MECHANICAL AND TRIBOLOGICAL PROPERTIES OF ULTRA HIGH MOLECULAR WEIGHT POLYETHYLENE WITH ZINC OXIDE ANTIBACTERIAL AGENT FOR JOINT IMPLANT

by

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Thesis submitted in fulfilment of the requirements

for the degree of

Doctor of Philosophy

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DECLARATION

I hereby declare that the work reported in this thesis entitled **"Mechanical and Tribological Properties of Ultra High Molecular Weight Polyethylene with Zinc Oxide Antibacterial Agent for Joint Implant"** is the result of my own research and it has not been submitted for the degree or diploma in any university previously. Materials taken from other sources are duly acknowledged by giving explicit references.

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TABLE OF CONTENTS

DECLARATION ii

ACKNOWLEDGEMENT iii

TABLE OF CONTENTS.. v

LIST OF TABLES xii

LIST OF FIGURES xv

LIST OF ABBREVIATIONS xxiii

NOMENCLATURE xxv

ABSTRAK xxvi

ABSTRACT... xxviii

CHAPTER ONE INTRODUCTION 1

1.1 The significance of total joint replacement.. 1

1.2 Bearing materials used in human joint implants.................................. 3

1.3 The development of UHMWPE composites 6

1.4 Problem statements 10

1.5 Research objectives.. 11

1.6 Scope of research 12

1.7 Thesis outlines 15

CHAPTER TWO LITERATURE REVIEW 17

2.1 Overview... 17

2.2 The natural human joints 17

2.2.1 Type of joint diseases 19

2.2.2 Tribology of the human joint 22

2.2.2.1 The history and meaning of tribology 22

2.2.2.2 Bio-tribology 23

2.2.3 Wear 24

2.2.3.1 Adhesive wear 25

2.2.3.2 Abrasive wear 26

2.2.3.3 Fatigue wear 27

2.2.4 Friction 27

2.2.5 Tribology of polymer composites 29

2.3 Total joint replacements 33

2.3.1 Total hip replacement 36

2.3.2 Total knee replacement 37

2.3.3 Other joint replacements 38

2.3.4 Infections in orthopaedic implant 39

2.4 Materials for total joint replacement 42

2.4.1 Bearing materials used in TJR 43

2.4.2 Ultra-high molecular weight polyethylene 45

2.4.3 The processing of UHMWPE 46

2.4.4 Problems of UHMWPE bearing materials 48

2.4.4.1 Production of wear debris 49

2.5 Current developments to improve wear properties of UHMWPE............... 51

2.5.1 Crosslinking of UHMWPE..51

2.5.2 Incorporation of micro- and nano-sized fillers 53

2.6 Additives for polymer.. 55

2.6.1 Antibacterial agents 56

2.6.1.1 Silver.. 57

2.6.1.2 Titanium dioxide.. 58

2.6.1.3 Zinc oxide (ZnO) 60

2.6.1.4 The effect of ZnO on the properties of polymers 61

2.6.2 Surface modification...63

2.6.2.1 Chemical coupling agents... 64

2.6.2.2 Silane coupling agent... 65

2.6.2.3 Silane coupling mechanism 66

2.6.2.4 Effects of silane coupling agents on performance of polymer composites... 68

2.6.3 Silicate mineral 70

2.6.4 Hybrid composite..72

2.7 Statistical analysis and optimization.. 73

2.7.1 Design of experiment...74

2.7.2 Response surface methodology..75

2.8 Research strategy on UHMWPE composites used in the present research . 77

CHAPTER THREE METHODOLOGY 80

3.1 Introduction 80

3.2 Materials and chemicals used in the experiment 80

3.3 UHMWPE composites preparation 81

3.3.1 Surface treatment of ZnO 81

3.3.2 Preparation of the UHMWPE composites 82

3.4 Characterization of UHMWPE composites 83

3.4.1 Fourier transform infrared (FTIR) spectroscopy analysis 83

3.4.2 Mechanical properties 84

3.4.2.1 Tensile properties 84

3.4.2.2 Tensile fracture analysis 84

3.4.2.3 Impact test 84

3.4.2.4 Microhardness 85

3.4.3 Wear and friction test 85

3.4.4 Worn surface and transfer film analysis 87

3.4.5 Antibacterial property evaluation 87

3.4.5.1 Agar diffusion technique 87

3.4.5.2 Spectrophotometric analysis 88

3.5 Thermal analysis and degree of crystallinity 89

3.5.1 Differential scanning calorimeter (DSC) 89

3.5.2 X-ray diffraction (XRD) characterization 90

3.6 Response surface methodology and design 90

3.6.1 Response surface design 90

3.6.2 Response surface methodology and optimization...........................92

CHAPTER FOUR RESULTS AND DISCUSSION 94

4.1 Introduction... 94

4.2 Effect of ZnO surface treatment on the performances of UHMWPE.......... 94

4.2.1 Characterization of surface treatment on the ZnO 95

4.2.2 Tensile properties 96

4.2.3 Tensile fracture analysis..100

4.2.4 Vicker's microhardness 101

4.2.5 Wear and friction properties 102

4.2.6 Effect of load and sliding speed on the wear properties of ZnO/UHMWPE 108

4.2.7 Average COF of U-ZPE and T-ZPE compared to pure UHMWPE...110

4.2.8 SEM observation of worn surfaces of UHMWPE and its composites…..113

4.2.9 Antibacterial properties assessment 116

4.2.9.1 Agar diffusion.. 116

4.2.9.2 Spectrophotometric analysis.. 117

4.3 Effect of ZnO nanoparticles on the mechanical, tribological and antibacterial properties UHMWPE composites... 122

4.3.1 Mechanical properties of the nano-ZnO/UHMWPE 122

4.3.2 Tribological properties of nano-ZnO/UHMWPE composites 125

4.3.3 Observation of worn surfaces and transfer films 131

4.3.4 Antibacterial properties...136

4.4 Comparative study on the tribological properties of micro- and nano-ZnO-reinforced UHMWPE composites 139

4.4.1 Effect of size and content on the wear behaviour of ZnO/UHMWPE 140

4.4.2 Effect of applied load and sliding speed on the wear behaviour ...145

4.4.3 Effect of size and content of ZnO on the average COF of UHMWPE……………………………………………………………146

4.4.4 Effect of counterface roughness on the tribological properties 148

4.4.5 SEM observation of worn surfaces and transfer films..................150

4.5 Effect of different silicate minerals on the degree of crystallinity, mechanical and wear properties of UHMWPE composites.. 157

4.5.1 FTIR analysis 158

4.5.2 Thermal analysis and degree of crystallinity 160

4.5.3 Crystallite structure analysis 162

4.5.4 Mechanical properties..164

4.5.5 Abrasive wear and coefficient of friction 169

4.5.6 SEM studies on worn surfaces and transfer films of UHMWPE composites……………………………………………………………175

CHAPTER FIVE MODELLING AND OPTIMIZATION OF UHMWPE HYBRID COMPOSITES…… 181

5.1 Introduction.. 181

5.2 Comparison on the wear performance of UHMWPE composites............. 182

5.3 Development of wear and friction models of UHMWPE hybrid composites.. 184

5.4 Effect of independent variables on wear volume loss of UHMWPE hybrid composites.. 194

5.5 Effect of independent variables on average COF of UHMWPE hybrid composites.. 199

5.6 Validation of the models.. 203

5.7 Optimization 204

5.8 SEM studies on worn surfaces and transfer film of UHMWPE hybrid composites.. 207

5.9 Wear mapping of the UHMWPE composites... 211

CHAPTER SIX CONCLUSIONS AND RECOMMENDATIONS 214

6.1 Conclusion 214

6.2 Recommendations for future research 219

REFERENCES 223

APPENDIX A LIST OF PUBLICATIONS AND CONFERENCES................ 241

LIST OF TABLES

Table 2.1: Kinetic and static coefficient of friction value for some materials sliding pairs (Klyosov, 2007).. 29

Table 2.2: Typical polymers used in tribological applications and its properties (Stachowiak and Batchelor, 2014).. 30

Table 2.3**:** Summary of literature on the improvement of wear properties of different types of filler-reinforced polymer composites and the optimum filler loading......... 32

Table 2.4: Materials combinations with UHMWPE in total hip replacement implant (Davis, 2003).. 35

Table 2.5: The infection of *S. epidermidis* and *S. aureus* in Total Joint Replacement (Wise et al., 1996).. 41

Table 2.6: Timeline of UHMWPE development for joint replacement (Steven, 2004). 44

Table 2.7: UHMWPE industrial applications (Kelly, 2002)...................................... 46

Table 2.8: Commercial coupling agents and its application (Sperling, 1997)........... 65

Table 2.9: A comparison of the pre-coating and *in situ* methods of filler treatment (Rothon, 2003).. 68

Table 3.1: General properties of UHMWPE GUR 4120 80

Table 3.2: The coded and actual values of experimental conditions for wear and friction test of UHMWPE hybrid composites and the investigated factors.............. 92

Table 4.1: Samples description for agar diffusion antibacterial test....................... 117

Table 4.2: Assessment of the antibacterial inhibition for the U-ZPE and T-ZPE composites against the *E.coli* and *S.aureus*. 118

Table 4.3: Material compositions of the UHMWPE composites and designation. . 140

Table 4.4: Average COF of micro- and nano-ZnO/UHMWPE as a function of filler loading, applied load and sliding speed. 148

Table 4.5: The composites designations, compositions and specific density of zeolite and talc-reinforced UHMWPE composites.. 157

Table 4.6: DSC data and calculated DOC of pure UHMWPE, and its composites at different filler-matrix ratios. 161

Table 4.7: XRD results of zeolite and talc-reinforced UHMWPE composites. 164

Table 5.1: The designation, composition and specific density of talc/nano-ZnO/UHMWPE and glass fibre/nano-ZnO/UHMWPE hybrid composites. 182

Table 5.2: The three levels coded and actual values of sliding conditions. 185

Table 5.3: Experimental design and results of T/nano-ZnO/UHMWPE hybrid composites.. 186

Table 5.4: Experimental design and results of GF/nano-ZnO/UHMWPE hybrid composites.. 187

Table 5.5: Analysis of variance and estimated regression coefficients for volume loss of T/ZnO/UHMWPE hybrid composites. 190

Table 5.6: Analysis of variance and estimated regression coefficients and for average COF of T/ZnO/UHMWPE hybrid composites. 191

Table 5.7: Analysis of variance and estimated regression coefficients and for volume loss of GF/ZnO/UHMWPE hybrid composites. 192

Table 5.8: Analysis of variance and estimated regression coefficients and for average COF of GF/ZnO/UHMWPE hybrid composites. 193

Table 5.9: Paired t-test for volume loss of T/ZnO/UHMWPE vs GF/ZnO/UHMWPE hybrid composites. 198

Table 5.10: Paired t-test for average COF of T/ZnO/UHMWPE vs GF/ZnO/UHMWPE hybrid composites. 202

Table 5.11: Comparison of the predicted and measured wear results of T/ZnO/UHMWPE 203

Table 5.12: Comparison of the predicted and measured wear results of GF/ZnO/UHMWPE 204

Table 5.13: The target value and upper value of responses of UHMWPE hybrid composites. 205

LIST OF FIGURES

Figure 1.1: Projected growth of primary hip and knee procedures in the United States of America over the next 30 years (Steven, 2004).. 3

Figure 1.2: The probability of failure versus implant period for total hip replacements schematic graph (Dumbleton, 1977).. 5

Figure 1.3: Research methodology adopted in the study.. 14

Figure 2.1: A natural human knee of synovial joint section (Furey, 2006)............... 19

Figure 2.2: The arthritis hip joint (Batchelor and Chandrasekaran, 2004)................ 20

Figure 2.3: Types of abrasive wear. (a) two-body wear and (b) three-body wear..... 27

Figure 2.4: Diagram showing location of implantation of total knee and total hip replacements (Davis, 2003).. 35

Figure 2.5: (a) Typical artificial hip replacement component and (b) the UHMWPE acetabular cup that on the inner shell of metal acetabular cup (Davis, 2003). 37

Figure 2.6: Components of total knee replacement implant (Davis, 2003).............. 38

Figure 2.7: Example of other joint implant (a) knee, (b) ankle and (c) wrist (Wang et al., 2006). 39

Figure 2.8: Comparison of different engineering thermoplastic on the abrasion resistance properties (Stein, 1999)... 46

Figure 2.9: Failure mechanism of total joint implants (Moreno, 2013).................... 50

Figure 2.10: Schematic drawing of photocatalysis principle and e-h pairs and radicals generation.. 59

Figure 2.11: Silane coupling agents bond to inorganic particle surfaces reactions (Sperling, 1997). 67

Figure 3.1: Surface treatment of the ZnO particles. 81

Figure 3.2: Ducom Pin-on-disc (POD) tester. 86

Figure 3.3: Box-Behnken Design. 91

Figure 4.1: FTIR spectra for silane APTES, untreated and treated ZnO. 96

Figure 4.2: Coupling reaction of APTES on the ZnO particles. 96

Figure 4.3: Tensile properties of ZnO/UHMWPE composites as a function of filler loading: (a) tensile strength, (b) modulus, and (c) elongation at break. 99

Figure 4.4: SEM micrographs of the tensile fracture surfaces of UHMWPE based composites: (a) 10 wt% U-ZPE, (b) 10 wt% T-ZPE, (c) 20 wt% U-ZPE and (d) 20 wt% T-ZPE. 100

Figure 4.5: Vickers microhardness of untreated and treated ZnO/UHMWPE. 102

Figure 4.6: Volume loss of different filler loading of U-ZPE composites as function of applied load at: (a) 0.033m/s; (b) 0.368m/s; (c) 1.022m/s compared to pure UHMWPE. 104

Figure 4.7: Volume loss of different filler loading of T-ZPE composites as a function of applied load at: (a) 0.033m/s; (b) 0.368m/s; (c) 1.022m/s compared to pure UHMWPE. 106

Figure 4.8: Wear volume loss of untreated and treated ZnO/UHMWPE composites as a function of filler loading at 30 N load and 0.033 m/s sliding speed. 108

Figure 4.9: Average wear volume loss of (a) U-ZPE and (b) T-ZPE composites at 35 N as function of sliding speeds. 110

Figure 4.10: The average COF of different filler loading of U-ZPE and T-ZPE composite as compared to pure UHMWPE as function of sliding speeds at: (a) 10 N; (b) 20 N and (c) 30 N. 111

Figure 4.11: Extracted average COF of UHMWPE composites at 0.368 m/s as a function of applied loads. 112

Figure 4.12: SEM micrographs of the worn surfaces for (a) Pure UHMWPE, (b) 5 wt% U-ZPE and (c) 5 wt% T-ZPE composites under a sliding speed of 0.368 m/s and 10 N applied load. The white arrows indicate the sliding direction. 114

Figure 4.13: SEM micrographs of the worn surface for (a) 20 wt% U-ZPE and (b) 20 wt% T-ZPE composites under a sliding speed of 0.368 m/s and 30 N applied load. The white arrows indicate the sliding direction. 115

Figure 4.14: Agar diffusion method of UHMWPE and its composites with different filler loading for both tested bacterial. 116

Figure 4.15: Mean and standard deviation of bacterial inhibition for both U-ZPE and T-ZPE composites. 119

Figure 4.16: Schematic diagram of the antibacterial mechanism with respect to surface treatment for (a) T-ZPE and (b) U-ZPE. 120

Figure 4.17: Mechanical properties of nano-ZnO/UHMWPE composites as function of filler loading: (a) tensile strength, (b) elastic modulus, (c) elongation at break and (d) Vickers microhardness. 124

Figure 4.18: Volume loss of the nano-ZnO/UHMWPE composites as a function of applied load and filler loadings at sliding speed of (a) 0.209 m/s and (b) 0.419 m/s. 126

Figure 4.19: Volume loss of the nano-ZnO/UHMWPE composites as a function of applied load and filler loadings at sliding speed of (a) 0.033, (b) 0.368 and (c) 1.022 m/s. 128

Figure 4.20: Average COF of the nano-ZnO/UHMWPE composites as function of applied load and filler loading at sliding speed of (a) 0.209 m/s and (b) 0.419 m/s.130

Figure 4.21: SEM micrographs of the worn surfaces under sliding speed of 0.209 m/s at 35 N for (a) Pure UHMWPE (b) 10 wt% nano-ZnO/UHMWPE (c) 20 wt% nano-ZnO/UHMWPE and under sliding speed of 0.419 m/s at 35 N (d) Pure UHMWPE (e) 10 wt% nano-ZnO/UHMWPE (f) 20 wt% nano-ZnO/UHMWPE. 132

Figure 4.22: SEM micrographs of the transfer films formed after sliding wear test under 35 N applied load at 0.209 m/s for (a) Pure UHMWPE, (b) 10 wt% nano-ZnO composite and (c) 20 wt% nano-ZnO composite. Arrow indicates the sliding direction. 134

Figure 4.23: SEM micrographs of wear debris particles of (a) Pure UHMWPE, (b) 10 wt% nano-ZnO composite and (c) 20 wt% nano-ZnO composite at 0.419 m/s and 35 N applied load. 135

Figure 4.24: Images show antibacterial properties of nano-ZnO/UHMWPE composites against *E.coli*. at (a) 5 wt%, (b) 10 wt%, (c) 15 wt% and (d) 20 wt% of nano-ZnO loadings. Light-coloured regions indicate the antibacterial zones meanwhile dark-coloured regions represent well-grown bacteria. 138

Figure 4.25: Images show antibacterial properties of nano-ZnO/UHMWPE composites against *S.aureus* at (a) 5 wt%, (b) 10 wt%, (c) 15 wt% and (d) 20 wt% of nano-ZnO loadings. Light-coloured regions indicate the antibacterial zones meanwhile dark-coloured regions represent well-grown bacteria. 138

Figure 4.26: Volume loss of the micro- and nano-ZnO/UHMWPE composites as a function of filler loading, applied load and sliding speed: (a) 0.033 m/s (b) 0.368 m/s and (c) 1.022 m/s... 141

Figure 4.27: Tensile fracture surface of the micro and nano-ZnO/UHMWPE composites at various magnifications; (a) 10 wt% micro-ZnO/UHMWPE composite (M10) and (b) 10 wt% nano-ZnO/UHMWPE composite (N10). 145

Figure 4.28: Volume loss of the ZnO/UHMWPE with different counterface roughness. 149

Figure 4.29: Average COF of the ZnO/UHMWPE with different counterface roughness 149

Figure 4.30: SEM micrographs of the worn surfaces for UHMWPE filled with micro- and nano-ZnO under a sliding speed of 0.368 m/s and 10 N applied load (a) P0, (b) M5, (c) M10, (d) M20, (e) N5, (f) N10 and (g) N20. Arrow indicates the sliding direction. 152

Figure 4.31: SEM micrographs of the worn surface for ZnO/UHMWPE filled with 20 wt% filler loading of (a) micro- and (b) nano-ZnO at a sliding speed of speed 0.368 m/s and at 20 N applied load. Arrow indicates the sliding direction. 153

Figure 4.32: SEM micrographs of the worn surface for micro and nano-ZnO/UHMWPE under a sliding speed of 1.022 m/s and 20 N applied load (a) P0, (b) M10 and (c) N10. Arrow indicates the sliding direction. 154

Figure 4.33: SEM micrographs of the transfer films of (a) Pure UHMWPE (b) 10 wt% micro-ZnO/UHMWPE composites and (c) 10 wt% nano-ZnO/UHMWPE composites under 20 N applied load and sliding speed of 0.033 m/s. 156

Figure 4.34: FTIR spectra of UHMWPE and its composites: (a) zeolite/UHMWPE composites and (b) talc /UHMWPE composites... 159

Figure 4.35: DSC thermograms for UHMWPE and its composites at different filler-matrix ratios (a) heating process and (b) cooling process....................................... 160

Figure 4.36: XRD diffraction patterns of UHMWPE and its composites at different filler-matrix ratios. 163

Figure 4.37: Comparison of (a) tensile strength, (b) tensile modulus and (c) elongation at break of UHMWPE and its composites as function of filler loading. 166

Figure 4.38: Comparison of impact strength of UHMWPE and its composites as function of filler loading. 167

Figure 4.39: Comparison of Vicker's microhardness of UHMWPE and its composites as function of filler loading. 168

Figure 4.40: Comparison of wear volume loss of UHMWPE and its composites as function of applied loads at sliding speeds of (a) 0.21 m/s and (b) 0.42 m/s........... 170

Figure 4.41: COF of UHMWPE and its composites as function of sliding time at 0.21 m/s for (a) 10 N, (b) 20 N and (c) 30 N. 172

Figure 4.42: COF of UHMWPE and its composites as function of sliding time at 0.42 m/s for (a) 10 N, (b) 20 N and (c) 30 N. 173

Figure 4.43: Average COF for UHMWPE and its composites as function of filler loading at 20 N under (a) 0.21 m/s and (b) 0.42 m/s. 174

Figure 4.44: SEM micrographs of the worn surfaces of (a) UHMWPE, (b) 10Z/U, (c) 20Z/U, (d) 10T/U and (e) 20T/U composites at 30 N applied load under sliding speed of 0.42 m/s. The white arrow indicates the sliding direction. 176

Figure 4.45: SEM micrographs of the transfer films of (a) UHMWPE, (b) 10Z/U, (c) 20Z/U, (d) 10T/U and (e) 20T/U composites at 30 N applied load under sliding speed of 0.21 m/s. 177

Figure 4.46: SEM and EDX analyses of the transfer film of 20Z/U composites at 30 N applied load under sliding speed of 0.42 m/s of (a) SEM micrograph and (b) EDX spectrum. 179

Figure 4.47: SEM and EDX analyses of the transfer film of 20T/U composites at 30 N applied load under sliding speed of 0.42 m/s of (a) SEM micrograph and (b) EDX spectrum. 180

Figure 5.1: Effects of the addition of nano-ZnO, talc/nano-ZnO hybrid and GF/nano-ZnO hybrid on the wear properties of UHMWPE composites as function of applied loads at sliding speeds of (a) 0.2094 and (b) 0.4188 m/s. 184

Figure 5.2: Typical residual plots for volume loss of UHMWPE hybrid composites. 186

Figure 5.3: Surface plots and contour plots of the combined effects of the independent variables on volume loss of T/ZnO/UHMWPE hybrid composites. (a) Load-Speed, (b) Load-Distance and (c) Speed-Distance. 195

Figure 5.4: Surface plots and contour plots of the combined effects of the independent variables on volume loss of GF/ZnO/UHMWPE hybrid composites. (a) Load-Speed, (b) Load-Distance and (c) Speed-Distance. 196

Figure 5.5: Surface plots and contour plots of the combined effects of the independent variables on average COF of T/ZnO/UHMWPE hybrid composites. (a) Load-Speed, (b) Load-Distance and (c) Speed-Distance. 200

Figure 5.6: Surface plots and contour plots of the combined effects of the independent variables on average COF of GF/ZnO/UHMWPE hybrid composites. (a) Load-Speed, (b) Load-Distance and (c) Speed-Distance. 201

Figure 5.7: Optimal conditions of independent variables on the responses of T/ZnO/UHMWPE hybrid composites. 206

Figure 5.8: Optimal conditions of independent variables on the responses of GF/ZnO/UHMWPE hybrid composites. 206

Figure 5.9: SEM micrographs of the worn surfaces of T/ZnO/UHMWPE ((a) 0.21 m/s, (c) 0.42 m/s, (e) 0.63 m/s) and GF/ZnO/UHMWPE ((b) 0.21 m/s, (d) 0.42 m/s, (e) 0.63 m/s) under 30 N applied load. Arrow indicates sliding direction. 209

Figure 5.10: SEM micrographs of the transfer films of T/ZnO/UHMWPE on the abrasive paper at (a) 0.21 m/s, (c) 0.42 m/s, (e) 0.63 m/s, and GF/ZnO/UHMWPE at (b) 0.21 m/s (d) 0.42 m/s (f) 0.63 m/s under 30 N applied load. 210

Figure 5.11: Wear mapping of the UHMWPE composites under different sliding speed conditions of (a) 0.2094 and (b) 0.4188 m/s. 212

LIST OF ABBREVIATIONS

Al_2O_3	: Aluminium oxide
APTES	: Aminopropyl-triethoxysilane
ASTM	: American Society for Testing and Materials
ATTC	: American Type Culture Collection
BBD	: Box-Behnken Design
CCD	: Centre Composite Design
CF	: Carbon Fibre
COF	: Coefficient of Friction
DF	: Degree of Freedom
DOE	: Design of Experiment
DSC	: Differential Scanning Calorimetry
FESEM	: Field Emission Scanning Electron Microscopy
FTIR	: Fourier Transform-Infrared Spectroscopy
GF	: Glass fibre
GUR	: Granular UHMWPE and Ruhrchemie
H_2O_2	: Hydrogen peroxide
MoS_2	: Molybdenum disulfide
PEEK	: Polyetheretherketone
PMC	: Polymer Matrix Composites
POD	: Pin-On-Disc
PP	: Polypropylene
PPS	: Polyphenylene sulfide
PRESS	: Predicted Residual Sum of Square
PS	: Polystyrene
PTFE	: Polytetraflouroethylene

RSM	: Response Surface Methodology
S	: Standard Deviation
SiC	: Silicon carbide
SS	: Sum of Square
TiO_2	: Titanium dioxide
TJR	: Total Joint Replacement
UHMWPE	: Ultra-high molecular weight polyethylene
XRD	: X-ray Diffraction
ZnO	: Zinc oxide

NOMENCLATURE

A	: Area [m^2]
H_v	: Vickers microhardness
β	: Half high width of diffraction peak [radian]
V	: Wear volume loss [mm^3]
W_r	: Specific wear rate [mm^3/Nm]
d	: Sliding distance [m]
L	: Applied load [N]
gf	: Gram-force [N]
T_g	: Glass transition temperature [ºC]
T_m	: Melting temperature [ºC]
wt%	: Filler weight percent
ΔH_m	: Melting enthalpy of fusion of the samples [ºC]
ΔH_{100}	: Melting enthalpy of 100% crystalline polymer [ºC]
L_{hkl}	: Crystallite size [nm]
λ_{hkl}	: Distance between adjacent crystal plane [nm]
λ	: wavelength of the X-ray [nm]
θ	: X-ray radiation angle [º]
n	: X-ray diffraction level
P	: Test load on the diamond indenter [g]
Y	: Response variables
X_i,X_j	: Independent variables
ε	: Residue error

SIFAT-SIFAT MEKANIKAL DAN TRIBOLOGIKAL POLIETILENA BERBERAT MOLEKUL SANGAT TINGGI DENGAN ZINK OKSIDA ANTIBAKTERIA AGEN UNTUK IMPLAN SENDI

ABSTRAK

Penggantian sendi keseluruhan (TJR) adalah rawatan yang berjaya untuk peringkat akhir penyakit sendi seperti osteoartritis. Kebanyakan peranti TJR digunakan dalam ortopedik melibatkan artikulasi antara aloi logam dan polietilena berberat molekul sangat tinggi (UHMWPE). Walaupun polimer ini mempunyai ciri-ciri yang sangat baik, sesuai untuk komponen TJR, tetapi partikel haus yang dihasilkan disebabkan oleh gerakan relatif antara komponen masih merupakan satu isu yang belum diselesaikan. Kajian ini membentangkan kaedah-kaedah untuk meningkatkan prestasi haus UHMWPE dalam aplikasi implan dengan pelbagai jenis pengisi tetulang. Komposit UHMWPE diperkuatkan dengan pelbagai jenis pengisi telah difabrikasi dengan menggunakan pengacuan mampatan hidraulik panas dengan nisbah pengisi-matrik yang berbeza. Pencirian dan perbandingan komposit-komposit ini dari segi sifat mekanikal dan tribologikal telah dijalankan. Ujian tribologikal telah dikaji dengan menggunakan penguji pin-atas-cakera di bawah beban dan kelajuan gelongsor yang berbeza. Permukaan lelasan dan filem-filem pemindahan yang terhasil selepas ujian geseran telah dikaji menggunakan mikroskop pengimbasan elektron (SEM). Kajian ini terdiri daripada empat bahagian. Bahagian pertama adalah untuk mengkaji kesan rawatan permukaan Zink Oksida (ZnO) ke atas sifat mekanikal, tribologikal dan antibakteria. ZnO tanpa rawatan (U-ZPE) dan terawat (T-ZPE) dengan aminopropyl-triethoxysilane (APTES) memperkuatkan UHMWPE telah dikaji dan dibuat perbandingan. Penilaian sifat antibakteria bagi UHMWPE komposit telah diuji menggunakan dua jenis bakteria yang biasa ada di badan manusia iaitu Escherichia coli (*E. coli*) dan Staphylococcus aureus (*S. aureus*). Keputusan telah menunjukkan

bahawa T-ZPE mempunyai sifat-sifat mekanikal dan ketahanan haus yang lebih tinggi berbanding U-ZPE. Kedua-dua U-ZPE dan komposit T-ZPE menunjukkan perencatan aktif terhadap bakteria *E. coli* dan *S. aureus*. T-ZPE menunjukkan perencatan peratusan lebih tinggi terhadap bakteria yang diuji. Bahagian kedua kajian adalah membandingkan prestasi mikro dan nano-ZnO sebagai agen penguat dalam komposit UHMWPE. Sifat-sifat haus bagi komposit nano-ZnO/UHMWPE adalah lebih baik daripada micro-ZnO/UHMWPE. Komposit nano-ZnO/UHMWPE menunjukkan sifat antibakteria yang lebih baik berbanding komposit micro-ZnO/UHMWPE. Bahagian ketiga kajian mengkaji pengaruh pengisi mineral silikat (zeolit dan talkum) terhadap sifat-sifat UHMWPE. Dari segi sifat mekanikal, zeolit/UHMWPE menunjukkan sifat-sifat mekanikal lebih unggul berbanding dengan talkum/UHMWPE. Walau bagaimanapun, bagi ujian ketahanan haus, talkum/UHMWPE menunjukkan sifat kehausan yang lebih baik berbanding zeolit/UHMWPE. Didapati bahawa tiada hubungan secara langsung antara darjah penghabluran dan sifat-sifat tribologikal komposit UHMWPE. Akhir sekali, dalam bahagian keempat kajian, kajian lanjut tentang pengaruh dua jenis pengisi iaitu partikel talkum dan gentian kaca sebagai pengisi sekunder di dalam UHMWPE komposit hibrid terhadap sifat tribologikal telah dijalankan. Model empirikal bagi hubungan pelbagai pembolehubah beban yang dikenakan, kelajuan gelangsar dan jarak terhadap kehilangan isipadu haus dan pekali purata pekali geseran kepada UHMWPE komposit hibrid telah dihasilkan dengan menggunakan Metodologi Permukaan Respon (RSM). Pengoptimuman fungsi pemboleh ubah bebas juga telah dianggarkan. GF/ZnO/UHMWPE menunjukkan prestasi kehausan yang lebih baik berbanding talkum/ZnO/UHMWPE komposit hibrid.

MECHANICAL AND TRIBOLOGICAL PROPERTIES OF ULTRA HIGH MOLECULAR WEIGHT POLYETHYLENE WITH ZINC OXIDE ANTIBACTERIAL AGENT FOR JOINT IMPLANT

ABSTRACT

Total joint replacement (TJR) is a highly successful treatment for end-stage joint disease like osteoarthritis. A prominent number of TJR devices used in orthopaedic involve articulation between a metallic alloy and ultra-high molecular weight polyethylene (UHMWPE). Although this polymer has excellent properties, suitable for TJR bearing materials, the wear particulate produced due to relative motion between components still remains an issue yet to be resolved. This study presents approaches to improve the wear performance of UHMWPE in implant applications by various types of fillers reinforcement. The UHMWPE composites were fabricated by compression moulding with different filler-matrix ratios. These composites were characterized and compared in terms of their mechanical and tribological properties. The filler which delivered the best performances were selected as the filler in the UHMWPE hybrid composites. The tribological properties was investigated using pin-on-disc tester under different loads and sliding speeds. The worn surfaces and transfer films produce after wear test were studied under scanning electron microscopy (SEM). This research consists of four parts. The first part was to investigate the effect of surface treatment of ZnO on the mechanical, tribological and antibacterial properties. Two variants of untreated ZnO-reinforced UHMWPE (U-ZPE) and treated ZnO-reinforced UHMWPE (T-ZPE) with aminoproply-triethoxysilane (APTES) were used to compare the improvement of properties. The antibacterial assessments of the composites were tested against two common human body bacteria i.e. *Escherichia coli (E. coli)* and *Staphylococcus aureus (S. aureus).*

Results have shown that T-ZPE possess higher mechanical and wear properties as compared to U-ZPE. Both U-ZPE and T-ZPE composites showed active inhibition against *E. coli* and *S. aureus* bacteria. T-ZPE showed higher percentage inhibition against the tested bacteria. The second part of the research was compared the performances of the micro- and nano-ZnO reinforcement in the UHMWPE composites. The wear properties of nano-ZnO/UHMWPE composites are better than micro-ZnO/UHMWPE. The nano-ZnO/UHMWPE composites impart superior antibacterial properties as compared to micro-ZnO/UHMWPE composites. The third part of the research studies the influence of silicate mineral reinforcements (zeolite and talc) on the properties of UHMWPE. In terms of mechanical properties, the zeolite/UHMWPE showed superior mechanical properties as compare to talc/UHMWPE. However, for wear resistance, talc/UHMWPE exhibited better wear behaviour as compared to zeolite/UHMWPE. There is no direct relationship of degree of crystallinity (DOC) on the tribological properties of UHMWPE composites. Finally, in the fourth part of the research, the effects of two types of filler reinforcements i.e. particulate (talc particles) and fibre (glass fibre (GF))-reinforced ZnO/UHMWPE hybrid composites on the tribological properties were carried out. The empirical models on the relationship of various variables of applied loads, sliding speeds and distances on the wear and friction of UHMWPE composites was developed using Response Surface Methodology (RSM). Optimization of the responses as function of independent variables were generated. GF/ZnO/UHMWPE exhibited better wear performance compared to talc/ZnO/UHMWPE hybrid composites.

CHAPTER ONE
INTRODUCTION

1.1 The significance of total joint replacement

Total joint replacement (TJR) is a surgical procedure in which the ailing and injured human joints are replaced with an artificial joint components. Over the last 40 years, TJR has been increasingly performed in many countries around the world which has brought relief to millions of people. Based on trends collected from both past decades and projected future ones, TJR is now becoming an important treatment for arthritis, trauma and joint disorders amongst the young active and elderly patients. Every year, millions of people suffer from arthritis and joint injuries worldwide. As the body ages, organs, joints and other body parts would wear out over time causing restrictions to the joint movements and pain. The most common forms of arthritis disease are osteoarthritis, rheumatoid arthritis and post-traumatic arthritis (Wang et al., 2006). The worn out components must be replaced for the body parts to function properly. In early 2000, the National Institutes of Health (NIH) reported that the number of patients undergoing total joint implant surgery treatments increased drastically over the years (Davis, 2003). According to a statistical study on the United States of America medical implant market, orthopaedics are the second most important field behind cardiovascular (Wang et al., 2006). It accounts for 24% of the U.S. medical device industry in the year 2003 and is projected to experience 7-9% growth rate (Kouidri, 2004). In Malaysia, TJR has been practiced since the late 1970s (Ahmad Hafiz et al., 2011). Dhillon et al. (1993) reported the number of surgery performed at

University Hospital Kuala Lumpur has increased intensely since 1986. The cumulative cost for hospital patients suffering from hip fracture incidents in 1997 was 6.8 million USD (approximately RM 22 million), and this is not counting nursing home care costs (Yeap et al., 2013). The joint disorder due to aging populations and injuries are expected to escalate. The knee, hip, and spine implant devices are the most dominant products in the orthopaedic sector (Wang et al., 2006). By referring to the statistics dated 30 years back, elderly patients above the age of 60 years dominated the majority number. However, there is an increasing trend of younger patients receiving TJR treatments has been reported (Kurtz et al., 2005). The number of patients which receive TJR treatment has increased significantly over the years. Figure 1.1 shows the statistical plot of the past, current and projected growth over the next 30 years of primary hip and knee procedures in the United States of America (U.S.) by the American Academy of Orthopaedic Surgeons (AAOS). The plotted data indicates an approximately 30% increment in every year for both total hip replacement (THR) and total knee replacement (TKR) performed. The TKR shows higher number of procedures than THR. Due to the thriving demand for TJR treatments, research on improvement and development of implant material is greatly important.

The clinical needs for TJR come from a variety of conditions such as joint disorder, tissue injuries, fractures, wear and tear of joint cartilage. Osteoarthritis and rheumatoid arthritis are two common joint disorders in which patients need to undergo TJR surgery. These joint disorders affect the structure of synovial joints, such as joints in the knee, hip, shoulder, elbow, and ankle; and causing pain in joints to the patients (Davis, 2003). The patients will possess limited joint mobility and suffer from numerous destructive processes such as inflammation, infection, fracture and cancer.

Under these conditions, the worn parts should be replaced with suitable artificial joint components in order to maintain the quality of life for the patients.

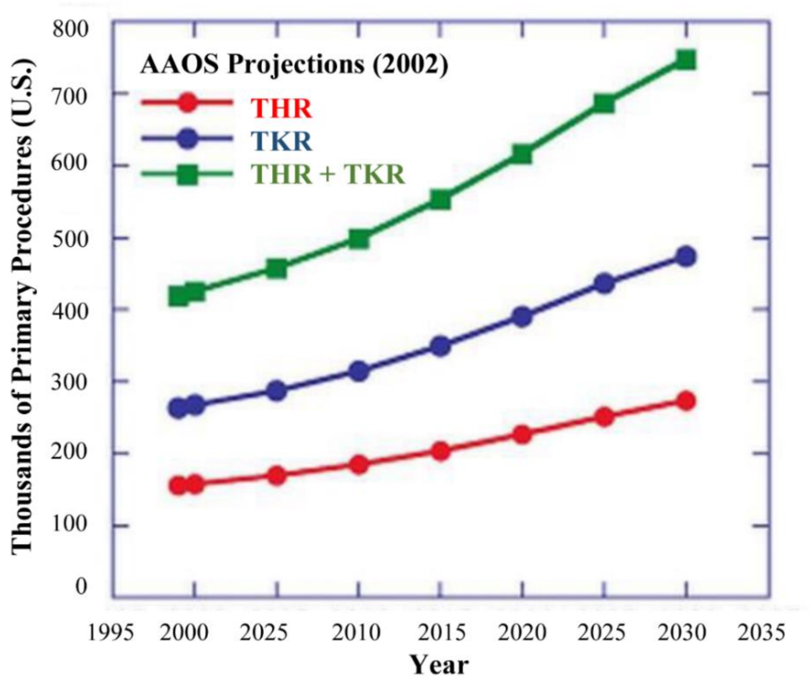

Figure 1.1: Projected growth of primary hip and knee procedures in the United States of America over the next 30 years (Steven, 2004).

1.2 Bearing materials used in human joint implants

Artificial joint components consist of metal stem and polymer bearing components. In this research, the focus is primarily on the TJR bearing materials i.e. materials produced by the polymer as interface of the TJR components to transfer load stress during joint motion, rather than with the metallic alloy stem, which are mainly involved in design to withstand different axes of forces. Ultra-high molecular weight polyethylene (UHMWPE) is one of the most important, high performance semi-crystalline engineering thermoplastics with excellent wear resistance. As the name indicates, UHMWPE is a type of linear structure polyolefin with extremely high molecular weight (>10^6 g/mol) which makes it an excellent comprehensive performance materials. Apart from its excellent wear resistance, UHMWPE also possesses low coefficient of friction (Barbour et al., 1999), bio-compatibility (Xiong and Ge, 2001), high impact strength (Abadi et al., 2010, Steven, 2004), light in weight, chemical inertness and corrosion resistance. Its popularity begin to take over conventional PE when it was first commercially used as implant bearing materials for human hip replacement bearing component by Sir John Charnley in the mid-1960s. By employing UHMWPE as bearing components of human joint implants, numerous human joint diseases were successfully resolved such as arthritis, and rheumatoid. The successful use of UHMWPE as a bearing material in TJR application makes it a popular material in the medical industry. UHMWPE has received the U.S. FDA (Food and Drug Administration) approval as a nontoxic medical material for biomedical applications such as heart valves, artificial joints bearing, tissue scaffolds, blood pumps and others. Besides artificial medical components, UHMWPE is extensively used in various engineering materials in other industry applications which include bearings and valves, dump truck liner, mining equipment, sport equipment, pharmaceutical materials, military armour and recreational engineering (Stein, 1999).

Despite the suitability and numerous advantages of UHMWPE, there are still challenges raised from this bearing material in artificial joint component, namely wear debris production. Same as other polyethylene families, UHMWPE also possesses similar weaknesses as conventional polymers, such as susceptible to creep upon loading (Dangsheng, 2005), low surface hardness, low modulus and prolonged wear-related problems. Beside the wear of UHMWPE bearing materials, there are several problems occurring on current human joint implants after a certain implant period as shown in Figure 1.2. Post-surgery bacterial infection is the early stage problem where implant failure may occur within 5 years' time (Dumbleton et al., 2002). The patients will experience swollen and inflammation on the implant location and finally leads to implant failure. The fracture of the implant is normally caused by the material design and stress transfer issue on metal alloy stem of the implant. According to Wang et al. (2006), the wear of bearing materials can be attributed to the usage of joints after implantation, as it will generate cyclic loading from the polymer against the metal or ceramic stem. In addition to that, significant localized contact stresses will be directed on the polymer material surface and may break off to form sub-micron sized wear debris. These wear debris generated by worn out polymer material will be released into the surrounding synovial fluid and tissues in which may cause adverse biological reaction in human body (Wang et al., 2006). Formation of wear debris will lead to osteolysis, implant loosening and finally cause implant failure.

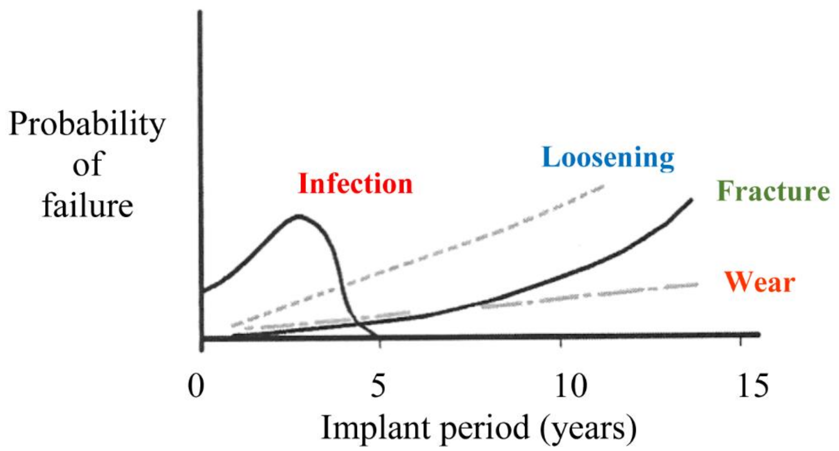

Figure 1.2: The probability of failure versus implant period for total hip replacements schematic graph (Dumbleton, 1977).

1.3 The development of UHMWPE composites

There are several hundred of thousand people accepted the treatment with total joints replacement components made from UHMWPE bearing materials. Patients undergoing TJR surgery are increasing over the years worldwide. Thus, the performance and service lifetime of TJR bearing components is undoubtedly important. The wear particles produce from UHMWPE is one of the major factors limiting the implant longevity and cause inconvenience problems to the patient (Harris, 2001). In order to increase the wear resistance of UHMWPE and life span of TJR, numerous research works on modification of UHMWPE have been extensively explored. Many research works have reported that the modification of UHMWPE by crosslinking with electron beam irradiation (McKellop et al., 1999a, Shi et al., 2001), heat treatment (Fouad et al., 2005), as well as incorporation with micro- and nano-sized filler in UHMWPE matrix can improve its wear performance significantly (Plumlee and Schwartz, 2009, Guofang et al., 2004, Ge et al., 2009). These approaches altered the physical and mechanical properties of the UHMWPE. Of all the approaches, filler reinforcement UHMWPE composite is the most widely used method due to its simplicity and low cost of processing. The influence of modification on wear properties of UHMWPE by adding different types of reinforcing fibres and particle fillers was widely investigated in recent years to improve the implant bearing materials. Therefore, the development of UHMWPE composites have become a famous research topic. One example is the introduction of carbon fibre-reinforced UHMWPE composites known as Poly II which has been commercialized and used clinically in the 1970s (Kurtz et al., 1999). There are researches which attempted to improve UHMWPE properties using carbon fibre (Dangsheng, 2005) carbon particle, and graphite powder as reinforcements (Galante and Rostoker, 1973). The results are very encouraging as the wear properties of UHMWPE enhanced significantly. Although polymer composites have been recognized as potential candidates for medical devices and implant materials, majority of them are still limited to laboratory investigation level at present (Ramakrishna et al., 2004). Therefore, extensive research has to be done in order to achieve further improvement of polymer composite materials in implant applications.

The type of filler or reinforcement used play a significant role in determining the properties of the final composites. The incorporation of inorganic nanoparticles into polymer has introduced a new pathway in engineering polymer technology. They can significantly improve the mechanical properties of the polymer with additional functional properties such as thermal and electrical conductivity as well as bacterial resistance. Hence, it offers additional advantages in the physical, mechanical and additional functional performances as compared to traditional additive in polymer. Zinc oxide (ZnO) as fillers in polymeric materials is not common in wear and friction researches as compared to other high hardness materials such as alumina (Al_2O_3), silicon carbide (SiC) and carbon fibre (CF). ZnO exhibits excellent mechanical and antibacterial properties (Zhang et al., 2008, Liu et al., 2009, Padmavathy and Vijayaraghavan, 2008), which can be suitable for implant application. The role of Zn element in the resistance to infection and anti-inflammatory response is well known (Shankar and Prasad, 1998). In particular, ZnO appears to exhibit excellent antibacterial properties (Liu et al., 2009, Zhang et al., 2007a). Although numerous researches have showed great improvements in tribological properties of the UHMWPE after being reinforced with different types of fillers, there are fewer researches concentrating on additional antibacterial fillers in UHMWPE for implant applications. The risks of bacterial infection after surgical implant may be reduced with the present of antibacterial filler in this composite material.

In order to fabricate a high performance composite materials, integrating of various functional filler is a principal route which cannot be achieved by using single filler alone (Friedrich et al., 2005b). The use of hybrid filler reinforced-polymer composite system increasingly explores in improving the performance further in single filler reinforced-polymer composite system. Nowadays, the development of hybrid polymer composite systems with more than one filler reinforcement is of great interest in many research capacities. The hybrid reinforcement system enables the incorporation of two or more functional fillers into a polymer matrix. Improvements in terms of mechanical properties can be greatly observed in hybrid composites as compared to single filler-reinforced composites (Thwe and Liao, 2002, Cho and Bahadur, 2005, Chang et al., 2005, Mohan et al., 2013). Silicate minerals are promising fillers that generally leads to reinforcing effect in polymer due to their outstanding mechanical properties. They are attractive materials as substitutes for expensive additives in polymer to reduce the material cost. Furthermore, silicate minerals are known as effective nucleating agents for polymer materials which can improve various polymer properties. The reinforcement of mineral initiate heterogeneous crystallization in polymer, thus changing the morphology of the polymer and conferring significant changes in properties. The use of silicate minerals (zeolite and talc) as secondary reinforcement in this research is due to their potential ability in enhancing the mechanical properties and also is a strong nucleating agent.

The investigation of various fillers reinforced-UHMWPE composites in improving the wear properties with additional antibacterial properties for artificial joint implant bearing is the major focal point of this research project. The mechanical and tribological properties of UHMWPE composites reinforced with micro- and nanoparticles ZnO as antibacterial agent (first filler), silicate minerals as further reinforcing filler (second filler) were studied. The filler which delivered the best performances was selected as the filler in the final UHMWPE hybrid composites system. There have been an increasing number of studies reported on composite performance improvement using hybrid filler systems. However, no study has been recorded yet regarding performance comparison between particulate and fibre form of secondary reinforcement in UHMWPE. This work stands out from other researches done as its novelty can be extracted from the improved wear resistance upon testing and the additional antibacterial properties included which is beneficial in reducing the bacterial infection after implant application. On the other hand, the mathematical modelling on the tribological properties of UHMWPE hybrid composites and optimization of the input parameters to the output parameters using Response Surface Methodology (RSM) were also implemented in this research study. RSM is a set of mathematical techniques that explains the relation between several independent variables and one or more responses. It can produce equation model in a given process system based on experimental results and obtain the optimization of the process either to yield maximization or minimization of the output through the input variables. Tribological studies of materials involve a complex process which not solely depends on material behaviour but also dependent on many external factors such as applied load, sliding speed and distance. With RSM modelling and optimization, the significance level of independent variables whose effect has a high impact on the responses can be identified and the optimal settings of these variables that minimize the wear of the materials can be determined. Therefore, RSM is a great tools to model the tribological properties of UHMWPE hybrid composites and optimize the wear conditions. The use of RSM in this study to model and optimize the wear and friction properties of this particular hybridization polymer system which is still novel. The effects of two types of filler reinforcements i.e. particulate and fibre as secondary reinforcements in UHMWPE-based composites on the wear and friction properties were compared. The RSM was employed to analyse the UHMWPE hybrid composites wear performances affected by the independent variables and interactive effect of the factors under different sliding condition. The wear of UHMWPE implicated several undesirable outcomes and cause failure to the implant, the enhancement of the wear resistance of UHMWPE may theoretically increase the service period and durability of the implant.

1.4 Problem statements

UHMWPE has been used in joint implant application for over 40 years. However, the long term wear problems and wear debris generated from commercially available artificial joint implants after a certain period of usage remains a challenge yet to be resolved. The UHMWPE wear debris causes adverse biological reaction to human body which leads to osteolysis, implant loosening and finally implant failure (Burger et al., 2007, Dumbleton et al., 2002). As a result, these TJR components have low lifespan and need to undergo revision for replacement every 5-10 years. Therefore, wear of UHMWPE bearing in TJR is a major factor limiting the implant longevity (Hallab et al., 2002).

Secondly, like other implant materials, the long term application of UHMWPE polymer will run the risk of infection from bacteria, fungi, and other microbial pathogens that is dangerous to human body and affect people's health and may even cost their lives. Moreover, this further complicates the surgery procedure to remove infected implant and replacement purposes. Currently, works are under way to reduce bacterial infection from the implants (Dallas et al., 2011, Jeong et al., 2005). In order to increase the wear resistance of UHMWPE, numerous research works on modification of UHMWPE composites using different types of reinforcement have been carried out (Plumlee and Schwartz, 2009, Schwartz et al., 2007, Ge et al., 2009). However, there are little emphasis on the use of antibacterial agent as reinforcement in the implant materials thus far. Antibacterial agent reinforced-UHMWPE composites is believed to be the solution to reduce undesirable bacterial infection after surgery.

1.5 Research objectives

In a nutshell, the main concern of the present study is the improvement of wear resistance for UHMWPE composite with additional antibacterial properties; seen as the best choice of material for human artificial joint replacement. The UHMWPE is modified with several types of reinforcement, which are expected to improve the tribological performance and will impart antibacterial properties to reduce the infection of the bacteria after the surgery of the implant into human body. Any attempt of the studies presented here is also to identify and study on the mechanisms responsible for good tribological properties of UHMWPE. The objectives of this research are listed as follows:

1. To investigate the mechanical and tribological properties of the UHMWPE through addition of antibacterial fillers at different loadings.
2. To evaluate the effects of ZnO antibacterial agent on the antibacterial properties of the UHMWPE composites against human body bacteria.

3. To generate empirical models with different independent variables on the tribological behaviour of UHMWPE hybrid composites (Talc/ZnO/UHMWPE) and optimize the output variables using response surface methodology (RSM) approach.

1.6 Scope of research

To execute the above-mentioned objectives, UHMWPE composites reinforced with different types of filler have been fabricated. Pure UHMWPE were used as control samples for comparison purposes on the improvement of the UHMWPE composites. The filler materials selected were metal oxide antibacterial agent which were micro- and nano-size of ZnO, silicate minerals i.e. talc and zeolite; and GF. The UHMWPE composites with different filler-matrix ratios were evaluated in terms of mechanical and tribological properties. The filler which delivered the best performances will be selected as the filler in the UHMWPE hybrid composites. For antibacterial assessment, the effects of ZnO loadings on the antibacterial activity of UHMWPE composites against two common human pathogenic bacteria i.e. *Escherichia coli (gram negative bacteria) and Staphylococcus aureus* (gram positive bacteria) were investigated. Furthermore, mathematical regression model of UHMWPE hybrid composites was developed and the relationship between the control factors (applied load, sliding speed and sliding distance) and the response factors (wear volume loss and coefficient of friction) were obtained using RSM.

The present research was categorized into five major phases and the research methodology flow is shown in .

Phase I – To study the effects of untreated and treated-ZnO on the mechanical, tribological and antibacterial properties of UHMWPE composites.

Phase II – To compare the performance of micro- and nano-ZnO-reinforced UHMWPE composites on the mechanical, tribological and antibacterial properties. The filler which delivered the best performances will be selected as the filler in the UHMWPE hybrid composites.

Phase III – To study and compare the performance of talc and zeolite on the mechanical and tribological properties of UHMWPE composites. The filler which delivered the best performances will be selected as the filler in the UHMWPE hybrid composites.

Phase IV – To develop and evaluate mechanical and tribological properties of UHMWPE hybrid composites. The mathematical regression model on the relationship between the control factors (applied load, sliding speed and sliding distance) and the response factors (wear volume loss and average coefficient of friction) were implemented in this phase as well.

Phase V – To validate on the mathematical model of the UHMWPE hybrid composites and optimize the wear behaviour as a function of variables. Construction of wear mapping for all the composites studied were also employed in this phase for clear comparison.

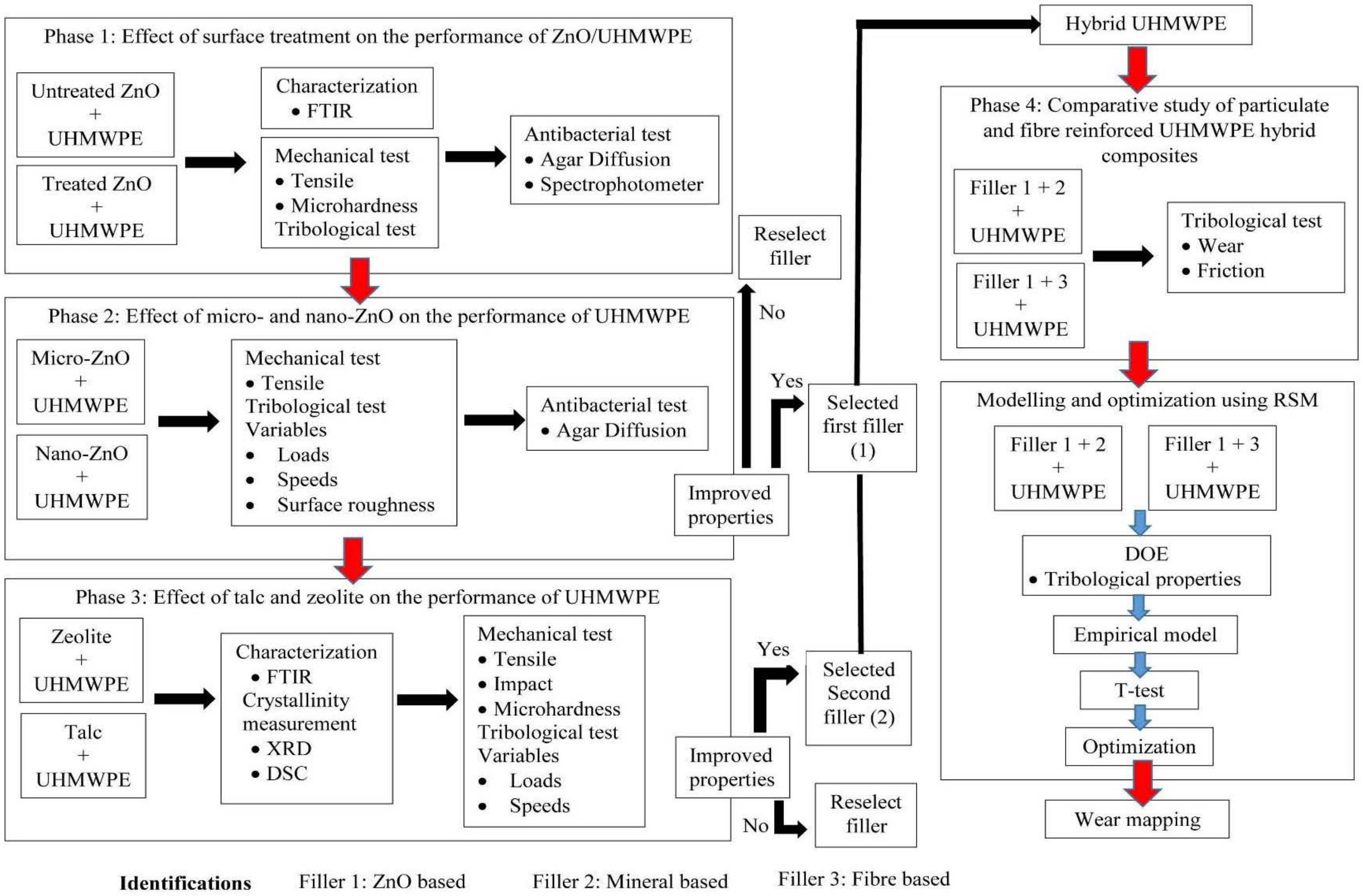

Figure 1.3: Research methodology adopted in the study.

1.7 Thesis outlines

This thesis is divided into six chapters which will explain and discuss the entire research in detail. Chapter 1 gives a general introduction and significance of TJR; problem statement of UHMWPE as bearing material in TJR and objectives behind this research.

Chapter 2 contains the history and background on materials used in artificial human implant application; fundamental concept of tribology of polymer composites; studies on polymeric composites and methods used in improving the properties of UHMWPE by various researchers. Subsequently, highlights of the important factors affecting the tribological properties of polymer composites. Overview of the literature review of various reinforcement and antibacterial agent in polymer composites is also discussed in this chapter.

The materials used, sample preparation, characterization and experiment techniques (physical, mechanical, tribological and antibacterial) of this research are elaborated clearly in Chapter 3. This chapter begins with a systematic review on the raw materials used, apparatus and methodology for all the tests.

Chapter 4 reports the results and discussion on the effect of different filler reinforcement in the performance of UHMWPE matrix. The effect of different size and loading of ZnO particles-reinforced UHMWPE on the mechanical, tribological and antibacterial properties as compared to pure UHMWPE was reported. In addition to that, the effects of silane coupling agent on the performances of ZnO/UHMWPE composites will be discussed as well in this chapter. In order to develop a high performance composite material, integrating another functional filler is now a vital necessity, in which cannot be achieved by a single filler system. Therefore, selection of the second reinforcement fillers was attempted in the last part of this chapter. An in-depth analysis was done to compare the performances of silicates mineral reinforced-UHMWPE i.e. zeolite/UHMWPE and talc/UHMWPE composites with different filler-matrix ratios. The filler which delivered the best performances will be selected as the second filler in the UHMWPE hybrid composites.

In Chapter 5, the further enhancement on the UHMWPE properties by using hybrid reinforcements system were described. The filler type and filler loading selection were made by referring to performances from previous results. This chapter focused on the mathematical modelling of tribological behaviour of UHMWPE hybrid composites using response surface methodology (RSM). The optimization of the wear conditions and validation of the tribological data on UHMWPE hybrid composites was also conducted and discussed in this chapter. The final part of this chapter depicts the wear and friction mapping of all the studied UHMWPE composite materials

Finally, Chapter 6 focuses solely on the conclusion and summary of the entire research and findings. This chapter also includes future work recommendations and possible improvements to be made specifically in this field for the near future.

CHAPTER TWO
LITERATURE REVIEW

2.1 Overview

This chapter presents the introduction of human joints, joint diseases and the importance of total joint replacements (TJR). This chapter also reviews the history of human joint implant surgery and the artificial bearing materials used since the early 1900s till now. Recent studies of improvement methods and literature review available at the time of writing on the UHMWPE composites used as artificial joint implant applications are thoroughly reviewed. Besides that, the additives use in polymer composites and highlight of some literature on tribological properties evaluation of polymer composite are discussed.

Finally, the chapter ends with discussion on the concept of Design of Experiment (DOE) and RSM that used in scientific as well as engineering researches. The studies using RSM approach in tribological properties of polymer composites are also reviewed.

2.2 The natural human joints

Human joints are located at the end of two or more bones that are connected by articulate tissues. Human joint systems are closely interconnected with tendons, cartilage, ligaments and muscles in our body. They allow free movements of our body parts. There are three types of joints; fibrous joints, cartilaginous joints and synovial joints. Fibrous joints are unmovable joints such as sutures that only bind skull bones. Cartilaginous joints are joints that connect cartilage with bones and only allow slight movements. Meanwhile, for the synovial joints, it is a moveable joint that allows body parts to move freely such as joints located inside the hip, knee, shoulder, elbow and ankle. The synovial joints can be categorized into three groups which are ball and socket joints (hip and shoulder), bi-condylar joints (knee), and multiple bone joints (wrist and ankle). Most of the human joint replacements surgeries are synovial types. Synovial joints in the human body will produce natural body fluid that acts as a lubricant to reduce wear and motion friction in the joint (Bhat, 2005). A typical human knee joint structure is shown in Figure 2.1. The end rigid bones are connected by articular cartilage. This thin layer of cartilage acts as a protection to cover all the joints articular surfaces and reduces movement friction. The main functions of human joints are to provide movements and act as stress or load transfer medium to reduce the applied stress on the bone. In a case where a joint disease or injury has occurred, these joints lost its functions to deliver movements to the bone which will result to substantial pains upon flexing. This particular joint disorder which causes pain, swellings and difficulty in joint movements is known as arthritis.

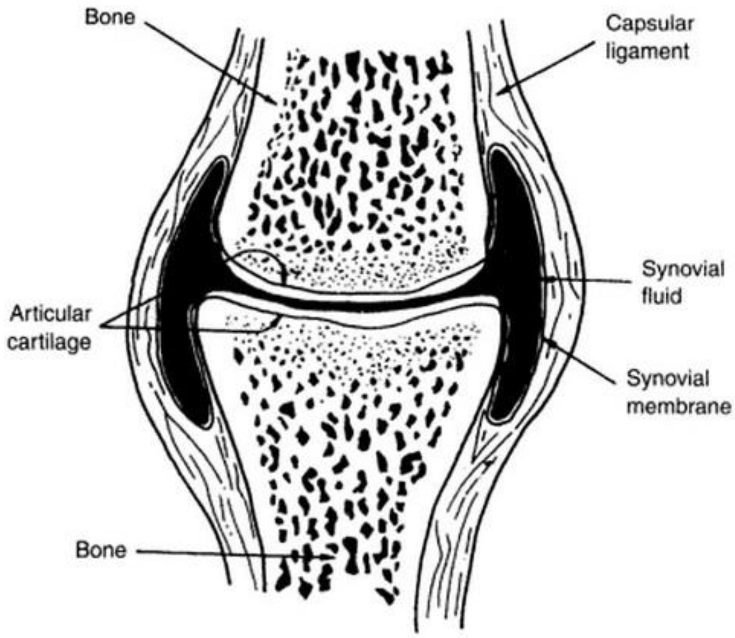

Figure 2.1: A natural human knee of synovial joint section (Furey, 2006).

2.2.1 Type of joint diseases

There are a number of joint diseases that can happen to human beings. Arthritis is a kind of joint disorder which is due to inflammation, infection, injuries or other factors that can cause the joint degeneration. The main symptoms of these joint disorders are swellings at the joint areas, joint pain and loss of joint functions. Osteoarthritis (OA) and rheumatoid arthritis (RA) are two commonly known joint disorders which affect human joints for both active youngsters and people from the middle age group (Kouidri, 2004). The degenerated and damaged articular cartilages will cause the two bones to be in contact directly. The knees and hips are two common joints which are susceptible to OA. A brief discussion on the types of arthritis is presented as follows:

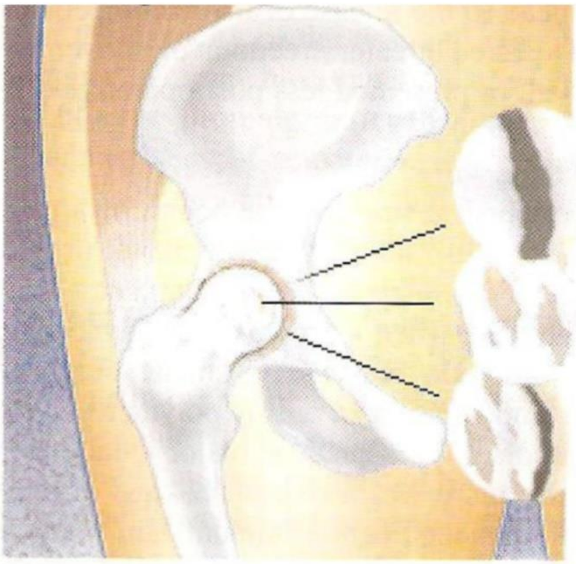

Figure 2.2: The arthritis hip joint (Batchelor and Chandrasekaran, 2004).

(a) Osteoarthritis

Osteoarthritis (OA), also known as degenerative joint disease, is a joint disorder in which the bones are in contact directly due to the articular cartilage cushioning on the bones wears away (Wang et al., 2006). It is estimated that more than 30 million people in the world are affected by OA (Hench, 2005). Clinical symptoms of osteoarthritis may include joint pain, stiffness, inflammation, and creaking of joints. The patient will experience pain and swelling, from walking and standing due to the loss of mobility at the joints. This condition may be due to an old injury or infection to the patients' joints. OA is the most common form of arthritis, and the leading cause of chronic disability (Cheatle, 1991). This arthritis normally happens to middle aged people. Most of the middle aged people will have bone spurs (small bone growths) around the joint. Clinical data reported that before the age of 45, the rate of infection is around 2%, whereas above the age of 65, the rate of infection is around 68% (Kouidri, 2004). However, the reported number of younger aged patient infected with OA has increased in recent years (Kurtz et al., 2005).

(b) Rheumatoid arthritis

Rheumatoid arthritis is a disease associated to inflammation of the synovial membrane surrounding the joints (Wang et al., 2006) where the auto-immune system of the body is induced to attack synovial joint instead of microbe and viruses (Batchelor and Chandrasekaran, 2004) This can cause deterioration of cartilage and other parts of the joint, resulting in the need for TJR. It is one of the inflammatory types of arthritis that may affect other areas of the body such as skin, kidneys etc. Unlike osteoarthritis, rheumatoid arthritis could occur to kids and also elderly people. Around 80% of patients are from the age group around 35-50.

(c) Post-traumatic arthritis

Post-traumatic arthritis is a type of joint destruction attributed from sport injuries or accident (Wang et al., 2006). It arises following an injury and abnormalities such as sprains, fractures and dislocations which cause excessive wear within the joint cartilage and leads to an unstable joint. This joint disease is widely reliant on the damage severity to the ligament, tendon, muscle tear and etc.

There are other types of joint diseases such as bursitis, infectious arthritis, hemarthrosis and etc. The specific cause of arthritis is still not fully comprehended. Wear of articulate cartilage due to excessive loading, ageing, release of wear particles and infection are some of the causes that may lead to degradation of human joints (Batchelor and Chandrasekaran, 2004). There is still no complete solution to cure arthritis entirely. Due to the increasing number of arthritis patients throughout the world, proper solution and treatment on arthritis are now considered very important.

2.2.2 Tribology of the human joint

Human joints provide mobile gestures between bones. From these joints, wear friction and lubrication occur in a biological environment due to performing daily activities. There is an intriguing relationship between human joint bearings and tribological properties. This section presents a brief account of the general introduction of tribology, bio-tribology, wear mechanisms and classical theories of friction. The current trend of literature review on tribological properties of polymer composites for both micro- and nanocomposites are summarized.

2.2.2.1 The history and meaning of tribology

The word "tribology" is derived from an old Greek word, where "tribo" means "rub" or "rubbing", and "logy" means "study of" or "knowledge of". It is later coined by British physicists David Tabor and Peter Jost as "tribology" in 1964 (Field, 2008). Tribology is defined as the study of wear, friction and lubrication in a contacting pair's motion. It is the science of surface engineering involving two interacting surfaces of motion in a given environment which is subjected to different loads or sliding speeds. Tribology is touted as a new field of scientific study in 1967 by a committee of the Organization for Economic Cooperation and Development (Stachowiak and Batchelor, 2014). The concept of tribology can be dated back to 3500 BC when the wheel was invented as a tool to reduce friction in a translationary motion. The use of water as lubricant to smother the surfaces of sledges which transported large statues can be seen in 1880 BC by the Egyptians to build the famous pyramids (Gohar and Rahnejat, 2012). Leonardo da Vinci was the first scientist to study on friction. He was the first to conduct an experimental setup on friction measurement and found that the coefficient of friction is the ratio of friction force to normal load. In everyday's life, we are experiencing tribology science without us realizing it. For example, when we walk, cycle, drive, grab hold on things, we experience friction. Without friction, walking, taking or holding anything would be impossible. Tribology is a multidisciplinary subject involving several areas of expertise i.e. materials science, solid and surface mechanics, chemistry, biochemistry and surface science (Furey, 2006). It is a very complicated subject which involves more than 30 types of wear mechanisms and also several types of lubrication and friction related sciences. The tribology knowledge will help to improve reliability of interacting machine system, service life, safety of the components and substantial economy benefits. Today, many manufacturing industries have emphasized the tribology knowledge to solve several industrial problems and reduce the cost of maintenance of machine components.

2.2.2.2 Bio-tribology

In the case of motion in human joints, the similar tribology concept is applied which also involves wear, friction and lubrication but in the biological environment. The tribology of human joints is also known as "bio-tribology" where the tribology specifically occurs in living organism system (bio-environment). The term bio-tribology was first used in 1973 (Dowson and Wright, 1973). Much attention has been focused in bio-tribology field by clinical studies on the human joint since it was first explored. The human joint is one of the most remarkable bearing known. The human joint bearing is covered with a layer of smooth tissue on the contacting surfaces with the bones, called articular cartilage. This articular cartilage will help to distribute the stress exerted by the bones. A natural lubricant called synovial fluid is present in the joints bearing to lubricate the joint during movement and provide nutrients to the cartilage. The design of the human joints allows uniform stress transfer to minimize the wear and friction to the joint structure of the person. It is very important to understand how the wear and friction during movement activities affect the human joints. Serious problems such as wear and tear may occur if not examined properly. The joint will suffer undesirable wear when the joint mechanism is changed due to joint lubricant decrease or joint disorder. Increase in friction and wear will result in the loss of articular cartilage and consequently, joint failure. This failed joint will cause pain and stiffness in which over time requires artificial joint replacement. Therefore, human joints and artificial joint implants represent the foremost topics in the field of bio-tribology. Besides human joints, there are other significant examples of bio-tribology in human biological system such as skin, hair, shaving, teeth and etc.

2.2.3 Wear

Wear occurs when two or more materials are involved in relative motion contact which causing progressive loss of material from the solid surface. The presence of load, frictional contact, mechanical forces and motion between surfaces will cause several wear problems. As a result, the surface material loses its mechanical cohesion and wear debris is produced (Briscoe and Sinha, 2005). The wide variety of applications that normally face this wear issue are bearings, piston rings and cylinders, gears, cams, brakes, articulation of human joints, machinery components, cutting tools, fastener and others. Wear of the materials results in reduced service lifetime of the components and leads to operating efficiency decrease. Factors which affect the severity of wear are often related to the sliding conditions such as applied load, sliding velocity, lubrication, temperature, counter face roughness and sliding duration. Different sliding conditions will result in different wear mechanisms to materials. The