Department of Engineering Sciences and Mathematics
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Luleå University of Technology 2013

Carbon Nanofiller Reinforced UHMWPE
for Orthopaedic Applications

Optimization of Manufacturing Parameters

Evelina Enqvist
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Abstract

Polymer composites research designed for orthopaedic applications are commonly focused on Ultra high molecular weight polyethylene (UHMWPE) reinforced by a variety of different nanoparticles. However, the high melt viscosity of UHMWPE renders conventional melt mixing techniques impossible for composite manufacturing. Either solvents that are often difficult to extract from the finished composite or addition of high density polyethylene is necessary in order to use conventional melt mixing techniques. Therefore, solid state mixing is convenient option for manufacturing of UHMWPE based nanocomposites.

The aim of this work is to optimize manufacturing parameters (rotational speed and mixing time) for CNT and ND reinforced UHMWPE prepared by planetary ball milling. Many reports have previously been presented, where UHMWPE has been reinforced by CNTs through ball milling, but typically, only mixing time is presented as the crucial variable in ball milling and the movement of the vials, size of the balls, ball-to-powder mass ratio, mixing media and even rotational speed are often overlooked.

During this work, both multi walled carbon nanotubes (MWCNTs) and nanodiamonds (NDs) as reinforcement in UHMWPE have been studied. Beginning with the optimal speed in a planetary ball mill for CNT reinforcement and continuing to time and mixing media for NDs. Scanning electron microscopy (SEM) has been used to study the dispersion of nanoparticles using an extreme high resolution SEM (XHR-SEM). Differential scanning calorimetry (DSC) was used to study the thermal properties of the nanocomposite and X-ray diffraction (XRD) was used to complement the crystallinity measurements obtained by DSC. The water contact angles were measured using the sessile drop method.

The results showed changes in morphology on UHMWPE powder due to ball milling, such as flattening, welding of powder and changes in powder particle size. The ball milling procedure also negatively affected the crystallinity of the powder; however the crystallinity of the sintered material did not show this negative trend for all composites. Furthermore, thermal analysis did not show any changes in melting temperatures, which indicates that any thermal effects on the powder due to ball milling is only temporary. SEM analysis also showed that a higher speed and longer mixing times more effectively distribute and break down nanoparticle clusters, but at the expense of flattening of the powder and reduced powder crystallinity. It was also shown that wet mixing with ethanol was more efficient and less detrimental to powder morphology compared to dry mixing. Water contact angles were overall increased for composites compared to UHMWPE.
Appended papers

Paper I

The effect of ball milling time and rotational speed on ultra high molecular weight polyethylene reinforced with multi walled carbon nanotubes.

Evelina Enqvist, Paula Marques, José Grácio and Nazanin Emami

This paper was presented at the 9th World Biomaterial Congress June 1-5, 2012, Chengdu, China and will be submitted for journal publication.

Paper II

Nanodiamond reinforced ultra high molecular weight polyethylene: comparison of dry and wet ball milling manufacturing techniques

Evelina Enqvist and Nazanin Emami

Submitted to journal publication and will be presented at the 3rd International Symposium of IFToMM, March 19-21, 2013, Luleå, Sweden.

Paper III

Tensile and fatigue crack propagation resistance of MWCNT-reinforced UHMWPE

Dmitrij Ramanenka, Evelina Enqvist and Nazanin Emami

This paper was presented at the 9th World Biomaterial Congress June 1-5, 2012, Chengdu, China and will be submitted for journal publication.

Author’s contribution to the papers

Paper I
Principal author, performed experimental work and analysis.

Paper II
Principal author, performed experimental work and analysis.

Paper III
Helped in manufacturing of composite and performed SEM analysis
Acknowledgements

The work has been carried out at the Division of Machine Elements at Luleå University of Technology. Part of the work has also been carried out at University of Aveiro, Portugal, in collaboration with Professor José Grácio, Director of the center for mechanical technology and automation.

The work presented in this thesis has been partially funded by the Swedish agency for economics and regional growth through CMTF. Swedish Research School in Tribology is also greatly acknowledged for financing the research trip to Aveiro, Portugal.

I would like to express my gratitude to my supervisor Nazanin Emami for guidance and support through this work. I would also like to thank my assistant supervisor Paula Marques at University of Aveiro, Portugal for advise and support especially during the startup of this work.

Gil Gonçalves and Nuno Almeida at University of Aveiro are greatly acknowledged for fruitful discussions. And of course all of my colleagues at the University of Aveiro who made my stay in Portugal a wonderful experience.

Dmitrij Ramanenka is acknowledged for valuable discussions on UHMWPE/MWCNTs composites.

I would also like to take the opportunity to thank Professor Kristiina Oksman and her research group wood and bionanocomposites at Luleå University of Technology for valuable help with laboratory work and for making much of the work possible.

Johnny Grahn and Lars Frisk at the division of Materials Science are acknowledged for valuable help in the lab.

Johanne Mouzon, Iftekhar Uddin Bhuiyan, Danil Korelskiy and Mattias Grahn from the division of Sustainable process Engineering are acknowledged for valuable discussions.

Thank's to all colleagues at division of Machine Elements, especially Gregory Simmons for proofreading this thesis and post doc Yijun Shi for valuable discussions.

Finally, I would like to thank my friends and my family for always supporting me. Although my priorities might seem to be elsewhere, you are always on my mind.
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Abbreviations

0-D Zero dimensional
1-D One dimensional
3-D Three dimensional
2-D Two dimensional
$\text{Al}_2\text{O}_3$ Aluminum oxide
$\text{BSE}$ Backscattered electrons
$\text{C}_2\text{H}_4$ Ethylene gas
$\text{CNF}$ Carbon nanofibers
$\text{CNT}$ Carbon nanotubes
$\text{CoCr}$ Cobalt Chromium
$\text{Co}$ Cobalt
$\text{CO}_2$ Carbon dioxide
$\text{Cof}$ Friction coefficient
$\text{C}_5\text{TiCl}_3$ Cyclopentadienyltitanium(IV) trichloride
$\text{CVD}$ Chemical vapor deposition
$\text{DSC}$ Differential scanning calorimetry
$\text{DWCNT}$ Double walled carbon nanotube
$\text{Fe}$ Iron
$\text{GO}$ Graphene oxide
$\text{HA}$ Hydroxyapatite
$\text{HDPE}$ High density polyethylene
$\text{HIPing}$ Hot isostatic pressing
$\text{HNO}_3$ Nitric acid
$\text{H}_2\text{SO}_4$ Sulfuric acid
$\text{HPHT}$ High temperature high pressure
$\text{HS}$ High speed
$k\text{Gy}$ KiloGray
$\text{KMnO}_4$ Potassium permanganate
$\text{LDPE}$ Low density polyethylene
$\text{LLDPE}$ Linear low density polyethylene
$\text{LS}$ Low speed
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>MDPE</td>
<td>Medium density polyethylene</td>
</tr>
<tr>
<td>MWCNT</td>
<td>Multi walled carbon nanotubes</td>
</tr>
<tr>
<td>ND</td>
<td>Nanodiamond</td>
</tr>
<tr>
<td>n-HA</td>
<td>Nano Hydroxyapatite</td>
</tr>
<tr>
<td>Ni</td>
<td>Nickel</td>
</tr>
<tr>
<td>OPBI</td>
<td>Poly[2,2′-(p-oxydiphenylene)-5,5′-bibenzimidazole]</td>
</tr>
<tr>
<td>PSD</td>
<td>Particle size distribution</td>
</tr>
<tr>
<td>PLA</td>
<td>Polylactic acid</td>
</tr>
<tr>
<td>PLLA</td>
<td>poly-L-lactide</td>
</tr>
<tr>
<td>PVA</td>
<td>Polyvinyl alcohol</td>
</tr>
<tr>
<td>Pt-Zr</td>
<td>Platinum-Zirconium</td>
</tr>
<tr>
<td>SE</td>
<td>Secondary electrons</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>Si3N4</td>
<td>Silicon Nitride</td>
</tr>
<tr>
<td>SWCNT</td>
<td>Single walled carbon nanotube</td>
</tr>
<tr>
<td>Td</td>
<td>Degradation temperature</td>
</tr>
<tr>
<td>Ti6Al4V</td>
<td>Titanium alloy with 6% aluminium and 4% vanadium</td>
</tr>
<tr>
<td>TiCl4</td>
<td>Titanium tetra chloride</td>
</tr>
<tr>
<td>TiO2</td>
<td>Titanium dioxide</td>
</tr>
<tr>
<td>TiBAl</td>
<td>Triisobutylaluminium</td>
</tr>
<tr>
<td>TJR</td>
<td>Total joint replacement</td>
</tr>
<tr>
<td>TLD</td>
<td>Through lens detector</td>
</tr>
<tr>
<td>Tm</td>
<td>Melting temperature</td>
</tr>
<tr>
<td>TpTiCl2(Et)</td>
<td>Tp = Hidrotris(pyrazolyl)borate, Ti = Titanuim, Et= ethyl</td>
</tr>
<tr>
<td>UHMWPE</td>
<td>Ultrahigh Molecular weight polyethylene</td>
</tr>
<tr>
<td>UNCD</td>
<td>Ultrananocrystalline diamond</td>
</tr>
<tr>
<td>UTS</td>
<td>Ultimate tensile strength</td>
</tr>
<tr>
<td>WAXS</td>
<td>Wide-angle X-ray scattering</td>
</tr>
<tr>
<td>wt%</td>
<td>Weight %</td>
</tr>
<tr>
<td>XHR-SEM</td>
<td>Extreme high resolution scanning electron microscopy</td>
</tr>
<tr>
<td>Xc</td>
<td>Crystallinity (%)</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>Y</td>
<td>Yttrium</td>
</tr>
<tr>
<td>ZrO2</td>
<td>Zirconium dioxide</td>
</tr>
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Part I

The Thesis
Chapter 1

Introduction

Ultrahigh molecular weight polyethylene (UHMWPE) has been used as one of the bearing surfaces in total joint replacements (TJR) for more than 50 years due to its wear resistance, low friction coefficient in TJR, high impact strength and toughness. Despite these superior properties compared to other polymers, the UHMWPE wear particles, produced when sliding against a metal counter face, induce osteolysis, which is the major cause of failure of TJR [1]. New materials with higher wear resistance are needed to increase the lifetime of these implants in such a way that revision surgeries can be reduced or even avoided. This is particularly important for younger and more active patients. Over the years, there have been many attempts to reduce the wear of UHMWPE bearing. In recent years crosslinking of the polymer has been recognized as one key feature for reducing wear. Other attempts include reinforcing UHMWPE with fibers or particles such as TiO$_2$ [2], AlO$_3$ [3], MWCNTs [4–10], CNFs [11], and HA [12], using different processing techniques including solvent casting [13–23], ultrasonication [24] [25], in situ polymerization [6], [26–32] and ball milling [7–9], [12], [33–41].

Ball milling is a simple and inexpensive technique where a jar filled with balls and the sample is shaken or rotated to effectively mill the material to be ground by the impact between the balls and the sample. Planetary ball milling is a ball milling technique where the rotating jar is situated at the periphery of a larger disc (sun wheel) which rotates in the opposite direction. Milling time, rotational speed, movement of the jars, size of the balls and ratio between the volume of the material to balls are important parameters to take into consideration when mixing composites for use in ball milling.

Nanoparticles are promising components as reinforcement in polymer based composites due to high mechanical properties and high surface energy. Some of the most interesting nanoparticles are carbonaceous nanoparticles. Carbon comes in a variety of forms with one structure having properties completely different from the other. Such an example is diamond, which is extremely hard, and graphite, which is considered as a soft material due to the weak bonds between its layers. Carbon nanotubes have been widely investigated as reinforcement in polymer based composites. A newer carbon nanoparticle is the nanodiamond, although it has been known in Russia since the 1960’s.

Carbon nanotubes (CNTs) are outstanding in many ways. Thanks to their small diameter (4-300 nm) and long length, CNTs exhibit high mechanical strength. These tiny particles can consists of one to several tubes stacked within one another, these are known as single walled and multi walled carbon nanotubes [42]. Nanodiamonds (ND) like CNTs are a class of carbon allotropes with great variety. They have a size range from about 1 to 100 nm and exist in the form of diamond films
and diamond particles. Ultrananocrystalline diamonds (UNCD) are a class of nanodiamonds with a size range of only a few nanometers as compared to other nanodiamond structures with typical sizes above 10 nm [43].

MWCNTs and NDs are promising as reinforcement in polymer matrices thanks to their small sizes and large aspect ratios and rich tailor able surfaces. Furthermore, several studies point to the increased oxidation stability of crosslinked UHMWPE reinforced with nanofillers [33] [44]. In the presented thesis manufacturing and processing parameters of UHMWPE reinforced with different weight% of either MWCNTs or NDs was investigated.

1.1 Ultrahigh Molecular Weight Polyethylene

Several kinds of polyethylene exist, such as, low density polyethylene (LDPE), linear low density polyethylene (LLDPE), medium density polyethylene (MDPE), high density polyethylene (HDPE) and ultrahigh molecular weight polyethylene (UHMWPE) all varying in molecular weight and density. UHMWPE is widely used in various applications and since the early 1960s in TJR when Sir John Charnley introduced it in total hip arthroplasty.

1.2 The Polymer

UHMWPE belongs to a family of polymers with a simple chemical formulation of carbon and hydrogen molecules. It is a linear homopolymer with a carbon backbone that can rotate, twist and fold into the crystalline phase providing a more complex structure at the molecular level. It can be explained as a set of crystalline regions embedded in an amorphous phase. The degree of crystallinity is important in any polymeric material since it is related to the mechanical properties, including: elastic modulus, yield strength, creep resistance, and fatigue resistance. UHMWPE is a viscoelastic material and many of its weaknesses originate from its low creep resistance and fatigue strength compared to the metal or ceramic counter-face in TJR. Polyethylene is formed from ethylene gas (C2H4) using the Ziegler process in a solvent using titanium tetra chloride (TiCl4) as a catalyst. Impurities of titanium, aluminum and chloride come from the catalyst. Medical grade UHMWPE is categorized into three grades: type 1, 2 or 3 depending on the molecular weight and manufacturer [26].

The most commonly used UHMWPE resins for medical applications are GUR 1020 and GUR 1050 from Ticona. Some typical mechanical properties of the GUR 1020 resin are molecular weight 3.5×10⁶ g/mol, density of 935 kg/m³, yield strength 21.9-22.3 MPa, Ultimate tensile strength 51.1-53.7 MPa and elongation to failure 440-452 %. These values were based on extruded and molded UHMWPE [26] and are based on both extruded and molded UHMWPE. The GUR 1050 resin, also from Ticona, has a higher Molecular weight 5.5-6×10⁶ g/mol, density of 930-931 kg/m³, yield strength 21-21.5 MPa, Ultimate tensile strength 46.8-50.7 MPa and elongation to failure 373-395 % [26]. GUR 1050 has, despite the larger molecular weight, slightly lower mechanical properties.
1.3 UHMWPE in Joint Replacements

As mentioned above, UHMWPE has been used as orthopaedic material since the early 1960's and has been constantly studied and developed to improve clinical performance. In the 1970's carbon fiber reinforced UHMWPE was introduced by Zimmer, Inc under the name of Poly II [45]. The most recent break through, was in the late 1990's when highly crosslinked UHMWPE was introduced in TJR [46]. Nevertheless the improved wear rate of highly crosslinked UHMWPE comes with the expense of increased risk for oxidation [47] and reduced mechanical properties [48]. The problem with oxidation could be solved by post irradiation treatments that include heating the material to either above or below the melting temperature [49]. However, the current solution is the addition of vitamin E that acts as antioxidant [50][51].

The main types of wear mechanisms in TJR are abrasive, adhesive, burnishing, fatigue and pitting, which depend on the type of joint and also the area of the implant that is investigated [52–54]. Wear of UHMWPE liners has been suggested to be caused by microstructural changes due to the frictional loading. As such the majority of wear debris are not generated from the very top of the surface, but that the microfibrils underneath the surface that break out [55]. The wear also depends on the type of counterface. Ceramic heads have shown lower wear rate in comparison to Cobalt-Chromium alloy (CoCr) heads in a hip simulator. Retrieved implants in the same study confirmed these results.[56]. Aging of the component is also largely affecting the performance of UHMWPE. More severe wear damage at the surface and subsurface was found for aged samples compared to un-aged samples. The severity of subsurface delamination and subsurface cracking was reported to increase as the subsurface oxidation increased, which in turn, increased with ageing. [57]. Higher crystallinity has been shown to improve the wear resistance [58]. Also different manufacturing techniques have been shown to affect the mechanical and tribological performance of UHMWPE [59]. On the other hand, it has also been shown that the consolidation temperature did not affect the wear of the polymer, and it was suggested that wear is a surface related phenomenon and not affected by the bulk inhomogeneities [60].

Materials such as metallic alloys [61] and ceramics [62], [63] have been investigated as suitable candidates to replace the polyethylene acetabular cup. These new systems have their drawbacks as well, for example squeaking [64], carcinogenicity [65], metal allergy, pusodotumor, more nanosized wear particles, revision difficulties and cost[66]. This is why UHMWPE is still dominant among orthopaedic materials in total hip and knee replacements after five decades on the market. Nevertheless, the wear particle induced osteolysis phenomena (aseptic loosening) still need to be dealt with.

1.4 Crosslinking of UHMWPE

Several important properties need to be considered in the search for alternative materials for high stress bearing joint implants such as high strength and stiffness, high wear- and fatigue resistance, and biocompatibility. The development of crosslinked PE began in the 1970’s [49] and has been in use since the late 1990s. Breaking of UHMWPE’s fibrils near the polymer surface has been recognized to be one of the main reasons for wear debris generation [55]. These fibrils increase the strength in the axial direction but when the direction of motion is changed to the transversal, the fibrils break easily leading to reduced strength and an increase in the generation of wear particles [67]. Crosslinking of UHMWPE was developed to slow down the formation of these fibrils, which is particularly important in multidirectional sliding
such as in the hip. Crosslinking of UHMWPE increases the wear resistance but also decreases molecular mobility, decreases ductility, fatigue and fracture resistance [49]. Crosslinking also increases oxidation due to free radicals that are induced through irradiation. This could be avoided by thermal treatments. Re-melting or annealing has been used to eliminate residual free radicals in crosslinked polyethylene, a processing step that further reduces the mechanical properties of the component. It has been shown that the crystallinity decreases further in crosslinked and re-melted UHMWPE and increases in crosslinked and annealed UHMWPE. Annealing also was shown to preserve the fatigue resistance better than re-melting [68]. Reductions in wear rate up to 93% of that of conventional UHMWPE has been reported for crosslinked and annealed X3 ® cups from Stryker Orthopaedics [69]. The differences of retrieved crosslinked and non-crosslinked UHMWPE acetabular components were recently investigated finding no significant difference between the two, which is contrary to what has previously been believed. The highly crosslinked UHMWPE is otherwise considered to be more wear resistant compared to conventional UHMWPE. This study found no differences in wear behavior, although the authors point out that long term studies of crosslinked liners are missing and that it is too early to draw any conclusions of the accuracy of their study. The accuracy may also have been affected by the differences between the retrieved components [70]. Nevertheless to make in vitro and laboratory studies relevant and applicable to in vivo and clinical situations is a well understood challenge in the orthopaedic materials development. Recently, vitamin E has been used to dope crosslinked polyethylene to eliminate free radicals and so remove the re-melting/annealing step.

1.5 UHMWPE Reinforced with Biomolecules

The extremely hydrophobic characteristics of UHMWPE hinder the acetabular liner from interacting with the synovial fluid in the joint implants, and prevent the lower friction that the synovial fluid can provide. The strive toward obtaining a material that meets the criteria of natural bone tissues to develop a more sustainable bearing material led to investigations of several reinforcing agents for UHMWPE. One of the latest studies investigated the use of biomolecules to obtain a natural lubricating and reinforcing filler. Hyaluronan was used to combine the high strength of UHMWPE and the lubricating ability of Hyaluronan. Hyaluronan is, along with lubricin, one of the major constituents of synovial fluid. It is also present in the soft tissue that surrounds and forms the capsular inside of the joint known as the synovial tissue. The cartilage surface is covered by a thin layer of special hyalurona-rich biomatrix called the lamina splendens. The hyaluronan keeps the layers together, gives structural elasticity and hydrates it while the lubricin is the lubricating agent. Reinforcing UHMWPE with hyaluronan was aimed to improve the lubrication and to reduce wear of the polymer by introducing a constituent which is not only naturally occurring in body fluids but is one of the main constituents of synovial fluid which lubricates the natural joints. Since UHMWPE is hydrophobic and Hyaluronan is hydrophilic, the two constituents mix poorly. Hyaluronan was thus functionalized to improve the interaction with UHMWPE. Despite the lower wear rate of UHMWPE-Hyaluronan composite compared to UHMWPE, the wear rate was higher compared to crosslinked UHMWPE [71][72]. Studies on the effect of hyaluronan addition in crosslinked UHMWPE is ongoing [72].
Chapter 2

Carbon Allotropes

Carbon comes in a variety of forms with vastly varying properties. Such an example is diamond, which is considered the hardest material in existence and graphite, which due to its weak interlayer bonds is considered to be a soft material. Carbon is the sixth element in the periodic table and is found as the first element in column IV. It has a total of six electrons with the ground state configuration: 1s²2s²2p². Four of these are valence electrons that can form three different hybridizations; sp, sp² and sp³. Carbon can form π-π multiple bonds such as C=C, C≡C, C=O, C=S, and C≡N, no other element in group IV has this ability. Carbon has a strong tendency to form bonds to its own atoms that can result in long structures. Carbon structures are mainly built from sp²- and sp³-bonded carbon atoms [42].

In the present study NDs and MWCNTs were used as a reinforcement system in UHMWPE matrix. Therefore in the next few pages these two specific groups of carbon nanoparticles will be explained in detail.

2.1 Carbon Nanotubes

Carbon nanotubes (CNTs) are outstanding in many ways. Thanks to their small diameter (4-300 nm) and long length, CNTs exhibit high mechanical strength, thermal and chemical stability, heat conduction and electrical properties. CNTs can be single-walled (SWCNT), double-walled (DWCNT) or multi-walled (MWCNT), where one, two or several graphene layers, respectively, are rolled up as tubes [42].

2.1.1 Synthesis

Generally, the methods for CNT synthesis can be divided into two categories which depend on the working temperature. Generally, techniques operating under high temperatures vaporize a graphite target while medium temperature techniques rely on catalytic chemical vapor deposition. High temperature techniques, which involve sublimation of graphite and condensation of the vapor produced after sublimation, mainly differ by the method used for sublimation. The different routes include forming an electric arc between two graphite electrodes, ablation using a pulsed laser or vaporization by a continuous laser. The processes used for producing SWCNTs and MWCNTs are the same and only differ in the use of a metallic catalyst in the formation of SWCNTs [73].
2.1.2 Structure of Carbon Nanotubes

CNTs basically consist of graphitic sheets rolled up into cylindrical tubes [74]. Two symmetric structures are possible for CNTs, these are known as zigzag and armchair. The unit cells of the zigzag and armchair are shown in figure 1. Although most CNTs are believed to have structures where the hexagons are arranged helically around the tube axis, chiral tubes. The graphene lattice structure can be described by a vector, \( \mathbf{C} \), that forms the nanotube’s circumference when it is rolled up so that \( \mathbf{C} \)'s endpoints meet. The vector \( \mathbf{C} \) is expressed by:

\[
\mathbf{C} = n \mathbf{a}_1 + m \mathbf{a}_2
\]

Where \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) are the unit cell base vectors and \( n \geq m \). \( m = 0 \) for zigzag tubes and \( n = m \) for armchair tubes (figure 1). The formation of chiral tubes is illustrated in figure 2.

![Figure 1: a) zigzag unit cell and b) armchair unit cell. Adapted from [75]](image1)

![Figure 2: Graphene sheet from which a CNT is rolled up, and the construction of the chiral unit cell. Adapted from [75]](image2)
The layer structure of MWCNTs can be formed in two different ways; one is the arrangement of individual tubes stacked in one another or rolled up like a scroll, or alternatively a mixture of both. The general opinion is however that the first arrangement is the most probable. The distance between the tubes is approximately 0.352 nm for the zigzag structure and 0.34 nm for the armchair structure. The structure for chiral tubes is more complicated. It is generally not possible to have the tubes separated by the graphite inter planar distance (0.34 nm) [75].

2.1.3 Mechanical Properties of Carbon Nanotubes

MWCNTs often appear fairly straight, which is a good indication of a stiff material. SWCNTs on the contrary often appear with a larger curvature. This is probably due to the thinner nature of SWCNTs compared to MWCNTs. This indicates both high Young's modulus as well as high breaking stress, especially since broken CNTs are hardly observed but bent CNTs are quite often observed. Values for the Young's modulus observed for MWCNTs prepared by the electric arc method range from 810 GPa to 1.28 TPa. For MWCNTs produced from catalytical methods lower Young's modulus was observed, from 27 GPa to 350 GPa. Tensile strengths as high as 150 GPa have been observed [76].

2.1.4 Toxicity of Carbon Nanotubes

It is useful to clarify that some carbon materials, like pyrolytic carbon and diamond-like carbon are presently used in medicine. However, the toxicity of smaller carbon black particles could be much higher than the toxicity of larger carbon black particles, suggesting that extra care needs to be taken regarding biocompatibility and cytotoxicity of carbon nanoparticles. It has also been shown that sidewall functionalized SWCNTs were less toxic than non-functionalized SWCNTs [77].

2.1.5 Functionalization of Carbon Nanotubes

Functionalization of carbon nanotubes can roughly be divided into two main categories, covalent functionalization and non-covalent functionalization. The aim of functionalization is often as simple as increasing the solubility of CNTs in various solvents, but it can just as well be to increase the interaction between CNTs and other compounds such as polymeric matrices or molecules in drug delivery [77].

2.1.5a. Covalent Functionalization

Acid functionalization is a common and easily performed method where the nanotube ends and defects are functionalized by formation of carboxyl or other groups. Acids used for functionalization are commonly \( \text{HNO}_3 \), \( \text{HNO}_3 + \text{H}_2\text{SO}_4 \), and \( \text{H}_2\text{SO}_4 + \text{KMnO}_4 \). After acid functionalization, further treatment can be carried out through reaction with the groups formed during acid functionalization. Grafting of polymers onto oxidized CNTs are one such treatment as well as silylation of CNT sidewalls. The reactions on sidewalls depend strongly on the curvature because an increased curvature results in higher pyramidalization of the sp² atoms and is then more likely to react. Since the curvature of CNTs is quite small except at the ends, functionalization of sidewalls will only occur if highly reactive reagents are used [77].
2.1.5b Non-Covalent Functionalization

Non-covalent functionalization consists of adding molecules to the CNTs without creating any chemical bonds between the molecule and the CNTs. Instead, van der Waal forces are created or molecules are wrapped around the CNTs. The idea of this type of functionalization is to preserve the pristine CNT properties. The usage of surfactants to disperse CNTs can be thought of as a type of non-covalent functionalization. Otherwise, two approaches are used; small molecules with planar groups adsorb onto the CNT surface using π-stacking forces or large polymeric molecules are stacked around the CNTs [77].

2.2 Nanodiamonds

Nanodiamonds (NDs) are, just as CNTs, a class of carbon allotropes with great variety. The size range is about 1-100 nm and can be everything from diamond films to diamond particles in the form of particle agglomerates, or particles incorporated into other materials. The range is from 0D particles to 1-D nanorods, 2-D diamond platelets and 3-D diamond films [43].

2.2.1 Synthesis of Nanodiamonds

There are a few methods for nanodiamond production, such as detonation of carbon explosive materials, gas-phase nucleation at ambient pressure, chlorination of carbide material at moderate temperatures, and HPHT graphite transformation with in shock-wave [43].

2.2.2 Structure of Nanodiamonds

Nanodiamonds are not nanosized diamond crystals, in fact, no agreement on their structure has been established [78]. They were discovered in the 1960’s in the former USSR, but it wasn’t until the 1980’s that they became known to the rest of the world [79]. Basically NDs consists of a diamond core with a graphitic shell [80]. The shape of detonation diamond is round with no distinct facets, with oxygen-containing groups present at the surface originating from the ND reaction with a cooling medium upon formation, or from the purification process. In addition to functional groups at the surface, graphitic carbon is also present at the surface. Core agglomerates are strongly bonded to each other and cannot easily be broken. The functional groups at the detonation ND surface are important in agglomeration due to the formation of covalent bonds that allow for formation of large agglomerate size [81].

2.2.3 Mechanical Properties of Nanodiamonds

The mechanical properties reported for UNCDs are 97 GPa in hardness, a Young’s modulus of 967 GPa and failure strength of 4.13 GPa [82]. But also Young’s modulus of 1.22 GPa has been reported as well as hardness 10 on the Mohr scale which is equivalent to diamond [83]. These values, especially the Young’s modulus makes NDs comparable and competitive with MWCNTs.
2.2.4 Toxicity of Nanodiamonds

It is well known that bulk diamond is chemically inert and is used as coatings on metallic components in orthopaedic surgery. Diamond coatings and diamond films have shown good biocompatibility. However, the biocompatibility of bulk material does not necessarily mean that fine particles of the same material are biocompatible [84]. However, NDs contain surface functional groups that were introduced during the purification process. Toxicity of NDs is most probably determined by the surface functionalization [85]. Considering the variety of surface modifications that exist for nanoparticles, testing of biocompatibility and toxicity of NDs should be thoroughly investigated in the future.
Chapter 3

UHMWPE based Composites

This thesis focuses on UHMWPE based composites in medical and orthopaedic applications. Composites reviewed in this chapter are mainly thought to apply as medical components, but also composites with primary application elsewhere are discussed which provides useful background for this work.

3.1 Synthesis of UHMWPE based Composites

In manufacturing of UHMWPE based components, due to the high melt viscosity of UHMWPE, conventional processing techniques such as injection molding, screw extrusion and blow molding are not suitable. UHMWPE has extremely high viscosity that works in such a way that the polymer tends to swell instead of melt. Because of this, UHMWPE is normally processed using one of a few processes including compression molding, ram extrusion and HIPing. In all three methods the most important parameters are time, temperature and pressure which affect the degree of crystallinity and the degree of consolidation in the final product. This makes UHMWPE based composite synthesis more challenging than other polymers as techniques such as melt-mixing is nearly impossible without the help of solvents or the addition of high density polyethylene (HDPE). However, only a few solvents are known to dissolve UHMWPE. These solvents include paraffin oil, Xylene and decahydronaphthalene, more commonly known as Decalin. Camphene is also mentioned as a solvent for UHMWPE [86], however it has not been widely investigated. Since these solvents are not easily removed after synthesis alcohol assisted dispersion of fillers in combination with ball milling or ultrasonication, is commonly used instead.

3.1.1 Solvent Casting

The challenge of dissolving UHMWPE limits the range of UHMWPE based composite-manufacturing techniques. One of many drawbacks of solvent casting of UHMWPE is the necessity of additional heat, which increases the risk of polymer oxidation during manufacturing. This is especially an issue in combination with simultaneously stirring of the solution. Decalin is a colorless industrial solvent suitable for UHMWPE dissolution which has been used in the manufacturing of CNT reinforced UHMWPE fibers through twin screw extrusion at elevated temperatures [13]. A combination of heating and stirring UHMWPE/MWCNTs with Decalin at 140-150 °C [14–16] or 80 °C [17] is done to produce thin films. The solvent can then be evaporated under ambient conditions or at 60 °C with further drying in an oven [14] or removed by extraction in acetone [15] or hexane [16] before further treatments. Hot drawing [13] or gel-spinning followed by hot drawing [16] are examples of further treatments. Dip coatings on Ti6Al4V surfaces have also been
manufactured with UHMWPE dissolved in decalin [18]. Paraffin oil has been used to
dissolve UHMWPE as well at temperatures close to the melting temperature while
screw extrusion[19] This technique has also been done at temperatures up to 250 °C
[14]. Benzene [14] and hexane [19], [20] have been used to extract excess paraffin oil.
Xylene [22] and toluene [23] are other examples of solvents for UHMWPE.

3.1.2 Ultrasonication

Ultrasonication in a water bath using various dispersing agents or solvents such as
ethanol [13],[87], xylene [22] and decalin [15][16] is often used to disperse the
reinforcement prior to the main mixing method together with UHMWPE. However,
composites produced solely using ultrasonic methods have also been reported. Toluene
was used to mix CNTs with a polymer matrix using ultrasonication [24]. Another
study discusses alcohol assisted dispersion of CNTs in an UHMWPE matrix using
ultrasonication that resulted in dispersion of CNTs at the matrix particle interfaces
[88]. Graphene oxide (GO) has been mixed with UHMWPE using both
ultrasonication and stirring. A mixture of water and ethanol was used. Water was used
to break the van der Waal forces between the graphene sheets and ethanol was then
used to disperse the UHMWPE in the solution [25]. Ultrasonication of UHMWPE
reinforced with silica nanoparticles in Decalin prior to gel spinning has been studied
[89] as well. An ultrasonic tip was used as the first step in mixing graphite nanoplatelets
with UHMWPE in toluene to homogenize the mixture and promote swelling of
UHMWPE before further processing using microextrusion [90].

3.1.3 Ball Milling

Ball milling is a common technique for grinding minerals, ceramics and paints into fine
powder, as well as a technique for mechanical alloying. It is a good alternative for
composite manufacturing where melting or dissolution of the matrix is not possible, as
it mixes the constituents in the solid state. The material to be milled is subjected to
compressive loads from impact with the balls. The properties of the resulting fine
powder depend on not only the inherent material properties such as mechanical
properties, chemical constitution, and structural properties but also on the ball milling
parameters such as ball-to-powder mass ratio, time, rotational speed, type of ball mill
(motion of the jar) and even the atmosphere [91]. Mixing by ball milling can be
performed either dry [7–9], [33–37] or wet, most commonly with ethanol [12], [38–
41]. Rotary ball mills use milling times of up to 8 hours in ethanol [12], [40], [41],
typically with a low rotational speed, 35 rpm has been reported [41] Some studies only
mention that the ball mill has “adjustable rotation” [40] up to 3000 rpm [12]. High-
energy ball mills operating with oscillating movements at high amplitude under dry
mixing have been used to mix UHMWPE and MWCNTs. The mixing in this case
was accomplished for 5 minutes at 250 rpm and 25 cycles [9]. Moreover, speeds up to
3500 rpm for 12 hours have been used to reinforce UHMWPE with Titanium [92].
Ball milling without balls was applied to mix of coconut shell powder and UHMPE
for 10 hours [93]. Another popular ball milling technique is the planetary ball mill
where the rotating jar is located at the periphery of a larger oppositely rotating wheel,
often referred to as the sun-wheel [7], [34–36]. In these cases, the rotational speed is
not mentioned [34] [35] or varies from 350 rpm [36], 450 rpm [7] up to 500 rpm [94].
Several authors have utilized ball milling without specifying the type of ball mill [8], [33], [39], only mentioning the milling time [8], [33], [93] or that wet or dry mixing was performed [39].

3.1.4 Melt Mixing

Melt mixing of UHMWPE can only be done at temperatures significantly above the oxidation temperature of UHMWPE. The melt mixing procedure is thus only possible without damaging the polymer if a lower molecular weight polymer or a solvent is added to the process. Melt mixing of UHMWPE and polypropylene has been conducted through single screw extrusion at 210 °C [95] and twin screw extrusion at 220-230 °C was used to reinforce carbon fibers with UHMWPE [96]. Twin screw extrusion has also been used to mix UHMWPE based composites with the help of paraffin oil [19], [97]. Addition of HDPE has been used to melt mix UHMWPE based composites with the help of a Brabender [98–100]. Toluene has been used to prepare UHMWPE based composites with a micro-extruder [90] and Paraffin oil has been used to prepare composites with a rheometer [20]. CNT reinforced UHMWPE was also manufactured using a rheometer [101], however no solvent or lower molecular weight polymer was added and consequently, the processing temperature had to be raised to 270 °C which is far above the oxidation temperature of UHMWPE.

3.1.5 In situ Polymerization

Polymerization of UHMWPE is generally accomplished by bonding ethylene monomers into long UHMWPE chains, this is typically done in a solvent using ethylene gas and titanium tetra chloride (TiCl₄) as a catalyst [26]. In situ polymerization relies on polymerization of UHMWPE with the nanofiller present. During polymerization, polyethylene is formed around the filler and the nanofiller become embedded in an otherwise intractable matrix. Compounds such as TpTiCl₂(Et) [27], TiBAl [28], TiCl₄ [6], [29], [30], CpTiCl₃ [31], [32] have been used to synthesize UHMWPE based nanocomposites.

3.1.6 Other techniques

Other techniques rely on dry mixing or wet mixing in a mortar or some kind of mechanical mixing technique. Among wet mixing techniques ultrasonicication followed by high speed stirring can be found [87] as well as solely high speed stirring in ethanol [102], [103] or acetone [104][105]. Dry mixing techniques involve using a vortex mixer [106], a theta-composer [107], a mortar [108] or more diffuse concepts such as “shaken vigorously in a sealed container” [109], mix-refiner [110], and “dry physical-mechanical blending” [111]. Mixing with a rheometer at 195 °C has also been reported [112]. One could argue that this technique would belong to the melt-mixing techniques since the processing temperature is above Tₘ of UHMWPE. However, to fully melt UHMWPE, either a much higher temperature needs to be applied, a solvent or a lower molecular weight polyethylene must be added.
3.2 Irradiation of UHMWPE based composites

Crosslinking of UHMWPE chains is already common for total hip replacements. The breaking and rearrangement of polymer chains increases the risk of oxidation over time; one solution to this is the incorporation of vitamin E as an antioxidant to prevent crosslinked UHMWPE from oxidizing. Other tradeoffs such as reduced elastic modulus and impact strength also affect crosslinked UHMWPE. Crosslinking of UHMWPE based composites have recently gained more interest since it is believed that fillers can prevent the mechanical losses or even prevent unwanted oxidation processes. Gamma irradiation of nano-hydroxyapatite (n-HA) reinforced UHMWPE showed the lowest wear rate at 150 kGy compared to unfilled UHMWPE and composites irradiated at 50 and 100 kGy [113]. However, the 100 kGy irradiation dose was chosen for the next study showing a reduced coefficient of friction and reduced wear rate for UHMWPE reinforced with 7 wt% n-HA compared to a lower concentration of n-HA and pure UHMWPE [114]. The same research group also irradiated UHMWPE reinforced by 6 wt% nano-TiO₂ at 500 kGy and reduced the wear rate by 70% [2]. Furthermore, they also showed that for nano-Al₂O₃, 2 wt% filler was needed to reduce the wear rate by the same amount at the same radiation dose [3]. MWCNT reinforced UHMWPE radiated with 90 kGy resulted in an increase in Young’s modulus for the irradiated composite [37] and it was shown that the MWCNTs may act as radical scavengers [44]. After 240 days of ageing, the loss of mechanical properties of MWCNT reinforced UHMWPE subjected to sterilization doses of 25 kGy and 50 kGy, was shown to be lower for the composite compared to pure UHMWPE [33].

3.3 UHMWPE Reinforced with Carbon Nanofillers

Due to the withdrawal from the market of the carbon fiber reinforced UHMWPE, Poly II, shortly after its introduction surgeons are skeptical towards this type of reinforced polyethylene for medical applications. However, one should keep in mind that the many refined characterization and analysis techniques have developed since the 1970’s. Also the introduction of nanoparticles, and especially carbon nanostructures, has once again raised the interest of many researchers to explore the possibilities of manufacturing UHMWPE based composites with superior long term properties as bearing surfaces in orthopaedic applications. This means that the challenges such as biocompatibility, increased wear of counter surface and poor interaction between UHMWPE and reinforcement must be addressed. One of the most noteworthy changes from reinforcing matrices with nanofillers, rather than microfibers, is the higher surface area to volume ratio. This leads to an associated improvement in mechanical properties due to the more effective load transfer between the fiber and the matrix. Biocompatibility is an important factor since the discussions on the effect of carbon nanotubes or any other nanoparticles on biological environments is a very important and complex matter. This needs to be addressed carefully for any nanocomposite to be used clinically. The debated nanofillers are widely studied as reinforcement in polymer based composites and thus also as reinforcement in UHMWPE. Their unique properties such as strength and stiffness and their high aspect ratio give them promise as reinforcements in polymer based composites in orthopaedic materials. In table 1, an overview of changes in mechanical properties of carbon nanofiller reinforced UHMWPE is shown. All properties are represented as
percentage. Tensile strength and Young’s modulus are typically increased while elongation at break is decreased.

Table 1: Mechanical properties of carbon reinforced UHMWPE

<table>
<thead>
<tr>
<th>Resin</th>
<th>Reinforcement</th>
<th>Concentration (wt%)</th>
<th>Processing</th>
<th>Tensile strength increase (%)</th>
<th>Young’s modulus increase (%)</th>
<th>Elongation increase (%)</th>
<th>Yield stress increase (%)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>80%GUR 2122/20%HDPE</td>
<td>MWCNT</td>
<td>0.2-2</td>
<td>Haake laboratory kneader at 210 °C</td>
<td>20</td>
<td>36</td>
<td>-</td>
<td>23</td>
<td>[4]</td>
</tr>
<tr>
<td>Mipelon</td>
<td>MWCNT</td>
<td>5</td>
<td>Jar mill</td>
<td>-13</td>
<td>82</td>
<td>6</td>
<td>-</td>
<td>[5]</td>
</tr>
<tr>
<td>UHMWPE</td>
<td>MWCN</td>
<td>0.5-3.5</td>
<td>In situ polymerization</td>
<td>~100</td>
<td>-</td>
<td>~150</td>
<td></td>
<td>[6]</td>
</tr>
<tr>
<td>GUR 4120</td>
<td>MWCNT</td>
<td>0.1-4</td>
<td>Planetary ball milling</td>
<td>17</td>
<td>-</td>
<td>73</td>
<td>-</td>
<td>[7]</td>
</tr>
<tr>
<td>GUR 1020</td>
<td>MWCNT</td>
<td>0.2-1</td>
<td>Ball milling</td>
<td>-26</td>
<td>-</td>
<td>-</td>
<td></td>
<td>[8]</td>
</tr>
<tr>
<td>GUR 1020</td>
<td>MWCNT</td>
<td>0.3-1</td>
<td>High energy ball milling</td>
<td>-13</td>
<td>28</td>
<td>21</td>
<td>-</td>
<td>[9]</td>
</tr>
<tr>
<td>GUR 1020</td>
<td>MWCNT</td>
<td>0.2</td>
<td>Ball milling</td>
<td>22.7</td>
<td>5</td>
<td>-</td>
<td></td>
<td>[10]</td>
</tr>
<tr>
<td>Supplied by Goodfellow</td>
<td>MWCNT</td>
<td>1-5</td>
<td>Ball milling</td>
<td>8</td>
<td>38</td>
<td>-</td>
<td>6</td>
<td>[37]</td>
</tr>
<tr>
<td>GUR 1020</td>
<td>CNFs</td>
<td>5-10</td>
<td>Stirred in paraffin + Brabender + washing in hexane</td>
<td>-</td>
<td>~26</td>
<td>-</td>
<td>-</td>
<td>[11]</td>
</tr>
<tr>
<td>Supplied by Beijing No. 2 Auxiliary Agent Factory</td>
<td>MWCNT or GO</td>
<td>0.2-2</td>
<td>High speed stirring in ethanol or H2O/ethanol</td>
<td>12.8 and 38</td>
<td>23.9 and 73.6</td>
<td>-</td>
<td>-</td>
<td>[103]</td>
</tr>
</tbody>
</table>
Table 2: Thermal properties of carbon nanofiller reinforced UHMWPE. Values within brackets are for pure UHMWPE.

<table>
<thead>
<tr>
<th>Resin</th>
<th>Reinforcement</th>
<th>Concentration (wt%)</th>
<th>Processing</th>
<th>$T_m$ ($^\circ$C)</th>
<th>$T_c$ ($^\circ$C)</th>
<th>$T_d$, peak ($^\circ$C)</th>
<th>Xc (% DSC)</th>
<th>Xc (% XRD)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mipelon</td>
<td>MWCNT</td>
<td>5</td>
<td>Jar mill</td>
<td>136</td>
<td>-</td>
<td>-</td>
<td>48 (58)</td>
<td>43 (55)</td>
<td>[5]</td>
</tr>
<tr>
<td>UHMWPE</td>
<td>MWCNT</td>
<td>-</td>
<td>In situ polymerization</td>
<td>131.44</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[31]</td>
</tr>
<tr>
<td>UHMWPE</td>
<td>MWCNT</td>
<td>0.5-3.5</td>
<td>In situ polymerization</td>
<td>-</td>
<td>-</td>
<td>476.4 (464.3)</td>
<td>-</td>
<td>-</td>
<td>[29]</td>
</tr>
<tr>
<td>UHMWPE</td>
<td>MWCNT</td>
<td>0.5-3.5</td>
<td>In situ polymerization</td>
<td>136-140</td>
<td>117-120</td>
<td>479-490 (477)</td>
<td>34-40 (28)</td>
<td>-</td>
<td>[6]</td>
</tr>
<tr>
<td>UHMWPE</td>
<td>MWCNT</td>
<td>0.1-1</td>
<td>In situ polymerization</td>
<td>134-137</td>
<td>116-118</td>
<td>-</td>
<td>42-47 (40)</td>
<td>-</td>
<td>[27]</td>
</tr>
<tr>
<td>-</td>
<td>MWCNT</td>
<td>0.1-0.5</td>
<td>Ultrasonication in toluene</td>
<td>-</td>
<td>-</td>
<td>~46-50 (50)</td>
<td>-</td>
<td>-</td>
<td>[24]</td>
</tr>
<tr>
<td>GUR 1020</td>
<td>MWCNT</td>
<td>0.3-1</td>
<td>High energy ball milling</td>
<td>132.7-133.6</td>
<td>-</td>
<td>-</td>
<td>53.4-56.6</td>
<td>-</td>
<td>[9]</td>
</tr>
<tr>
<td>Supplied by Goodfellow (Huntingdon, England)</td>
<td>MWCNT</td>
<td>1-5</td>
<td>Ball milling</td>
<td>134.2-135.3</td>
<td>-</td>
<td>42-48 (396)</td>
<td>47.9-53.7</td>
<td>(54.8)</td>
<td>[37]</td>
</tr>
<tr>
<td>GUR1020</td>
<td>CNF</td>
<td>5-10</td>
<td>Stirred in paraffin + Brabender + washing in hexane</td>
<td>136.8-137.7 (137.2)</td>
<td>115.3-115.9 (114.6)</td>
<td>-</td>
<td>44-47.4 (51.0)</td>
<td>[11]</td>
<td></td>
</tr>
</tbody>
</table>

The wear rate of carbon nanofiller reinforced UHMWPE is typically decreased while the coefficient of friction (Cof) is increased as shown in table 3. The increase in friction coefficient could be explained by the increased shear strength due to nanofillers.
Table 3: Tribological properties of carbon nanofiller reinforced UHMWPE

<table>
<thead>
<tr>
<th>Resin</th>
<th>Reinforcement</th>
<th>Concentration (wt%)</th>
<th>Processing</th>
<th>Cof</th>
<th>Wear rate decrease (%)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>80% GUR 1020/HDPE</td>
<td>MWCNTs</td>
<td>0.2-2</td>
<td>Haake laboratory kneader at 210 °C</td>
<td>~0.12</td>
<td>(±0.12)</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>MWCNTs</td>
<td>1</td>
<td>Haake rheomixer at 270 °C</td>
<td>0.12-0.5 (0.6-0.9)</td>
<td>53-83</td>
<td>[101]</td>
</tr>
<tr>
<td></td>
<td>MWCNTs</td>
<td>0.1-0.5</td>
<td>Ultrasonication in toluene</td>
<td>~0.07-0.12 (0.05)</td>
<td>~86 (mass loss)</td>
<td>[24]</td>
</tr>
<tr>
<td>GUR 4120</td>
<td>MWCNTs</td>
<td>0.1-4</td>
<td>Planetary ball milling</td>
<td>0.28 (0.24)</td>
<td>-</td>
<td>[7]</td>
</tr>
<tr>
<td>GUR 1020</td>
<td>MWCNTs</td>
<td>0.2</td>
<td>Ball milling</td>
<td>-</td>
<td>26</td>
<td>[10]</td>
</tr>
<tr>
<td>60%GUR1020/40% HDPE</td>
<td>CNFs</td>
<td>0.5-3</td>
<td>Haake rheometer</td>
<td>-</td>
<td>56</td>
<td>[115]</td>
</tr>
<tr>
<td>GUR1020</td>
<td>CNFs</td>
<td>0.5-3</td>
<td>Magnetic stirring in paraffin oil + Haake rheometer washing in hexane</td>
<td>0.13-0.135 (0.24)</td>
<td>~58</td>
<td>[20]</td>
</tr>
<tr>
<td>GUR1020</td>
<td>CNFs</td>
<td>5-10</td>
<td>Stirred in paraffin + Brabender + washing in hexane</td>
<td>-</td>
<td>34</td>
<td>[11]</td>
</tr>
</tbody>
</table>

Further processing was done for some of the carbon nanofiller reinforced UHMWPE composites such as irradiation [37] or drawing to increase reinforcement orientation [7]. Irradiation increased degradation temperature by up to 44 °C, while Young’s modulus was increased by up to 37% and yield stress was increased by 16% compared to un-irradiated composites [37]. When the mechanical properties of irradiated and un-irradiated UHMWPE/MWCNTs composites were compared after shelf aging, the losses of mechanical properties were slightly lower compared to irradiated UHMWPE [33]. After drawing of UHMWPE/MWCNT composites, the tensile strength was improved further by about 290% and the coefficient of friction reduced from about 0.28 for the composite to 0.14 for the drawn composite [7].

One study investigates the effect of NDs on UHMWPE microstructure. The composites were prepared using solvent casting in Xylene, and showed higher crystallinity for porous composites but only slightly higher compared the solid composite [116].
3.4 UHMWPE Reinforced with other particles

This section will cover the various types of nanofillers used as reinforcement in UHMWPE for medical applications. The composites are reviewed in terms of thermal, mechanical and tribological properties, for an overview see table 4. n-HA reduces the friction coefficient as well as the wear rate of UHMWPE [113], [114]. Irradiation of UHMWPE/n-HA composites further reduced the wear rate by 4.9 times compared to UHMWPE [114]. However, tensile strength, elongation and Young’s modulus were decreased by irradiation of UHMWPE/n-HA composites [113]. The mechanical properties are also generally increased, except for a decrease in tensile strength for n-HA reinforced UHMWPE manufactured by planetary ball milling [117]. Crystallinities increased for TiO₂ [2], Al₂O₃ [3], and n-HA [113] prepared with ball milling but decreased for n-HA manufactured by planetary ball milling [117] and graphite nano-platelets manufactured by ultrasonication [90]. Increased hardness, wettability and decreased friction coefficients in serum and saline of UHMWPE reinforced with ZrO₂ has also been reported [110]. The extensive study of thermal properties for carbon nanofiller/UHMWPE composites is lacking for UHMWPE reinforced with other types of nanofillers.

Micro-sized reinforcements in an UHMWPE matrix intended for medical applications include HA [12], [97], [98] Bovine-HA [40], [41], natural coral [39], Zirconium [106], ZrO₂ [32], Pt-Zr quasicrystals [118], Al-Cu-Fe quasicrystals [109], Ti [92], and quartz [104].
Table 4: UHMWPE based composites. Values within brackets are for UHMWPE.

<table>
<thead>
<tr>
<th>Resin</th>
<th>Reinforcement (size)</th>
<th>Concentration (wt. %)</th>
<th>Processing</th>
<th>Xc (%), DSC</th>
<th>Tensile strength increase (%)</th>
<th>Yield strength increase (%)</th>
<th>Young’s modulus increase (%)</th>
<th>Elongation increase (%)</th>
<th>Wear rate decrease (%)</th>
<th>Cof</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>GUR 1020</td>
<td>Graphite nanoplatelets (10nm)</td>
<td>0.5</td>
<td>Ultras-sonication in toluene + micro-extrusion</td>
<td>43 (50) (WAXS)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>23</td>
<td>0.83 (0.83)</td>
<td>[90]</td>
</tr>
<tr>
<td>Supplies by Shanghai institute of chemistry</td>
<td>TiO$_2$ (5nm)</td>
<td>1-10</td>
<td>Ball milling</td>
<td>~70 (~48)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>50</td>
<td>-</td>
<td>[2]</td>
<td></td>
</tr>
<tr>
<td>Supplies by Shanghai institute of chemistry</td>
<td>Al$_2$O$_3$ (&lt;80nm)</td>
<td>1-10</td>
<td>Ball milling</td>
<td>48.5-54 (49)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[3]</td>
<td></td>
</tr>
<tr>
<td>Polinit-2</td>
<td>Al$_2$O$_3$ (50nm)</td>
<td>3</td>
<td>Planetary ball milling</td>
<td>-</td>
<td>25</td>
<td>20</td>
<td>58</td>
<td>33</td>
<td>-</td>
<td>-</td>
<td>[34]</td>
</tr>
<tr>
<td>SSL-5020</td>
<td>n-HA (100nm)</td>
<td>1-7</td>
<td>Ball milling</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>23</td>
<td>0.75-0.84 (0.86)</td>
<td>[114]</td>
<td></td>
</tr>
<tr>
<td>SSL-5020</td>
<td>n-HA (100nm)</td>
<td>1-7</td>
<td>Ball milling</td>
<td>56.9-61.8 (55.6)</td>
<td>~42</td>
<td>-</td>
<td>5-18</td>
<td>-</td>
<td>0.092-0.12 (0.152)</td>
<td>[113]</td>
<td></td>
</tr>
<tr>
<td>GUR 2122</td>
<td>n-HA (20-30nm)</td>
<td>0.1-2</td>
<td>Planetary ball milling</td>
<td>45 (58.4)</td>
<td>~3-12</td>
<td>-</td>
<td>-</td>
<td>13-20</td>
<td>67</td>
<td>-</td>
<td>[117]</td>
</tr>
</tbody>
</table>


Chapter 4

Objectives of the presented thesis

Many studies today are using ball milling as a mixing technique to manufacture nanocomposites which require solid state mixing. However, little is known about the parameters of different types of ball mills and their effects on final product.

The objective of this work are to optimize the rotational speed, mixing time and mixing conditions (wet or dry) for nanocomposite manufacturing.

During research planning, extra attention was paid to the following goals:

- To determine the optimum rotational speed when a Retsch PM4 planetary ball mill was used in manufacturing
- To determine the effect of rotational speed on MWCNT dispersion on UHMWPE powder particles
- To determine the effect of rotational speed on UHMWPE powder morphology
- To determine whether wet milling or dry milling more effectively distribute nanofillers.

Naturally, other factors such as movement of the vials, jar loading, ball size and jar-, and ball material are also important. However, these parameters are not investigated in this work. Ultimately, the objective of this work is to improve the tribological properties of UHMWPE used for total joint replacements.
Objectives of the presented thesis
Chapter 5

Materials and Experimental procedures

5.1 Materials

5.1.1 Ultra High Molecular Weight Polyethylene

The UHMWPE resin used in this work is GUR 1020 from Ticona GmbH (Germany), with average molecular weight $3.5 \times 10^6$ g/mol and average particle size 140 µm. GUR 1020 together with GUR 1050 from Ticona are the most commonly used resins for orthopaedic materials. A powder particle and the fibril structure of GUR 1020 are shown in figure 3. Some typical GUR 1020 properties are given in table 5.

![Figure 3: a) UHMWPE powder particle and b) UHMWPE powder fibril structure](image)

<table>
<thead>
<tr>
<th>Physical properties of GUR 1020 [26]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>GUR 1020</strong></td>
</tr>
<tr>
<td>Density (kg/m$^3$)</td>
</tr>
<tr>
<td>Yield strength (MPa)</td>
</tr>
<tr>
<td>Ultimate tensile strength (MPa)</td>
</tr>
<tr>
<td>Elongation to failure (%)</td>
</tr>
</tbody>
</table>

5.1.2 Multi Walled Carbon Nanotubes

The multi walled carbon nanotubes (MWCNT) were purchased from Nanocyl, Belgium, (research grade) with a purity of >95% and an average particle diameter of 5-10 nm with an average length of 1.5 µm. Figure 4 a) shows the SEM image of MWCNTs at purchase.
5.1.3 Nanodiamonds

The nanodiamonds (ND, cubic diamond phase) were purchased from International Technology Center (ITC, Raleigh, NC, USA). ND’s have an average primary particle size of 4 nm and a cluster size of about 200 nm in water suspension (according to ITC). Their purity is >98%, figure 4b) shows a SEM image of ND particles at purchase.

![SEM image of ND particles](image)

Figure 4: Nanofillers at 65000X magnification a) MWCNTs, and b) NDs

5.2 Manufacturing of nanocomposite

The processing of the composites was carried out in four general steps; 1) ultrasonication of nanofillers in ethanol, 2) ball milling of ultrasonicated nanofillers together with UHMWPE, 3) removal of excess ethanol, and finally 4) compression molding of composite and UHMWPE. Each step is described below in figure 5.

![Schematic of processing steps](image)

Figure 5: Schematic of processing steps
5.2.1 Ultrasonication

The nanofillers were first ultrasonicated in ethanol in a water bath for 10 minutes before ball milling. The reason was not to break down the nanoparticle clusters but primarily to distribute the nanoparticles in the ethanol before introducing the UHMWPE.

5.2.2 Ball Milling

In this work a planetary ball mill was used. Preliminary studies were done on a ball mill from Ceramic Instruments (Sassuolo, Italy) with a rotational speed of 400 rpm. UHMWPE was ball milled for 8 hours and a sample was taken after 4 and 8 hours. Figure 6 shows the detrimental effect of ball milling for 4 and 8 hours at 400 rpm. This shows that not only was the powder deformed, but also the polymer fibrils were ruptured.

Figure 6: SEM images of a) UHMWPE, b) UHMWPE after 4 hours of ball milling, and c) UHMWPE after 8 hours of ball milling

For experimental work in paper I, paper II and paper III, a planetary ball mill PM4 (Retsch) was used, Figure 7 shows a schematic image of a planetary ball mill. The ethanol/nanofiller mixture was poured into the ball mill jar together with UHMWPE and balls. A Si₃N₄ jar and balls were used. The volume of the jar was 500 ml and the sizes of the balls were 10 and 16 mm.

One experiment was dedicated to measuring the temperature in the ball mill. The temperature was measured after 1, 2, 3 and 4 hours of both dry- and wet mixing, table 6.

Figure 7: Schematic of a planetary ball mill and milling balls
### Table 6: Temperatures inside the ball mill jar

<table>
<thead>
<tr>
<th>Time (hours)</th>
<th>Wet mixing (°C)</th>
<th>Dry mixing (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>31</td>
<td>46</td>
</tr>
<tr>
<td>2</td>
<td>34</td>
<td>49</td>
</tr>
<tr>
<td>3</td>
<td>35</td>
<td>50</td>
</tr>
<tr>
<td>4</td>
<td>35</td>
<td>54</td>
</tr>
</tbody>
</table>

#### 5.2.3 Sintering

First the excess solvent was removed in an oven. Sintering of the samples was done with a Fontune hot press. The powder was weighed and placed in the manufactured and preheated mold, after which a modified pressing cycle was developed to suit this particular experiment from that used by A Fonseca et al [8]. The sample was then pressed for 30 minutes. This procedure is illustrated in Figure 8. After pressing the samples were cooled with water for approximately 5 minutes until the temperature in the mold had reached 40 °C.

#### 5.3 Characterization of UHMWPE-Carbonfiller Nanocomposite

There are several methods and routes to choose for bulk characterization of nanocomposites. Two methods have commonly been used. The first, scanning electron microscopy (SEM), reveals a great deal about the material microstructure and filler dispersion. The second, differential scanning calorimetry (DSC), can provide information on the thermal properties of the final product. Crystallinity can easily be measured by DSC but since the thermal conductivity of UHMWPE changes with temperature, the accuracy of such measurements is debatable. Therefore, x-ray diffraction measurements were used for comparison purposes. Variation in contact angle helps to understand differences in nanoparticle distribution as well as changes in microstructure and surface energy.
5.3.1 Scanning Electron Microscopy

In scanning electron microscopy (SEM) images are formed through acquisition of signals produced when an electron beam interacts with a sample. Backscattered electrons (BSE) and secondary electrons (SE) are used for image analysis. These interactions can be either elastic or inelastic. Negligible energy loss is characteristic for elastic scattering as the incident electron is deflected by an atomic nucleus or outer shell electrons with similar energy. Electrons elastically scattered with an angle larger than 90° are referred to as backscattered electrons and are useful for imaging of the sample. On the contrary, inelastic scattered electrons undergo a significant loss of energy. This energy loss depends on how the electrons are excited (singly or collectively) and the binding energy. The excitation of the specimen results in secondary electrons. SE are mainly used for topography contrasts (surface texture and roughness). This image depends on how many SE reach the detector. SE that cannot reach the detector will manifest as shadows or dark contrast compared to the regions where SE can easily reach the detector. BSEs provide both topographic and compositional information on the sample. Apart from BSE and SE, other signals are produced including characteristic x-rays, Auger electrons and cathodoluminescence.

The penetration of the electron into the sample before it collides with a sample atom creates a zone of primary excitation or interaction volume, where different signals are produced. The electron beam energy and the atomic number of the sample determine the shape and size of this zone. A high electron beam energy and lower atomic number (low density) increase the depth of penetration and on the contrary, low electron beam energy and high atomic number decrease the penetration depth. This is why a high accelerating voltage causes loss in surface sensitivity of the sample, since the depth of penetration and primary excitation zone will be large.

In this work, an extreme high-resolution SEM (XHR-SEM, Magellan 400) has been used. The ultrahigh vacuum and through-lens detector (TLD) makes it possible to use beam voltages of only 1 kV which decreases the interaction volume, as described above. This makes the Magellan 400 extremely surface sensitive. Figure 9 shows the difference between coated and uncoated samples with two images taken of UHMWPE/ND composite powder. Figure 9a is uncoated and b) has been coated with a thin layer (3nm) of tungsten. It is clear that even this thin coating changes the quality of the SEM image. The coated sample appears smoother than the uncoated sample. The arrows point to NDs and the flatter areas in the images are UHMWPE. As can be seen, much of the UHMWPE powder surface is covered by NDs. The images presented in paper I are from uncoated samples the SEM images presented in paper II from coated samples.
5.3.2 Differential Scanning Calorimetry

In differential scanning calorimetry (DSC), changes in heat flow between the specimen and the reference are measured as a function of time and/or temperature as the sample is subjected to a controlled temperature program. Melting temperatures, crystallisation temperatures and Crystallinity were measured by Differential scanning calorimetry (DSC, Mettler Toledo DSC821e). When calculating the crystallinity (equation 1) it is assumed that no melting or crystallization occurs during heating. The crystallinity measured by DSC will not represent the crystallinity close to ambient temperature or working temperature of the composite, but instead represents the crystallinity rather close to melting temperature.

\[ X_c = \frac{\Delta H_c}{\Delta H_c^0} \times 100\% \]  

\( \Delta H_c^0 \) is the enthalpy of fusion of 100% crystalline UHMWPE and set to 289 J/g and \( \Delta H_c \) is the enthalpy of the composite. Both powder and sintered samples were investigated by DSC. Each sample was run for two heating cycles. The samples were first scanned from 30 °C to 200 °C with a heating rate of 10°C/min. After the first heating cycle, the samples were held isothermally at 200°C for 5 minutes to remove any thermal history. The samples were cooled at a rate of 10 °C/min to 30 °C before the second heating cycle was started. The measurements were run in a nitrogen atmosphere (80 ml/min). All samples were tested three times.

5.3.3 X-ray Diffraction

The degree of crystallinity of semi-crystalline polymers is dependent on temperature. Therefore, a PANalytical Empyrean X-ray Diffractometer was used to study the crystallinity of sintered UHMWPE and composites. From the XRD spectra, the crystallinities were calculated by integrating the peaks corresponding to the two crystalline planes (110), (200), and the peak corresponding to the amorphous phase. The crystallinity is then calculated using equation 2:
\[ X_c = \frac{A_{110} + A_{200}}{A_{110} + A_{200} + A_a} \times 100\% \] (2)

Where \( A_{110} \) is the area of the peak corresponding to (110), \( A_{200} \) is the area corresponding to (200) and \( A_a \) is the area of the amorphous peak.

### 5.3.4 Contact Angle Measurements

Contact angle was measured by STFi sessile drop method. A 4 μl drop was deposited on the sample surface and the contact angle was measured after 1 second. 5-10 drops were measured for each sample. Figure 10 illustrates how the contact angles are measured.

![Figure 10: Contact angle measurements](image)

### 5.3.5 Particle Size Distribution

Particle size distribution (PSD) was performed using a CILAS 1064 particle size analyzer where the composite powder was dispersed in ethanol and the particle size measured by laser diffraction. Each measurement was repeated three times. An example of the data obtained for UHMWPE and UHMWPE/MWCNT processed by planetary ball milling at 270 rpm for 2 hours is shown in figure 11. The particle size of UHMWPE ranges from 85 – 235 μm with an average particle size of about 147 μm. For the composite the values range from 71-281 μm with average size 167 μm.

![Figure 11: Particle size distribution of a) UHMWPE and b) UHMWPE/MWCNT composite processed by Planetary ball milling for 2 hours at 270 rpm.](image)
Chapter 6

Summary of papers

Paper I
During the ball milling process and manufacturing of the nanocomposites, the effect of rotational speed and mixing time affect the bulk properties of the final composite significantly and they are strongly correlated. Also other parameters such as ball to powder mass ratio and movement of the jars are important factors. These factors have been identified and studied carefully and the most important factor was found to be the mixing time when other parameters are decided. In this paper, both mixing time and rotational speed were studied. Six MWCNTs reinforced UHMWPE composites were studied, all were prepared with varying mixing parameters. Two speeds were chosen 135 rpm (Low Speed, LS) and 270 rpm (High Speed, HS). Mixing times were 45 min and 2 hours. All samples were analyzed using SEM, DSC, PSD and contact angle measurements. SEM image analysis revealed more efficient MWCNT cluster break down of the HS samples compared to LS samples, but HS samples also showed greater flattening of the UHMWPE powder particles than LS. Melting temperatures were not affected by the ball milling but crystallinity revealed that the mixing technique had some thermal effect on the samples. HS samples showed a decrease in crystallinity in a first heating cycle, however, in a second heating cycle, no differences were observed. PSD also confirmed the effect of rotation speed on powder morphology, particle size was increased for HS samples compared to UHMWPE. Contact angles were measured for LS samples mixed for 2 hours. 0.5 and 1 wt% were studied and the water contact angle was found to increase by increasing the quantity of MWCNTs. It was concluded that 270 rpm more effectively distributed the MWCNTs in the UHMWPE matrix. Figure 12 shows the dispersion of MWCNTs on the UHMWPE powder surface of a) LS sample and b) HS sample.

Figure 12: UHMWPE/MWCNT composites at 5000X magnification. a) LS and b) HS
Summary of papers

CHAPTER 6

Paper II
Since ethanol decreases the viscosity of the sample, it was assumed that wet ball mixing would be favorable to dry ball mixing. It was also assumed that the ethanol would improve the acid functionalized nanofiller dispersion. This paper continues the previous work of planetary ball milling parameters. 270 rpm was chosen as rotational speed since this was shown in the previous study as the optimal rotational speed. MWCNT clusters were more effectively broken down compared to the lower speed. In this paper dry and wet mixing of UHMWPE/ND nanocomposites were investigated. SEM, DSC, XRD and contact angle measurements were used to study the bulk characteristics of the manufactured composites to determine the most efficient and optimal manufacturing condition. It could be shown that wet mixing more effectively distributed the NDs on the UHMWPE powder surface. By looking at the pressed composites this became evident as shown in figure 13. Large ND agglomerates appeared in the bulk for the dry mixed samples.

![Figure 13: digital photos of a) 1hWM and 1hDM, b) 2hWM and 2hDM, c) 3hWM and 3hDM and d) 4hWM and 4hDM](image)

SEM images also revealed a greater flattening and welding of powder from dry mixed samples indicating increased temperatures during dry mixing. This was also confirmed by measuring the temperature in the jar during mixing. Decreased powder crystallinity also indicated a thermal effect from ball milling of the powder. Water contact angles were shown to increase after 4 hours of mixing for both dry and wet mixed samples. Overall, it was concluded that wet mixing is the preferable option for nanofillers in an UHMWPE matrix.
Paper III

Tensile testing and Fatigue crack propagation resistance of the composites prepared in paper I were studied. The tensile tests were performed using an Instron 3366 and showed a slightly increased ultimate tensile strength of composites prepared at 270 rpm for 2 hours. A decrease in UTS was observed for samples prepared with 135 rpm. The Young’s modulus was also slightly increased for the composites compared to UHMWPE. No significant differences between composites with 1 wt% MWCNTs and 0.5 wt% MWCNTs were observed and the fatigue crack propagation resistance was unaffected by MWCNT incorporation for all mixing conditions.

![Figure 14](image-url) Results of ultimate (a.) and yield (b.) strength, and Young’s modulus measurements (c.). Upper and lower measurements in c. represent measurements according to ASTM and ISO standard respectively.
Chapter 7

Suggestions for Future Work

The results presented in this thesis indicate that MWCNTs and NDs are promising as reinforcement in a UHMWPE matrix.

The future work will focus mainly on two topics. First, the study of parameters which affect manufacturing of the UHMWPE nanocomposites for orthopaedic application will be completed. Secondly, the mechanical properties of the two composites will be investigated further. Future work includes:

- Optimization of wt% of MWCNTs and ND particles
- Tribological study of UHMWPE/MWCNTs and UHMWPE/NDs composites compared to virgin UHMWPE and highly crosslinked UHMWPE
- Mechanical testing of UHMWPE/NDs composite
- Biocompatibility of the wear particles of UHMWPE/NDs
- Fatigue and oxidation of the nanocomposites in comparison to commercially available virgin UHMWPE and highly crosslinked UHMWPE
References


References


Part II

Appended papers
**Paper I**

The effect of ball milling time and rotational speed on ultra high molecular weight polyethylene reinforced with multi walled carbon nanotubes.

Evelina Enqvist, Paula A. A. P. Marques, José Grácio and Nazanin Emami
The effect of ball milling time and rotational speed on ultra high molecular weight polyethylene reinforced with multi walled carbon nanotubes.

Evelina Enqvist, Paula A. A. P. Marques, José Grácio and Nazanin Emam

Abstract

Ultra high molecular weight polyethylene (UHMWPE) composites reinforced with multi walled carbon nanotubes (MWCNT) were produced using planetary ball milling. The aim was to develop a more wear resistant composite with improved mechanical properties to be used in stress bearing joints. The manufacturing technique, using ball milling to incorporate MWCNT into the UHMWPE matrix was investigated. The effect of manufacturing parameters such as the effect of ball milling time and rotational speed on the final composite were analyzed by scanning electron microscopy (SEM), differential scanning calorimetry (DSC), particle size distribution and contact angle measurements. Ball milling as a mixing technique for UHMWPE based composites is not a new approach but yet, the effect of time, rotational speed, loading of milling jar and type of ball mill has not been reported properly for UHMWPE. Material with 0.5 and 1 wt% UHMWPE/MWCNTs were manufactured with different rotational speeds and mixing times. The results indicate that rotational speed rather than mixing time is important for dispersing MWCNTs using planetary ball milling.

Keywords: UHMWPE, MWCNT Hip implant, ball milling, thermal characterization
1. Introduction

Total joint arthroplasty (TJA) is considered as the 20th century's greatest surgical successes, starting in 1958 when Sir John Charnley introduced PTFE in total hip replacements (THR). Despite the low coefficient of friction of PTFE, the wear rate lead to failure of the implants and PTFE was soon abandoned and replaced by ultra high molecular weight polyethylene (UHMWPE) [1], [2]. Since its introduction in total joint arthroplasty in 1962 by Charnley, UHMWPE has been used as the acetabular cup with metal or ceramic femoral heads. The joint replacement has a limited lifetime due to wear particles generated at the UHMWPE-metal interface. The osteolysis induced loosening is one of the most common reasons for implant failure. Improving the mechanical and tribological properties of UHMWPE could increase the lifetime of implants for younger patients with higher demands on longevity and sustainability. Other solutions using metal alloys [3] or ceramics instead of UHMWPE are constantly being investigated, but in these systems other problems are introduced such as implant failure, pseudo tumors, metal toxicity or squeaking [4], [5].

Multi walled carbon nanotubes (MWCNTs) have been investigated as reinforcement in an UHMWPE matrix in order to improve mechanical and tribological properties. The high mechanical properties and high aspect ratio of MWCNTs has caught the attention of many researchers working to develop a more wear resistant and tougher UHMWPE based composite. Different manufacturing methods have been employed in order to mix the nanoparticles with the polymeric matrix. One simple technique is ultrasonic mixing, where the constituents are mixed either in an ultrasonic bath [6] or with a sonotrode [7], [8]. The ultrasonic waves introduce high energies and care must be taken to avoid damaging of the materials. Melt mixing is a good way to mix polymer based composites as it increases the polymer chain mobility and eases the incorporation of fillers in between the polymer chains. UHMWPE can be melt mixed either by mixing with high density polyethylene (HDPE) [9], [10] or by using a solvent such as paraffin oil [11–13] or Decalin (decahydronaphthalene) [14], [15], however, these solvents are difficult to remove.

Ball milling is a common method used to reduce the size of minerals and ceramics and has recently been adopted as a mixing technique for UHMWPE based composites. It is a rather simple technique existing in different forms such as a jar rotating around its axis but it can also be attached to a rotating wheel as in a planetary ball mill. Some of the important parameters that affect the final product when employing ball milling is the type of ball mill, rotational speed, mixing time, loading of the ball mill jar, mixing media and if wet or dry mixing is employed. Composites prepared with ball milling based on low density polyethylene (LDPE) [16–19] and medium density polyethylene [20] have previously been reported. Mechanical and tribological properties of ball milled UHMWPE/CNT composites have also been reported [21–24] but the parameters used in these investigations are poorly reported and a thorough investigation of the parameters affecting the final ball milled composite is lacking. This paper investigates the effect of time and rotational speed on UHMWPE/MWCNT nanocomposites prepared with planetary ball milling. Different rotational speeds and times were investigated. It was assumed that a higher rotational speed would decrease the time needed for efficiently distributing the MWCNTs. The resulting composite was investigated by scanning electron microscopy (SEM), differential scanning calorimetry (DSC), particle size distribution and contact angle measurements.
2. Materials and methods

2.1. Nanocomposite manufacturing:

UHMWPE, GUR 1020 was supplied by Ticona GmbH (Germany), with an average molecular weight of $3.5 \times 10^6$ g/mol and an average particle size of 140 $\mu$m (Figure 1a). It has a density of 0.93 g/cm$^3$. The multi walled carbon nanotubes (MWCNT) were purchased from Nanocyl (Nanocyl-3101, Belgium) with a purity of $>95\%$, an average particle diameter of 5-10 nm and an average length of 1.5 $\mu$m (Figure 1b). Prepared with catalytic carbon vapor deposition (CCVD), these MWCNTs were functionalized with carboxylic group groups ($\leq 4\%$) by the manufacturer.

![Figure 1: a) UHMWPE powder particle and b) MWCNTs](image)

To investigate the effect of mixing time and rotational speed, 7 samples were prepared according to Table 1, describing the composition and codes. Low speed (LS) was set to 135 rpm and high speed (HS) was set to 270 rpm. The concentration was fixed to 0.5 wt% MWCNTs. Previously 4 and 8 hours of ball milling were tested by authors and all those samples were damaged, therefore in this study 2 hours is chosen as the maximum time for ball-milling.
<table>
<thead>
<tr>
<th>Composite/code</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>UHMWPE</td>
<td>100% GUR 1020</td>
</tr>
<tr>
<td>PE005CNT_LS_45min</td>
<td>UHMWPE + 0.5 wt% MWCNT</td>
</tr>
<tr>
<td>PE005CNT_LS_1h</td>
<td></td>
</tr>
<tr>
<td>PE005CNT_LS_2h</td>
<td></td>
</tr>
<tr>
<td>PE005CNT_HS_45min</td>
<td></td>
</tr>
<tr>
<td>PE005CNT_HS_1h</td>
<td></td>
</tr>
<tr>
<td>PE005CNT_HS_2h</td>
<td></td>
</tr>
</tbody>
</table>

All composites were manufactured in the same way; first the nanofillers were dispersed in ethanol using an ultrasonic bath for 10 minutes. Dispersed MWCNTs were poured in a planetary ball-mill (Retsch, PM4, Germany) and mixed in ethanol with UHMWPE for 45 min, 1 hour, and 2 hours with a rotational speed of 135 or 270 rpm using a jar volume of 500 mL in Si$_3$N$_4$ and balls in the same material with varying diameter from 10 mm to 16 mm. The volume ratio between the free volume in the jar and the balls was 3:1 and mass ratio between composite and balls were 22:1. According to Retsch specifications, the 500 mL jar should be filled with slurry from 75 mL to 220 mL [25], the volume of UHMWPE, MWCNT and ethanol in this study was approximately 75 mL. Figure 2 illustrates a schematic of a planetary ball mill and the shape and sizes of the balls used. After ball-milling the samples were dried in an oven for 2 days at 60 °C.

![Figure 2: Schematic image of a planetary ball mill and the size and shape of balls.](image)

### 2.2 Scanning electron microscopy

Scanning electron microscopy (SEM, FEI Magellan 400) was used to analyze the surfaces of the ball-milled powders. The dispersion of MWCNTs was also studied with SEM. The Magellan 400 is an extreme high resolution SEM (XHR-SEM) that enables scanning of the sample surface without any coating, giving a more surface sensitive image of the studied specimen. A beam voltage of 1 kV and a beam current of 3.1 to 6.3 mA were used depending on the magnification and detector (Through lens detector (TLD) or Everhart-Thornley detector (ETD)) used.
2.3 Differential scanning calorimetry

Differential scanning calorimetry (DSC, Mettler Toledo DSC821e) was used to investigate the crystallinity, melting temperatures and crystallization temperatures. Specimens of 6-9 mg of either virgin UHMWPE or nanocomposites (based on table 1) were prepared in a sealed standard 40 µL aluminum crucible. Each sample was tested for five times. The samples were heated from 30 °C to 200°C at a heating rate of 10 °C/min, they were then cooled to 30 °C with a heating rate of 20 °C and operating under nitrogen atmosphere. A second heating step was performed and the crystallinity of the two steps was compared. The crystallinity was calculated according to the following formula:

\[
X_c = \frac{\Delta H_c}{\Delta H_{c0}} \times 100\%
\]

where \(\Delta H_{c0}\) is the enthalpy of fusion of 100% crystalline UHMWPE and set to 289 J/g [26] and \(\Delta H_c\) is the enthalpy of the composite, calculated from the peak area in the DSC measurements. The integration range was 50 °C to 160 °C.

2.4 Particle size distribution

Particle size distribution was analyzed with a CILAS 1064 particle size analyzer where the composite was dispersed in ethanol and the particle size measured by laser diffraction. Any changes in size due to ball milling were investigated.

2.5 Contact angle

Wettability was investigated with a STFi contact angle machine. A 4 µL water drop was deposited on the surface and the droplet angle was measured with a microscope. The angles were measured after one second. All samples were washed with ethanol, rinsed in distilled water and dried prior to testing. For this test three different compositions were investigated, pure UHMWPE, 0.5 wt% MWCNT and 1 wt% MWCNTs, both composites were ball milled for 1 hour with a rotational speed of 135 rpm (LS) and pressed in a hot press. Each sample was tested five times.

3. Results

3.1 Scanning electron microscopy

Figure 3 shows overview images of ball milled composites as described in table 1, the composites ball milled with the higher speed are more flattened than those prepared with the lower speed, this difference can be observed after only 45 minutes of mixing while the samples prepared with the lower speed seem to be less affected by the mixing time. After two hours, a small flattening of the surface was observed.
Clusters of MWCNTs were observed for all samples, but it appeared that they were broken down for higher mixing speeds and better dispersed on the UHMWPE particle surface. Figure 4a) shows large MWCNT clusters on PE005CNT LS_2h. Inside the clusters, the MWCNTs are dispersed into the matrix. Figure 4b) shows the dispersion of MWCNTs on the PE005CNT HS_2h powder, the cluster size has been reduced and MWCNTs are better dispersed on the powder as shown by a whiter surface compared to the LS sample. This is due to the difference in conductivity between UHMWPE and MWCNTs, where the MWCNTs appear whiter. In Figure 5 a magnification of the cluster and MWCNT dispersion from Figure 4 is shown. Figure 5 shows PE005CNT HS_2h, here the size of the clusters have clearly been reduced.
compared to figure 4. The MWCNTs seem to have dispersed better on the polymer powder.

**Figure 4**: SEM images of MWCNT dispersion on powder surfaces of a) PE005CNT_LS_2h and b) PE005CNT_HS_2h. 50000X magnification

**Figure 5**: PE005CNT_HS_2h a) Cluster, 50000X magnification and b) 100000X magnification of an area around the clusters.

**Figure 6a** represent the typical fibrils of UHMWPE GUR 1020 resin. Composites prepared with low speed still show some of the fibril characteristics, as shown in **figure 6b**), a MWCNT cluster can also be observed in this image and how single MWCNTs reside on the fibrils. These fibrils are not observed for the composites prepared with high speed, **figure 6c**.).
3.2 Differential scanning calorimetry

The crystallinity of the ball milled samples have increased for the LS samples and decreased for the HS samples compared to UHMWPE. Melting temperatures didn’t change for LS or HS ball milled composites. No significant difference in crystallinity was observed for the second heating cycle, table 2.

Table 2: Melting temperatures and crystallinity of nanocomposites prepared with different rotational speeds and milling times. The values are the average of five runs and ± is the standard deviation.

<table>
<thead>
<tr>
<th>Material</th>
<th>First heating cycle</th>
<th>Second heating cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_m$ (°C)</td>
<td>$X_c$ (%)</td>
</tr>
<tr>
<td>UHMWPE</td>
<td>142.3±0.5</td>
<td>63.6±3.7</td>
</tr>
<tr>
<td>PE005CNT_LS_45min</td>
<td>142.7±0.2</td>
<td>63.0±2.8</td>
</tr>
<tr>
<td>PE005CNT_LS_1h</td>
<td>142.7±0.3</td>
<td>65.4±2.4</td>
</tr>
<tr>
<td>PE005CNT_LS_2h</td>
<td>142.6±0.3</td>
<td>65.4±1.8</td>
</tr>
<tr>
<td>PE005CNT_HS_45min</td>
<td>142.8±0.5</td>
<td>61.4±3.3</td>
</tr>
<tr>
<td>PE005CNT_HS_1h</td>
<td>142.9±0.9</td>
<td>61.0±4.7</td>
</tr>
<tr>
<td>PE005CNT_HS_2h</td>
<td>142.4±0.0</td>
<td>61.4±2.3</td>
</tr>
</tbody>
</table>
Table 3 shows the cooling cycles for the DSC measurements. The crystallization temperatures for high speed samples have decreased slightly and the peak widths have increased by 1 °C, but these values are still within the standard deviation.

Table 3: Cooling behavior of nanocomposites.

<table>
<thead>
<tr>
<th>Material</th>
<th>Cooling cycle</th>
<th>( T_c ) (°C)</th>
<th>Peak width (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UHMWPE</td>
<td></td>
<td>115.6 ± 0.8</td>
<td>11.2 ± 1.1</td>
</tr>
<tr>
<td>PE005CNT_LS_45min</td>
<td></td>
<td>115.3 ± 0.5</td>
<td>11.4 ± 1.0</td>
</tr>
<tr>
<td>PE005CNT_LS_1h</td>
<td></td>
<td>115.4 ± 0.5</td>
<td>11.2 ± 1.1</td>
</tr>
<tr>
<td>PE005CNT_LS_2h</td>
<td></td>
<td>115.6 ± 0.4</td>
<td>11.4 ± 0.5</td>
</tr>
<tr>
<td>PE005CNT_HS_45min</td>
<td></td>
<td>115.0 ± 0.4</td>
<td>11.5 ± 0.5</td>
</tr>
<tr>
<td>PE005CNT_HS_1h</td>
<td></td>
<td>114.5 ± 1.0</td>
<td>12.7 ± 0.8</td>
</tr>
<tr>
<td>PE005CNT_HS_2h</td>
<td></td>
<td>114.7 ± 0.7</td>
<td>12.0 ± 0.5</td>
</tr>
</tbody>
</table>

3.3 Particle size distribution

Table 4 shows the particle size distribution of the samples. The mean diameter has decreased for the LS samples while they have increased for the HS samples.

Table 4: Particle size distributions of composites. All values are average of 3 measurements with standard deviation.

<table>
<thead>
<tr>
<th>Material</th>
<th>Mean diameter (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UHMWPE</td>
<td>153.5 ± 1.1</td>
</tr>
<tr>
<td>PE005CNT_LS_45min</td>
<td>144.6 ± 5.3</td>
</tr>
<tr>
<td>PE005CNT_LS_1h</td>
<td>146.6 ± 1.0</td>
</tr>
<tr>
<td>PE005CNT_LS_2h</td>
<td>146.1 ± 1.7</td>
</tr>
<tr>
<td>PE005CNT_HS_45min</td>
<td>163.5 ± 4.1</td>
</tr>
<tr>
<td>PE005CNT_HS_1h</td>
<td>155.9 ± 2.0</td>
</tr>
<tr>
<td>PE005CNT_HS_2h</td>
<td>172.8 ± 2.3</td>
</tr>
</tbody>
</table>

3.4 Contact angle

Table 5 illustrates the contact angles for composites with 0.5 wt% and 1 wt% of MWCNTs. The contact angle of the composites has increased compared to pure UHMWPE.
Table 5: Contact angles of 0.5 wt% and 1 wt% MWCNT composites. All values are the average of five measurements with standard deviation.

<table>
<thead>
<tr>
<th></th>
<th>UHMWPE</th>
<th>PE005CNT</th>
<th>PE01CNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact angles (°)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>82.6±2.3</td>
<td>85.6±2.8</td>
<td>88.0±3.1</td>
<td></td>
</tr>
</tbody>
</table>

*PE005CNT contains 0.5 wt% MWCNTs and PE01CNT contains 1 wt% MWCNTs. Both composites were prepared by 1 hour LS ball milling.

4. Discussion

It is well known that nanoparticles, due to their high surface energy, are difficult to disperse as fillers in a matrix. In most SEM image analysis, specimens must be coated to avoid electron charge up. This makes it difficult to observe the nanotubes in the composite, even at a very high magnification. Fonseca et al [23] report on well dispersed MWCNTs in an UHMWPE matrix, but it should be noted that the MWCNTs that were used in their study are 60-100 nm in diameter and 5-15 μm in length, which is about 10 times larger than the MWCNTs used in this study. Figure 4 shows the MWCNTs clusters on the UHMWPE particle surface. These clusters, however, are homogeneously distributed on the powder surfaces and inside the bulk; the MWCNTs are dispersed in the polymeric matrix. Figure 3 (b, d and e) and figure 4 together show the effect of time and rotational speed on MWCNTs dispersion, where the white patches (due to the conductivity differences between the polymeric matrix and the MWCNTs reinforcement), indicate where the MWCNTs reside. Longer mixing time seems to result in better dispersion of MWCNTs in the polymeric matrix and also better reduction of cluster size. This is probably due to the larger impact force between balls and powder at higher rotational speed. Subjecting a polymeric material to ball milling increases the risk of chain scission. The powder must therefore be carefully studied to ensure that the polymer has not been degraded. In this work, the HS samples were flattened and the fibrils disappeared. However, no debris was observed on the powders which would be a strong indication of chain scission. This debris on ball milled powder was observed in a pre-study made by the authors. Plastic deformation of the powder does not necessarily harm the thermal properties, as was also indicated by DSC results where the melting temperature had not decreased for the HS samples.

Crystallinity has an influence on the mechanical properties of semicrystalline polymers and is therefore a major concern when it comes to preparation of polymer based composites. The effect of ball-milling speed and time was analyzed by dynamic DSC thermal analysis. The result indicated a decrease in crystallinity for ball milled samples produced using high speed compared to low speed and untreated UHMWPE, as illustrated in table 2. After consolidation of UHMWPE, the melting temperature and crystallinity are decreased, this is illustrated by the second heating cycle. Only the sample ball milled for 1 hour at low speed, showed an increase in crystallinity, however this is within the statistical error. The decreased crystallinities of HS samples compared to LS seems to have been restored in the second heating cycle, this could indicate that any damage or disturbance of the crystal limit for these samples is regained upon heating. This also indicates that the flattening of powder due to high speed mixing does not damage the particles. Regarding the ball milling rotational speed, results from different investigations are contradictory. A decrease in crystallinity was observed by...
Martínez-Morlanes et al [22] and Bakshi et al [29]. Some investigations have, on the contrary, shown an increase in crystallinity due to CNT addition, which can be attributed to the CNTs acting as nucleation sites for polymer crystallization [24], [30]. On the other hand, Zoo et al did not observe any change in crystallinity with CNT addition [6]. DSC measurements on consolidated nanocomposites could more clearly describe the effect of ball milling time and speed on crystallinity, as consolidation is the final stage of form shaping the nanocomposite.

The cooling cycles indicated slightly lower crystallization temperature for the samples ball milled at 1 or 2 hours and HS, this is shown in table 3. This indicates that the ball milling procedure affects the crystallization temperature. This could signify that the ball milling speed, in particular, hinders the nucleation process of UHMWPE crystallization. Increased crystallization temperature due to CNT reinforcement for UHMWPE prepared through in situ polymerization has been reported [31]. An increase in crystallization temperature was also observed for MDPE with increasing ball milling times of up to 30 hours [32].

It should also be noted that in the present investigation, the peak width has also increased slightly, indicating a somewhat lower crystallization rate for HS samples ball milled for 1 and 2 hours. The first four composites had the same peak width (no significant differences), indicating that the addition of 0.5 wt% MWCNTs does not affect the crystallization rate. On the other hand, the peak width of the composites prepared at HS for 1 and 2 hours are slightly larger, indicating that the effect of speed and time is more important to the crystallization behavior.

The mean particle size was increased with increasing rotational speed and it was at the maximum for 2 hours of ball milling and HS, as shown in table 4. This was probably due to the more effective flattening of the polymer particles which is induced at HS. For the LS samples, the particles seem to be slightly reduced. This could be due to compaction rather than flattening of the polymer particles which could also explain the slightly higher degree of crystallinity for LS samples in the first heating cycle. It is believed that the impact of the balls together with the heat produced as the balls and powder collide in the ball mill plastically deforms (flattens) the ductile polymer particles. This impact and the heat generated is probably higher for higher rotational speeds and results in a more effective flattening process.

The contact angles seem to be low compared to other studies of pressed UHMWPE [33], [34]. But it should also be remembered that the contact angles depend on factors such as type of resin, manufacturing, preparation of samples and surface roughness. The addition of MWCNTs seems to increase the hydrophobicity of UHMWPE. The addition of 0.5 wt% MWCNT slightly increased the hydrophobicity and it seems like the contact angles increase with increasing amount of MWCNT. The highest contact angle was observed for 1 wt% MWCNTs. The hydrophobicity of UHMWPE is an important factor in low wear rate in metal-on-polymer and ceramic-on-polymer implant devices. In another parallel study the wear rate has been tested for UHMWPE with 0.5 or 1 wt% MWCNTs reinforcement system and it was found that wear rate was reduced up to 40% for nanocomposite manufactured with 1 wt% MWCNTs compared to virgin UHMWPE [35].

5. Conclusions

In the current study, ball milling was used to disperse MWCNTs in an UHMWPE matrix. It is hypothesised that ball milling’s rotational speed affects the final nanocomposite more profoundly than the ball milling time. Therefore the optimization
of rotational speed for any given ball milling procedure is highly important in order to enhance the manufacturing procedure for the UHMWPE/MWCNTs nanocomposite. The findings in the current investigation support the hypothesis and the results show that rotational speed and time are critical factors affecting the dispersion of MWCNTs. Optimized rotational speed, in particular, is an important factor to reduce MWCNTs cluster size and better disperse MWCNTs on the UHMWPE particle surfaces. SEM image analysis showed flattening and clustering of nanocomposite powder. Therefore it can be concluded that the rotational speed rather than the time is important for an optimal dispersion of MWCNTs in UHMWPE, in this experimental set-up. Of course, once the rotational speed is optimized, the time should be optimized accordingly.

**Acknowledgements**

This work has been partly funded by the Swedish agency for economics and regional growth through CMTF. The authors would also like to acknowledge Professor Kristiina Oksman and her research group at Luleå University of Technology for valuable help during the experimental work. Gregory Simmons at Luleå University of technology is also acknowledged for valuable comments on this work.

**References**


Paper II

Nanodiamond reinforced ultra high molecular weight polyethylene: A comparison of dry and wet ball milling manufacturing techniques

Evelina Enqvist and Nazanin Emami
Nanodiamond reinforced ultra high molecular weight polyethylene: a comparison of dry and wet ball milling manufacturing

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Evelina.enqvist@ltu.se

Abstract: Nanodiamonds (NDs) were investigated as reinforcement for ultra high molecular weight polyethylene (UHMWPE). Dry and wet mixing with planetary ball milling was compared and analysed by scanning electron microscopy (SEM), differential scanning calorimetry (DSC), X-ray diffraction (XRD) and contact angle measurements. The composites were mixed from one to four hours to study the dispersion of the nanoparticles. It was concluded that wet mixing is more effective at distributing nanodiamonds in comparison to dry mixing. It could also be concluded that dry mixing increases the temperature by 20°C more than wet mixing which resulted in a more distinct welding process of the UHMWPE powder.

Key words: UHMWPE, Nanodiamonds, DSC, SEM, XRD

1. INTRODUCTION
Ultrahigh molecular weight polyethylene (UHMWPE) has been used as a bearing surface in total joint replacements (TJR) for 50 years. It has been a favoured polymer due to its wear resistance and low friction, high impact strength and toughness. Despite these superior properties compared to other polymers, the UHMWPE wear particle produced when sliding against a metal/ceramic counter face induces osteolysis, which is the major cause of failure in TJR. New materials with higher wear resistance are needed to increase the lifetime of these implants so that revision surgeries can be avoided. This is particularly important for younger and more active patients.

Studies on UHMWPE based nanocomposites have increased tremendously during the last decade thanks to sophisticated analysis tools and improved manufacturing methods. Carbon nanoforms are of great interest due to their, often, unique mechanical properties. Carbon nanotubes have large aspect ratio with high elastic modulus and strength. Interest in graphene has increased since its isolation which resulted in the awarding of a Noble prize [1]. However, have not yet gained as much attention as reinforcement...
material as CNT and graphene. They are considered as zero-dimensional particles whereas CNT and graphene are 1-D and 2-D respectively [2]. The unique structure of detonation NDs with a stable diamond core and a tailor able outer graphitic shell makes them intriguing for nanocomposite applications. And where the biocompatibility of CNTs and graphene are debated, NDs are considered to have high potential in the biomedical field [3]. NDs have been investigated as UHMWPE reinforcement in one previous study [4]. NDs have also been investigated as reinforcement of epoxy [5] [6], PVA [7], PLA [8] and PLLA [9].

Planetary ball-milling is a simple and cost effective mixing technique which is widely used in composite manufacturing. Ball milling methods are studied for nanocomposite manufacturing and could be used in dry [10–17] or wet [18–22] mixing. In this work wet manufacturing processing was tested versus dry mixing. It was assumed that the wet mixing would more effectively distribute the ND particles due to the hydrophilic nature of NDs, using a hydrophilic disperser such as ethanol.

2. MATERIALS AND METHODS

2.1. Manufacturing of nanocomposite

UHMWPE, GUR 1020 was supplied by Ticona GmbH (Germany), with an average molecular weight of 3.5x10^6 g/mol, average particle size 140 µm and density of 0.93 g/cm^3. The nanodiamonds (ND, cubic diamond phase) were purchased from International Technology Center (ITC, Raleigh, NC, USA) and were prepared using the explosion detonation technique. NDs have an average primary particle size of 4 nm, an agglomerate size of about 200 nm in water suspension and a purity of >98%. Dry (DM) and wet (WM) ball milling, and different mixing time were investigated. A Retsch PM4 planetary ball mill was used. The speed was set to 270 rpm 1,2,3, and 4 hours of mixing was evaluated for both dry and wet mixing and compared to pure UHMWPE. The jar was cooled for 15 minutes in an ice bath, after each hour. The ball milled powder was dried in an oven at 60°C for two days to evaporate excess ethanol. Two additional experiments were performed during which the temperature in the jar was measured after each hour of wet and dry ball milling using a thermocouple, table 1.

A Fontune hotpress was used to consolidate the nanocomposite powder. The powder was evenly distributed in the mold and pressed. After preheating for 10 minutes, the composites were pressed under a pressure of 10 MPa and 190 °C in five cycles with 90 seconds of pressure and 90 seconds without pressure. The pressure was thereafter held for 30 minutes. This process was based on the procedure described by Fonseca et al [11]. It was then rapidly cooled to 40 °C and removed from the hot press. Eight samples containing 0.5 wt% ND were prepared according to table 1 and compared to UHMWPE.

<table>
<thead>
<tr>
<th>Table 1 Sample composition and codes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composite/code</td>
</tr>
<tr>
<td>UHMWPE</td>
</tr>
<tr>
<td>1hWM</td>
</tr>
<tr>
<td>2hWM</td>
</tr>
<tr>
<td>3hWM</td>
</tr>
<tr>
<td>4hWM</td>
</tr>
<tr>
<td>1hDM</td>
</tr>
<tr>
<td>2hDM</td>
</tr>
<tr>
<td>3hDM</td>
</tr>
<tr>
<td>4hDM</td>
</tr>
</tbody>
</table>

2.2. Scanning electron microscopy

The ball milled nanocomposite powder and the consolidated material were analysed with an extreme high resolution scanning electron microscopy (XHR-SEM, Magellan 400), using a 1 kV beam voltage. SEM is a useful tool for investigation of the dispersion of the nanoparticles and cluster break down as well.
as the interfaces between the polymer and the nanoparticles. The samples were sputter coated with ~3 nm thick tungsten.

2.3. Differential scanning calorimetry

Differential scanning calorimetry (DSC, Mettler Toledo DSC821e) was used to investigate the crystallinity and melting temperature of both powder samples and consolidated samples. Specimens of 6-9 mg of either virgin UHMWPE or nanocomposites were prepared in a sealed standard 40 µL aluminum crucible. During each of the three repeat tests the samples were heated two times from 30°C to 200°C at a heating rate of 10 °C/min and then cooled to 30°C with a cooling rate of 10°C/min, in a nitrogen atmosphere. The samples were held isothermally at 200°C after the first cycle to remove any thermal history. The crystallinity was calculated according to the following equation:

$$X_c = \frac{\Delta H_c}{\Delta H_{c0}} \times 100\%$$  \hspace{1cm} (1)

where $\Delta H_{c0}$ is the enthalpy of fusion of 100% crystalline UHMWPE, set to 289 J/g [23], and $\Delta H_c$ is the enthalpy of the composite, calculated from the peak area in the DSC measurements. The integration range was 50°C to 160°C.

2.4. X-ray diffraction

X-ray diffraction spectroscopy (XRD) was used as a means of verifying measurement of the degree of crystallinity with DSC. It made it possible to determine the degree of crystallinity at room temperature in contrast to DSC measurements where the enthalpy changes are measured during crystallisation. The phases in the samples were identified by XRD using a Cu-Kα radiation source. The degree of crystallinity calculated by XRD measurements was made using equation 2:

$$X_c = \frac{A_{110} + A_{200}}{A_{110} + A_{200} + A_a} \times 100\%$$  \hspace{1cm} (2)

where $A_a$ is the integrated intensity of the amorphous peak and $A_{110}$ and $A_{200}$ are the integrated intensities of the crystalline peaks.

2.5. Contact angle

Contact angle (CA) measurements were used to study any possible changes in wettability of the polymer using a STFi sessile drop method. A 4 μl water drop was deposited on the surface and ten drops were measured for each sample. Each drop was measured for 12 seconds and the values reported after 1 second. All samples were cut from the same part of the consolidated material to avoid any differences in microstructure.

3. RESULTS

The sintered composites were first visually inspected, and large ND clusters were observed for all dry mixed samples as shown in Fig. 1. Only 2 and 4 hours of dry mixing shows smaller ND clusters, although 2 hours tests have a darker color than the other samples. The following photos are evidence that dry mixing is not as efficient as wet mixing in distributing ND particles.

![Figure 1: images of dry and wet mixed samples. Wet mixed (WM) sample are to the left and dry mixed (DM) to the right. a) 1hWM and 1hDM, b) 2hWM and 2hDM, c) 3hWM and 3hDM and d) 4hWM and 4hDM](image)

The temperatures measured in the ball mill are shown in table 2. During the dry mixing the
temperature in the jar was increased significantly more than during wet mixing

<table>
<thead>
<tr>
<th>Time (hours)</th>
<th>Wet mixing (°C)</th>
<th>Dry mixing (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>31</td>
<td>46</td>
</tr>
<tr>
<td>2</td>
<td>34</td>
<td>49</td>
</tr>
<tr>
<td>3</td>
<td>35</td>
<td>50</td>
</tr>
<tr>
<td>4</td>
<td>35</td>
<td>54</td>
</tr>
</tbody>
</table>

3.1. Scanning electron microscopy

Fig. 2 shows overview images of pure UHMWPE, 1 to 4 hour wet mixed samples and 2 hour dry mixed samples. From images 2e and 2f, the welding process due to heat generated from the collisions between balls and between balls and powder in the ball mill jar is evident. Both samples have been flattened and particles are welded together. This means that the welding process starts after 2 hours for dry mixing but does not start until after 4 hours for the wet mixed samples.

Fig. 3 shows UHMWPE at 25000X magnification. Fig 3a shows the typical fibril structure of the GUR 1020 resins and Fig 3b shows the flat areas of the GUR 1020 resin.

The ND clusters are presented in Fig. 4.

Fig. 5 shows the dispersion of NDs in UHMWPE powder. 3hWM and 4hWM samples show less and smaller ND clusters compared to the 2hWM sample. This could be due to either the ND clusters being broken down into smaller clusters or due to embedding of ND clusters in the UHMWPE matrix. 2hWM, Fig. 5a shows the largest clusters, this suggests that the ND clusters break down into smaller clusters with time. The differences in cluster size are better shown in Fig. 6 where 50000X magnification was used.

3.2. Differential scanning calorimetry

Table 3 shows the melting temperatures of the powder samples and the sintered samples. $T_{m1}$ is the melting temperature from the first heating
cycle and $T_{m2}$ is the melting temperature from the second heating cycle. No large differences in melting temperatures could be observed for the composites.

Table 3 Mean melting temperatures of powder samples and sintered samples with standard deviation

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{m1}$ (°C) Powder</th>
<th>$T_{m2}$ (°C) Powder</th>
<th>$T_{m1}$ (°C) Sintered</th>
</tr>
</thead>
<tbody>
<tr>
<td>UHMWPE</td>
<td>141.6±0.4</td>
<td>132.5±0.1</td>
<td>134.7±1.3</td>
</tr>
<tr>
<td>1hWM</td>
<td>141.9±0.2</td>
<td>132.9±0.2</td>
<td>134.7±2.7</td>
</tr>
<tr>
<td>2hWM</td>
<td>142.3±0.5</td>
<td>133.4±0.4</td>
<td>135.5±1.2</td>
</tr>
<tr>
<td>3hWM</td>
<td>142.3±0.6</td>
<td>133.6±0.5</td>
<td>135.7±1.6</td>
</tr>
</tbody>
</table>

Figure 5 ND dispersion in the UHMWPE matrix, a) 1hWM, b) 2hWM, and c) 4hWM

Figure 6 50000X magnifications of a) 2hWM and b) 4hWM
To determine the crystallinity of the samples, DSC and XRD measurements were conducted. Table 4 shows the crystallinities from powder and sintered samples. $X_{c1}$ is the crystallinity from the first heating cycle, $X_{c2}$ is the crystallinity from the second heating cycle and $X_c$ is the crystallinity obtained from XRD measurements. As seen in Fig. 7, the crystallinities of the powders decrease for both wet mixing and dry mixing compared to UHMWPE.

**Table 4 Crystallinities calculated from DSC and XRD**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$X_{c1}$ (%)</th>
<th>$X_{c2}$ (%)</th>
<th>$X_c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UHMWPE</td>
<td>67.0±1.3</td>
<td>50.3±2.1</td>
<td>49.0±0.9</td>
</tr>
<tr>
<td>1hWM</td>
<td>67.8±1.3</td>
<td>51.0±1.1</td>
<td>51.5±1.1</td>
</tr>
<tr>
<td>2hWM</td>
<td>66.0±2.2</td>
<td>48.3±1.5</td>
<td>50.0±1.1</td>
</tr>
<tr>
<td>3hWM</td>
<td>65.7±3.0</td>
<td>49.0±1.0</td>
<td>48.2±5.1</td>
</tr>
<tr>
<td>4hWM</td>
<td>65.2±0.6</td>
<td>50.7±0.7</td>
<td>50.6±0.6</td>
</tr>
<tr>
<td>1hDM</td>
<td>60.3±0.5</td>
<td>50.7±2.1</td>
<td>50.5±4.7</td>
</tr>
<tr>
<td>2hDM</td>
<td>60.0±1.4</td>
<td>50.2±2.5</td>
<td>50.4±1.0</td>
</tr>
<tr>
<td>3hDM</td>
<td>58.4±3.7</td>
<td>50.6±1.5</td>
<td>48.0±4.3</td>
</tr>
<tr>
<td>4hDM</td>
<td>59.7±0.7</td>
<td>50.1±1.3</td>
<td>47.5±3.3</td>
</tr>
</tbody>
</table>

It is known that degree of contact angle is dependent on microstructure and roughness of the surfaces. Fig. 8 shows the trend of contact angles for the composites compared to UHMWPE. After 2 hours of mixing the contact angle decreases and slightly starts to increase after 3 hours of mixing.

**4. DISCUSSION**

As seen from Fig. 1, dry mixing does not distribute the NDs as efficiently as wet mixing. This could be due to the lower viscosity of the sample using ethanol. Considering the functionalization of the NDs and the pre-distribution process in ethanol in the ultrasonic bath prior to ball milling, wet mixing has an advantage. Fang [20] also found that ball milling in ethanol is advantageous as the number of collision events increases and also prevents the powder from re-agglomerating. For this reason, most analysis was focused on the wet mixed samples.

No previously reported studies on UHMWPE/ND composites prepared by solid state mixing are known to the authors. Therefore, the knowledge on ND distribution in polymeric matrices is limited. However, ND reinforced UHMWPE prepared by solvent casting showed large agglomerates of NDs at 0.5 wt% ND [4]. SEM analysis on the dispersion of NDs on powder surfaces was focused on the wet mixed samples to determine the effect of mixing time on dispersion. According to the SEM images, longer mixing times yielded smaller agglomerates. However the flattening and welding effect of longer mixing...
time could result in ND embedding in the matrix as well. This could make the ND clusters appear smaller.

It was also observed from the SEM images that the fibrils from the UHMWPE powders had disappeared (ruptured), this is probably due to plastic deformation of the powder due to the collisions between the powder and the balls and the heat produced during these collisions.

For the same reason, the ND’s effect on thermal properties has not yet been reported. In this study, the thermal effects of ball milling, especially from dry mixing, was manifested as decreased powder crystallinity and a flattening-welding process. Studies on multi walled carbon nanotube reinforced UHMWPE with dry ball milling have shown both decreased [17] and increased [10] crystallinity of sintered composites. The increased temperature was also indicated by the temperatures measured in the ball milling jars.

From the temperatures in table 2 it is clear that not only does the ethanol more efficiently distribute the NDs on the UHMWPE powder surface, it also keeps the temperature at lower. After 4 hours of mixing, the temperature in the dry mix jar was about 20°C higher compared to the wet mixed jar even though the jar was cooled to about 17°C after each hour of mixing in both dry and wet mixing procedures. The flattening and welding process was shown in Fig 2. After 2 hours dry mixing, the temperature had reached 49°C, but only 34°C for the wet mixed samples. The increased temperature in the dry mixed samples could explain the more rapid flattening and decrease in degree of crystallinity in the first heating cycle of the ball milled samples.

The crystallinity in the first heating cycle decreased from 67% for UHMWPE to 58.4% for 3hDM. This suggests that ball milling has some thermal effect on the samples, especially on the dry mixed samples which were also shown in table 2. The second heating cycle of the powder and the first heating cycle of the sintered material correspond well to each other. This implies that Thermal characterisation (DSC measurement) is a reliable method to measure the degree of crystallinity. However, since the crystallinity is measured after heating, melting and re-crystallisation, there is the potential for the introduction of small errors. Crystallinity obtained with XRD shows slightly higher values compared to DSC measurements. The crystallinity slightly increased from 52% for UHMWPE to 57.2% for 3hWM and 59.2% for 4hDM.

Avoiding re-melting and crystallization during measurements are by using XRD, along with the range of instrument settings and adjustment of the XRD spectra could explain the higher crystallinity as measured with XRD.

The effect of different weight percent of the nanoparticles should also be studied. The contact angle measurements were performed to investigate the wettability (hydrophobicity and hydrophilicity) of the prepared nanocomposites in comparison to the UHMWPE. Any significant changes in wettability of the manufactured composites could be an indication in behavioural change toward lubricity of these nanocomposites, which is an important factor when new materials are developed as bearing surfaces in load bearing implants in human joints. The synovial fluid is a water based lubricant and further investigation of wettability of new composites is essential to understand the lubricity behaviour of these nanocomposites. The differences in contact angle could be due to the differences in microstructure due to the welding mechanism during ball milling. As was seen in the SEM studies, the primary UHMWPE powder is deformed due to ball milling and after 4 hours of mixing, a welding process could be seen. It could be hypothesized that at first, the powder particle size is decreased resulting in more grain boundaries in the consolidated material, which could reduce the contact angle. After 4 hours of mixing and increased particle sized due to the welding mechanism, fewer grain boundaries are present in the consolidated material which thus results in a larger contact angle.
Although wet ball milling under the given conditions show promising effects on distribution of NDs, further investigations on the effect of oxidation and thermal stability of UHMWPE are needed. Mixing NDs alone in the ball mill before introducing the UHMWPE could perhaps break down the ND clusters and reduce the mixing time in the ball mill. In such a way, the flattening and welding process of the UHMWPE could be avoided.

5. CONCLUSIONS

- Wet mixing manufacturing procedure is preferred for ND dispersion in an UHMWPE matrix.
- Flattening and welding is more pronounced when dry mixing was applied in manufacturing of the nanocomposites
- 2-3 hours of wet mixing shows the most optimal dispersion without extensive flattening and welding of the UHMWPE powder.

6. ACKNOWLEDGEMENTS

This work has been partly funded by the Swedish agency for economics and regional growth through CMTF. The authors would also like to acknowledge Professor Kristiina Oksman and her research group at Luleå University of Technology for valuable help during the experimental work. Gregory Simmons at Luleå University of Technology is also acknowledged for valuable comments on this work.

7. REFERENCES


Paper III

Tensile and fatigue crack propagation resistance of MWCNT-reinforced UHMWPE

Dmitrij Ramanenka, Evelina Enqvist and Nazanin Emami
Abstract

For many reasons, the numbers of total joint replacements (TJRs) are expected to increase in the future. Expectation and requirements from orthopaedic materials are therefore increased too. Ultra-high molecular weight polyethylene (UHMWPE) has for a long time been used in TJRs with rather good rate of success. Nevertheless, improvement of mechanical properties such as ductility, fatigue crack propagation (FCP) resistance and fracture toughness would have positive impact of life time of the UHMWPE as orthopaedic material. Due to the relatively new advances in the field of nanotechnology novel nano-scaled materials are introduced as potential fillers for materials in biomedical applications. The objective of this study was to evaluate the effect of incorporation of multi-walled carbon nanotubes (MWCNTs) into the UHMWPE matrix (GUR 1020). UHMWPE, UHMWPE/MWCNT- composites containing 0.5 and 1 wt% MWCNTs prepared by high (HS) and low speed (LS) ball milling were prepared and examined. Tensile and FCP-resistance tests were performed. It was found that longer ball milling and HS favored ultimate strength of the composites. LS ball milling had a negative influence on the UTS of composites in comparison to the UHMWPE. Yield strength was relatively unaffected in all cases, while stiffness of the composites tended to slightly increase with incorporation of MWCNTs. Though small improvement of FCP was observed, FCP-resistance tests indicated that no significant improvement was achieved after incorporation of MWCNTs.
1 Introduction

For many years, the acetabular cup in total joint replacements (TJRs) has been made of ultra high molecular weight polyethylene (UHMWPE) [1]. Due to its toughness, durability and biocompatibility the use of UHMWPE together with metal or ceramic counter faces in TJRs has so far outrivaled the use of pure metal-on-metal or ceramic-on-ceramic bearing couples. The lifetime expectancy for such metal- or ceramic-on-plastic bearing couples is in average 10-15 years. Nevertheless, regardless its success, failure of UHMWPE is one of the leading causes of failure of TJRs. Furthermore, it is expected that, due to number of reasons, the number of TJRs will augment in the future, and a higher percentage of these patients are expected to be younger and more active than before. This pushes requirements on UHMWPE to a higher level and thus, in terms of performance and reliability, for orthopaedic UHMWPE, further improvements are desirable in order to be able to meet future demands [2].

The improvement of mechanical and tribological properties of orthopaedic UHMWPE has been the focus of many investigations over the years. One of the important milestones was to change the sterilization procedure from gamma radiation in air (due to its negative effect on the long-term stability of UHMWPE [3,4]. This was a common sterilization technique used until late 1990 which was replaced by methods (non-ionizing methods such as ethylene oxide gas or gas plasma sterilization but also ionizing sterilization by weak gamma irradiation is still used) that do not jeopardize the long term properties of the polymer. Another breakthrough during the years has been the utilization of cross-linking radiation with purpose of improving wear resistance of UHMWPE. This has resulted in a substantial reduction of adhesive and abrasive wear [5,2]. These grades of UHMWPE have been introduced into clinical use in the late 90th.

However, studies have showed that improvement in wear resistance by cross-linking affected some other important mechanical properties such as strength, stiffness, ductility, fatigue crack propagation resistance, and fracture toughness reversibly [2, 5,15]. The significant reduction in these mechanical properties is mainly due to the post-crosslinking thermal treatments (usually involving melting). If no neutralization of free radicals is made the risk of detrimental long-term oxidation of the material is imminent. These grades of UHMWPE are often referred to as the 1st generation of highly cross-linked UHMWPE (HXLPE). As a result of the mentioned drawbacks of the 1st generation of HXLPE a 2nd generation of HXLPE is under investigation.

Naturally, the driving force is to keep the superior wear resistance of the 1st generation HXLPE while also preserving the favorable mechanical properties of the conventional (non-cross-linked) UHMWPEs [2]. Numbers of methods have been developed in order to preserve these mechanical properties, for example sequential annealing and vitamin E- doping of HXLPEs- to avoid re-melting of the polymer. These methods have showed positive effect on the final mechanical properties of the HXLPE [6-8,16]. In fact, vitamin E-doped HXLPE has been in clinical use since 1998 [9]. However, despite the promising results of the 2nd generation of HXLPE, improvement of mechanical properties by these methods is limited.

One traditional and well-established way of enhancing mechanical properties of polymers is by incorporation of fillers into the polymeric matrix. The common denominator for the traditional fillers is their size, which is in the order of microns [10]. However, previous experience of incorporation of short fiber fillers into medical grades of UHMWPE has been without success. One product known as Poly 2TM was developed by incorporation of carbon-fibers into UHMWPE. Later studies showed
that Poly 2™ performed rather poorly in clinic compared to conventional UHMWPE, possibly due to poor interface between polymer matrix and fibers [1]. Nevertheless, due to the relatively new advances in the field of nanotechnology novel nano-scaled materials have raised as potential fillers for materials in biomedical applications. Carbon nanotubes (CNTs) exceptional mechanical properties and their high aspect ratio make them advantageous reinforcement system for polymer matrices. Many studies have shown increased mechanical properties of the polymers reinforced by CNTs. Zoo et al. reported enhanced tribological properties of UHMWPE/CNT-composite [11]. Qian et al. investigated addition of MWCNTs in polystyrene (PS). They found that an addition of 1 wt% of MWCNT to PS increased tensile stress at break and tensile modulus by up to 25 and 42 % respectively [12]. Ruan et al. reported enhancement in tensile strength, tensile modulus and ductility after the addition of MWCNTs into gel-spun UHMWPE fibers [13]. However, the main challenges for polymeric nanocomposites still concern homogenous dispersion and interfacial bonding of nanofillers to polymer matrix [10,14]. Moreover, the health effect of various nanoparticles is also under investigation by different authorities. Several in vivo bio distribution studies on the influence of carbon nanotubes have showed no signs of acute toxicity or negative health effects. Other studies have shown considerable toxicity of pristine SWCNTs (Single-walled CNTs) in contact with skin. On the other hand, it has also been shown that modification of CNTs can lead to significant reduction in toxicity. Another concern is the long-term bio-effect of CNTs, which tend to accumulate in organs. This problem should however be less evident when nanoparticles are incorporated into polymer matrices as reinforcement. In any case, more studies in this area are necessary [17, 18].

The objective of this study was to evaluate influence of incorporation of MWCNTs on the mechanical properties of the UHMWPE. Tensile and FCP resistance tests were performed on UHMWPE/MWCNTs-nanocomposites prepared at different manufacturing conditions and weight percentages.

2 Materials and Methods

2.1 Materials

Totally seven groups of materials (pure polymer and nanocomposites) based on UHMWPE orthopaedic grade GUR 1020 kindly supplied by Ticona (Germany) were tested in this study. These were: pure UHMWPE, UHMWPE/MWCNT-composites containing 0.5 and 1 wt% MWCNTs prepared in ethanol solution by high speed (HS = 270 rpm) ball mixing during one and two hours and low speed (LS = 135 rpm) ball mixing prepared during one hour. Table 1 shows all seven groups of tested materials. Additionally, in some cases also a commercially compression-molded GUR 1020 (Orthoplastics Ltd, UK) was used as a reference to our UHMWPE. Tensile tests and FCP resistance measurements were performed on each group of the materials.
Table 1. Summary of the materials tested in this study

<table>
<thead>
<tr>
<th>Notation of the materials</th>
<th>HS0.5%1h</th>
<th>HS0.5%2h</th>
<th>HS1%1h</th>
<th>HS1%2h</th>
<th>LS0.5%1h</th>
<th>LS1%1h</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNTs (wt%)</td>
<td>0.5</td>
<td>0.5</td>
<td>1</td>
<td>1</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>Mixing Speed (rpm)</td>
<td>270</td>
<td>270</td>
<td>270</td>
<td>270</td>
<td>135</td>
<td>135</td>
</tr>
<tr>
<td>Mixing Duration (h)</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

*HS stand for high speed and LS for low speed.

Bulk materials were manufactured by hot press molding in plate form in two thicknesses, approximately 2 and 4.5 mm. First, the powder was evenly placed in the mold on a brass foil (~0.05 mm). The mold was then pre-heated in the hot press for 10 minutes at 190 °C at zero pressure. Thereafter, pressure was slowly (during 2-3 min) raised to 10 MPa. The load cycle procedure was repeated five times, with a holding time of 90 seconds at in between. Finally, pressure of 10 MPa was held for 30 minutes at 190 °C whereupon the mold was removed from the hot press and cooled down at room temperature under a 5.5 kg weight (approx. 4.5 kPa).

2.2 Methods

2.2.1 Tensile testing

The samples for tensile testing were made from the 2 mm compression molded composite plates. Rectangular-shaped specimens were cut with 120 mm length and 10 mm width. The edges were polished on SiC sandpaper. Tensile tests were performed on Instron 3366 testing machine. A 10-kN load cell and air-driven grips were used. The tests were conducted at 23 ± 2 °C and 5-25 %R.H. Test specimens were chosen randomly from different batches of the prepared specimens. The air pressure to the grips was set to 20 psi, resulting in approximately 10 psi on lower and upper part of the sample. Testing speed was set to 1 mm/min while the gauge of the sample was set to 40 mm when elastic modulus was measured. An extensometer with a gauge length of 25 mm was used to measure the strain. The tests were conducted to approximately 0.5 % of strain (4-5 MPa) whereupon the tests were stopped and the load was released for further tensile tests until break. Elastic modulus was measured between 0.2-0.5 % strain where the most linear behavior could be found, ASTM 638 [19], and also between 0.05-0.25 % strain, ISO 527-1 [20]. The measurements were carried out until break point of the specimens at speed of 50 mm/min and specimens width was 20 mm. Ultimate tensile stress and stress at yield were calculated according to ASTM 638 [19]. For some selected tests a digital system camera was rigged to measure the extension at brake.
2.2.2 Fatigue crack propagation resistance

Rectangular compact tension samples for the FCP-resistance tests were machined from the UHMWPE/MWCNTs plates with thickness of 4.5±0.05 mm according to the guideline for shape proportions of ASTM E 647 [21], figure 1. A sharp crack was generated prior to the tests by slowly pressing an unused razor blade into the specimens [21]. The razor blade was fixed simply to Instron 4411 at controlled speed (1mm/min), Instron 4411.

Fatigue tests were performed on a hydraulic testing machine, Instron 1272. The R-ratio was set to 0.1 and a sinusoidal waveform at frequency of 5Hz was used. The maximum load was 220 N. In order to minimize heating of the samples an air-jet was aimed at the gap of the sample for cooling purpose. The tests were performed at room temperature (23-25°C). No controlled conditioning of the samples prior the tests was made. The specimens were tested until the crack length, \( a \), reached approximately 15 mm.

The crack growth was observed and measured using a high-speed camera (SensiCam) equipped with a Nikon 105 mm objective and controlled by software (CamWare v.2.19). An image was captured every 1000th cycle. Accordingly, the number of cycles was also recorded for each period of crack growth. Measurement of the crack extension was calculated in Matlab.

The stress-intensity factor range, \( \Delta K \), was calculated according to [21]:

\[
\Delta K = \frac{\Delta P}{B\sqrt{W}} f(\alpha) \tag{1}
\]

Where \( \Delta P \) is the force range, \( B \) thickness of the specimen, and \( W \) width of the specimen. \( f(\alpha) \) is a geometrical correction factor for rectangular compact tension specimens, where \( \alpha = a/W \) (equation 1 is valid for \( \alpha \geq 0.2 \) only).

Relevance of plane strain loading conditions relative to the geometry of the samples was evaluated according to [21]:

\[
B, a, (W - a) \geq 2.5 \left( \frac{K_{\text{max}}}{\sigma_{YS}} \right)^2 \tag{2}
\]

Where \((W-a)\) is the specimen’s uncracked length and \( \sigma_{YS} \) is the yield strength of the material. \( K_{\text{max}} \) was calculated using equation 1 by substituting \( \Delta K \) with \( K_{\text{max}} \) and \( \Delta P \) by \( P_{\text{max}} \).
The stress-intensity factor ($\Delta K$) and the crack growth rate ($da/dN$) of the samples were plotted where $\Delta K$ and $da/dN$ are known to be correlated by the Paris equation in the stable crack propagation regime:

$$\frac{da}{dN} = C(\Delta K)^m$$

Parameters $C$ and $m$ are material and test dependent. Since test conditions are constant material properties can be compared. By a bi-logarithmic plot of Paris region ($10^{-4}<da/dN<10^{-3}$) the slope and the intercept were found which represent parameters $m$ and $C$ respectively.

### 2.2.3 Scanning electron microscopy

Scanning electron microscopy (SEM, FEI Magellan 400) was used to analyze the surfaces of the ball-milled powders. The dispersion of MWCNTs was also studied with SEM. A beam voltage of 1 kV and a beam current of 3.1 to 6.3 mA were used depending on the magnification and detector (Through lens detector (TLD) or Everhart-Thornley detector (ETD) used. All samples were uncoated.

### 3 Results and Discussion

#### 3.1 Tensile testing

Tensile tests (Figure 1) indicate that UHMWPE/MWCNTs nanocomposites prepared at HS- ball milling for 2hr favors in ultimate strength (US). Composites prepared by LS- ball milling resulted in lower US compared to UHMWPE. Yield strength tends to reduce after incorporation of MWCNTs, but only insignificantly. Tested composites indicate slight enhancement of stiffness in both LS- and HS-groups. No significant differences were observed between Young’s modulus of LS- and HS-groups. 0.5 and 1 wt% groups show some differences in some cases. Average of extension at break for some selected tests (UHMWPE, LS 0.5%1h and LS 1%1h) was measured to 455-467 %.
Gripping technique, how specimens were attached to the Instron, was affected the results of UTS measurements significantly. The use of sandpaper as commonly made during gripping was found to influence the results substantially, depending on the grip pressure and the grit size of the sandpaper. In the tests presented here no sandpaper was used for gripping of the samples.

3.2 Fatigue crack propagation resistance

The data from the FCP- tests of the same material was pooled together since the data scattered insignificantly from test to test. The tests indicate that FCP resistance of the tested materials is approximately the same, figure 2.
Plane strain loading conditions were not fulfilled for any period of crack growth during these tests. This is a limitation for the used geometry in the performed tests; however in practice useful information can still be concluded. As Gencur et al. [15] have observed the size criteria plays relatively small role when conducting FCP – tests compared to when determining static fracture toughness. Exponent \( (m) \) and coefficient \( (C) \) found in these tests (Table 2) indicates that no significant difference is presented between the tested materials after initiation of stable crack growth. \( C \) and \( m \) suggest that as the stable crack growth is established the crack propagation accelerates similarly from one to another tested material.

<table>
<thead>
<tr>
<th></th>
<th>UHMWPE</th>
<th>HS0.5%2h</th>
<th>HS0.5%1h</th>
<th>LS0.5%1h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exponent ( (m) )</td>
<td>7.57</td>
<td>8.24</td>
<td>8.14</td>
<td>7.93</td>
</tr>
<tr>
<td>Coefficient ( (C) ) ((\text{mm/cycle})/(\text{MPa}^{1/2}))</td>
<td>(2.22\times10^{-7})</td>
<td>(1.03\times10^{-7})</td>
<td>(1.04\times10^{-7})</td>
<td>(1.23\times10^{-7})</td>
</tr>
</tbody>
</table>

An attempt to measure fracture toughness according to ASTM D5045 was also performed. Compact tension samples with thickness of 4.5 mm were used. However, as for the FCP- tests the plane-strain requirements of the standard was not possible to fulfill in the room temperature. In order to render the fracture more brittle the tests were performed at temperatures below 0 °C; at -100 °C as the lowest temperature. A more brittle fracture was obtained but not sufficiently in order to fulfill plane-strain requirements.
3.3 Scanning electron microscopy

Microscopy studies have showed that manufacturing and processing parameters play significant role in the dispersion of nanoparticles in the polymer matrix. SEM images reveal that HS-preparation at 2 hours favors distribution of MWCNTs in the polymeric matrix. As figure 3 shows at shorter mixing time (45 and 60 min) MWCNTs tend to form agglomerates, (a) and (b), while after two hours of mixing the cluster formation is significantly reduced, (c). Additionally, it can be concluded that LS- ball milling is less efficient when compared to HS- ball milling at the same mixing duration, (d). Images presented in figure 3 (c to f) respectively confirms that. Composites prepared at LS- ball milling at 2h have large areas where MWCNTs are poorly presented, while in HS- samples after 2h mixing such areas were less evident.
Figure 3. SEM images of UHMWPE reinforced with 0.5 wt% MWCNTs prepared by HS-ball mixing at duration of (a) 45 min, (b) 1 h, (c) 2 h and (d) LS-ball mixing at duration of 2 h. Areas marked in (c) and (d) respectively are magnified in (e) and (f).
4 Conclusion

- Manufacturing parameters affect significantly the distribution of MWCNTs into the UHMWPE matrix.
  - High speed ball milling at 270 rmp and longer mixing time (2hr) favor distribution of MWCNTs. Accordingly mechanical properties were influenced by the dispersion of MWCNTs.
- Ultimate strength of composites tends to increase when prepared at 270 rmp and for 2 hours.
  - No positive trend observed between 0.5 and 1 wt% of MWCNTs reinforced composites.
- Yield strength seems to be unaffected by the incorporation of MWCNTs.
- A slight increase of stiffness can be correlated to the incorporation of MWCNTs at favored mixing conditions.
- Fatigue crack propagation resistance was increased but insignificantly affected.

5 References


