE composite were then subjected for incorporation with chitosan for hybridization purposes with 1, 2 and 3wt% chitosan loadings. The ZnO was further experimented by treatment with silane as a coupling agent. All composite specimens were prepared by using a hot compression mold by mixing via dry ball milling process. Other means of plastic fabrications such as extrusion, pultrusion or injection molding are not suitable in forming the UHMWPE inserts because of the low melt flow index of the UHMWPE. The specimens were subjected to characterization via Fourier Transform Infrared (FTIR) for the treated ZnO samples, thermal behavior through Differential Scanning Calorimetry (DSC) and Thermogravimetry Analysis (TGA), mechanical and wear test. Biocompatibility test are also done towards all composite. This was to ensure that the fillers were compatible with the human body after installation. Using human mesenchymal stroma cells (HMSC) as the cell, the composite was observed for their interactions with the activity of the cells such as the cell growth and the cell attachments. The test was done in-vitro because it was considered as sufficient to indicate the cytotoxicity effect with the Alamar Blue assay technique.

1.4 Objectives

The objectives of this study are:

- i. To investigate the effects of ZnO particle loading on the thermal, mechanical and biocompatibility properties of UHMWPE hybrid composites.
- ii. To investigate the effects of ZnO-Chitosan hybrid fillers on the thermal, mechanical and biocompatibility properties of UHMWPE hybrid composites.
- iii. To investigate the effect of filler treatment on the thermal, mechanical properties and biocompatibility of UHMWPE hybrid composites.

1.5 Thesis Organization

There are five chapters in this research thesis, consisting of introduction, literature review, methodology, results and discussion, and conclusion.

Chapter 1 Introduction (Introduce the topic of the research through background of the UHMWPE advancement in the recent years, problem statement, and objectives of the research. These three elements provide the overview and relevance of project to the readers).

Chapter 2 Literature review (It is an introduction to the research done by previous or existing researchers on the advancement development of the UHMWPE and the review of the fillers that are being used in this study).