

Tribological Behaviour of Hybrid Carbon Filled UHMWPE Composites in Water

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Declaration

I hereby declare that except where specific reference is made to the work of others, the contents of this thesis are original and have not been submitted in whole or in part for consideration for any other degree or qualification in this, or any other university. This thesis is my own work and contains nothing which is the outcome of work done in collaboration with others, except as specified in the text and Acknowledgements.

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Abstract

There is a increasing emphasis in today's world to use environmental friendly solutions for tribological and lubrication purposes. Use of water as a lubricant presents a cost effective and easy method of bio friendly lubrication. But, as water has low viscosity, it is necessary that the materials used in water lubricated contacts perform exceedingly well in boundary lubricated conditions. Polymer Based Materials (PBMs), are one such group of materials which have been proven to perform well in such conditions. In particular, Ultra High Molecular Weight Polyethylene (UHMWPE) has been extensively used in water lubricated contacts. But, PBMs still suffer from wear and related problems and there is room for improvement. Various methods have been tried with mixed results to improve the qualities of polymers and consequently their performance in water lubricated contacts. One such method is by inclusion of fillers. Conventionally, micron sized fillers have been used to form composites with a polymer resulting in materials with better properties. Recently, nanometer sized reinforcements have been attracting more attention due to their unique mechanical and tribological properties. Combining micrometer and nanometer sized filler in a polymer composite could help form materials with excellent properties. Such composites would be termed as a hybrid material. Therefore, the aim of this project and thesis is to experimentally investigate the influence and interaction of micro and nano carbon-based fillers on tribological behaviour of UHMWPE composites and provide further understanding of the mechanisms involved.

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Chapter 1

Introduction

From a maintenance and economical point of view, it is advantageous to replace metal parts in various industries and applications with Polymer Based Materials (PBMs). The advantages include light weight, low maintenance, and also lower cost [1–3]. Usage of PBMs as bearing surfaces and in tribological contacts has been witnessing an increase in popularity lately. Thin polymer film monolayers that are created by chemisorption or physical adsorption of organic polymer molecules in a tribological contact represent promising surface lubricants.

Lately, emphasis has been on using environmental friendly solutions for lubrication. Two primary ways in which this can be done are by using Environmentally Adapted Lubricants (EALs) and water. The former generally have a specific half-life and degradation period inside which they still can cause harm to the environment, the extent of which is still being researched. Therefore, using water is the next best option. But, using water in tribological contacts involving conventional materials like steel and other metals has many disadvantages associated with it. Due to the low viscosity of water, the contact tends to function in boundary lubrication regime resulting in considerable friction and wear. Corrosion in water lubricated systems is a major drawback. Owing to their excellent corrosion resistance and self-lubricating properties, PBMs have emerged as the leading replacement for metals in such applications. Application of polymers in water lubricated bearings introduces many other advantages which cannot be achieved with conventional metallic bearing materials, coatings or ceramics. PBMs possess properties which are desirable in cases like bearings in hydro-power plants, prosthetic joints, marine applications and many more. In spite of this, mixed results have been obtained for using water as a lubricant in polymer contacts [4–6]. Significant wear is still observed for PBMs in water lubricated applications. Also, PBMs has been shown to absorb water during a extended period of time. Absorption of water can cause ageing issues and hysteresis which ca lead to swelling and affect wettability and tribological performance consequently.

Introduction

The majority of the PBMs used as tribological materials at present incorporate fillers and reinforcements, not only to improve the tribological, mechanical and thermal properties, but also to reduce the material costs and improve processability of the polymer. The range of materials that can be used as fillers in polymer composites is vast and out of scope of this report. In general, fillers can be categorised into two on the basis of their size: micro and nano sized fillers. Micrometer scale fillers have been traditionally used to reinforce composites while nano scale fillers are gaining in popularity. The selection of suitable fillers is usually a compromise between the properties of the polymer and its friction and wear behaviour.

1.1 State of the art

Many of the well-established polymeric materials still cannot fulfil all technological needs for the various new applications. Hence, the tremendous possibility to tailor properties offered by hybrid materials make them a strong candidate to replace conventional materials. Hybrid polymer based composite materials combine both micro and nano reinforcements to obtain properties which are better than when just a single type of filler is used. The usage of different fillers cause a synergistic effect and most of the resulting materials show improved mechanical properties. Ability to functionalise the fillers provides a better control over the properties [7, 8]. This possibility of generating complex systems from simpler building blocks can be compared to a kind of *LEGO*® approach [9]. The above description of hybrid materials is not to be confused with hybrid composites which use only different fibres as reinforcing materials or any other definition. In some cases, the composite can even contain more than one polymer.

The behaviour of hybrid composites is a weighed sum of the individual components in which there is a more favourable balance between the inherent advantages and disadvantages. Advantage of one type of filler could complement with what is lacking in another. As a consequence, a balance in cost and performance can be achieved through proper material design [10]. Considerable improvement in properties has been observed in such hybrid materials [11]. The crucial properties are mechanical behaviour of composite, its thermal conductivity and lubricity. The complex structure of polymer-based composites reflects in complex tribological behaviour of polymeric tribosystems. Nano scale fillers work by having a large surface area to volume ratio which allows more interaction with the matrix material. Therefore, a lower concentration of filler can be utilised to improve the composite. Studies have shown that the addition of an optimum amount of micro- and nano-scale of fibres, inorganic particles, ceramic, and bio-material with UHMWPE matrix would significantly

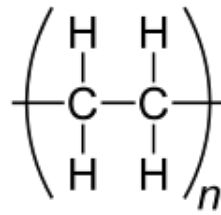


Fig. 1.1 Structure of UHMWPE with n greater than 100,000

reduce the wear rate under sliding wear conditions [12]. UHMWPE composite with both micro- and nano-hydroxyapatite reinforcement has exhibited better performance than the same composite having just either one of them. [13]. Combination of Graphene and nanodiamonds has shown to lead to macro-scale lubricity [14].

In the same manner, it can be hypothesised that with proper design of material and selection of fillers and corresponding properties, good performance under water lubrication can be achieved. The next few sections in this chapter will talk about which materials are used for the purpose of the work presented in this thesis and why.

1.2 Materials

1.2.1 UHMWPE

UHMWPE stands for Ultra High Molecular Weight Polyethylene. It is a PBM, defined as "polyethylene with molecular weight over three million." It is a semi-crystalline thermoplastic polymer and consists of long chains of ethylene groups, which is the monomer, all aligned in the same direction. The carbon backbone can rotate, twist and fold into the crystalline phase providing a more complex structure at the molecular level. It is a general purpose plastic which is relatively cheap and also exhibits low friction and very good wear resistance. UHMWPE has shown superior performance in load bearing systems where water is used for lubrication [15]. Its long linear chains provide great impact strength, abrasion resistance and toughness. It is also non toxic in nature [16]. The polymer finds applications in orthopaedic implants, food and beverage machinery, personal armour, recreation and general manufacturing [16, 17]. Figure 1.1 shows the structure of UHMWPE in terms of its most basic unit.

Although significant research has been conducted to ensure good tribological performance of UHMWPE in water lubricated applications, significant wear particle generation has been reported. To overcome these issues, the polymer can be incorporated with various kinds of fillers to significantly improve its properties [18]. The additives include carbon fibre,

Introduction

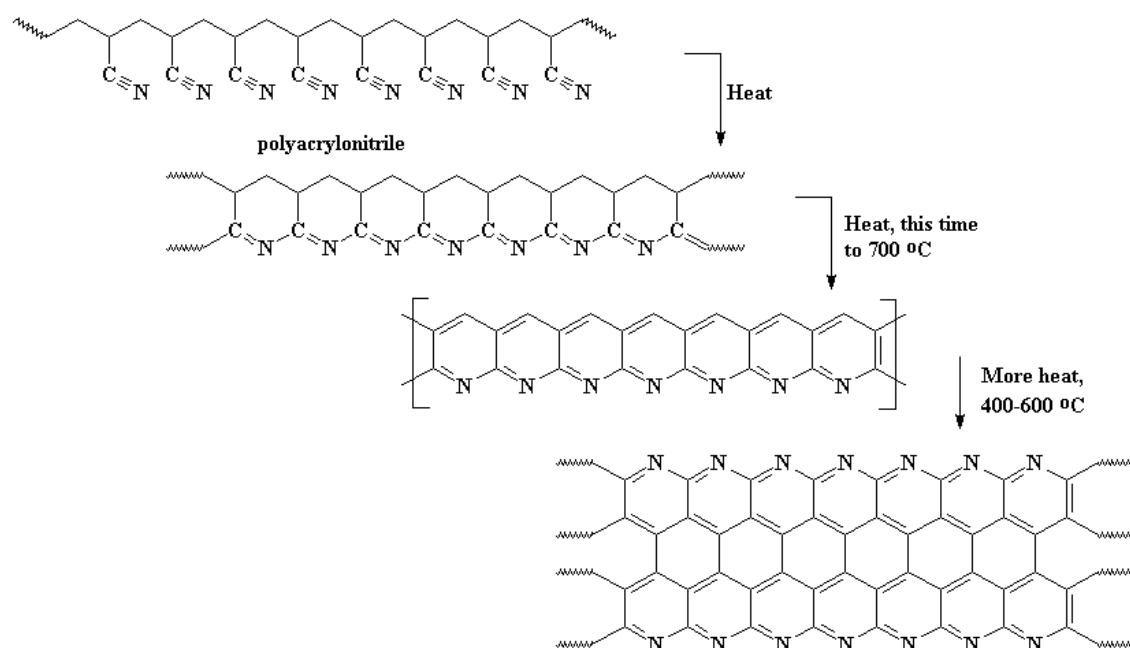


Fig. 1.2 Synthesis of Carbon fibre [21]

kaolin, natural coral particles, Zirconium particles, Titanium dioxide, Aluminium oxide and carbon nanotubes among others [19, 20]. The long chains make it difficult to manufacture UHMWPE products through process like extrusion or injection moulding. Compression molding is the most commonly used method at present.

1.2.2 Short Carbon fibres (SCF)

As the name suggests, carbon fibres are fibres composed mostly of carbon atoms. The usefulness of carbon reinforcing fibres rests on the characteristics of the graphite crystal's hexagonal layer structure. Because of the highly anisotropic nature of the graphite crystal it is necessary to arrange for the layer planes to be aligned preferentially with the fibre axis to produce a carbon fibre having a high elastic modulus. At present, most carbon fibres are manufactured from polyacrylonitrile (PAN) precursors. Carbon fibres produced in this way are not composed of perfect crystalline material and consist, in the main, of turbostratic graphite [22]. Figure 1.2 is a simplified representation of the process of producing carbon fibres.

SCFs are nothing but shorter form of the conventional carbon fibres. SCF composites are easier and cheaper to produce than continuous fibre reinforced composites. A compromise between cost and performance is made when SCF is used as a filler in a composite. They are one of the most popular candidates for the development of structural and functional

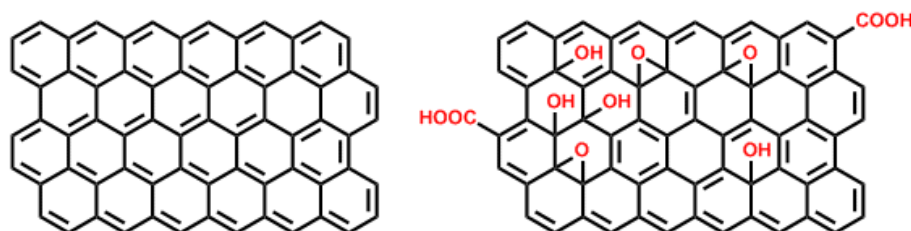


Fig. 1.3 Graphene(left) and Graphene oxide [28]

reinforced polymer composites because of their high surface-to-volume ratio, outstanding thermal, mechanical and electrical properties and good dispersion in polymer matrices [23–25]. SCFs improve wear resistance of polymers by carrying main load between contact surfaces and protecting polymer matrices from severe abrasion [23, 24, 26]. The use of SCF reinforcement in polymers reduces the fibre length reinforcing efficiency compared with long fibres, but offers economic and design advantages in applications with complex geometries, for example injection molding of composite parts with complex shapes [27].

1.2.3 Graphene oxide (GO)

Graphene oxide (GO) could be regarded as Graphene functionalised by carboxylic acid, hydroxyl, and epoxide groups. By analogy to Graphene, Graphene oxide are monomolecular sheets of graphite oxide. Graphite oxide is obtained by treating graphite with strong oxidisers. This introduces oxygenated functionalities in the graphite structure which expand the separation between different layers of Graphite and make the material hydrophilic. This enables the Graphite Oxide to be exfoliated in water using sonication, ultimately producing Graphene Oxide. The presence of oxygen functionalities makes it possible to easily disperse GO in water and other organic solvents, as well as in different matrices [29, 30]. Figure 1.3 shows the structures of Graphene and Graphene Oxide in a simplified manner.

With its carbon-based mono-layer structure and densely packed and atomically smooth surface, GO has excellent tribological properties. It also possesses good mechanical properties such as a high Young's Modulus, excellent flexibility, hardness, stiffness and strength which make it an excellent filler material. The high specific surface area, two-dimensional geometric structure and good interfacial adhesion of GO are beneficial to the stress transfer between GO and the polymer matrix [31]. Wear behaviour of polymers filled with GO in dry friction have been investigated and the results show that the deformation and fracture of composites were reduced, whereas wear resistance was improved. Also, it has been demonstrated that addition of GO to UHMWPE shows good bio-compatibility [31–34]. These properties combined with the fact that GO shows a lower surface energy than the surface tension of

water make it an interesting candidate for use as a tribological material and particularly in water lubricated contacts.

1.2.4 Nanodiamonds (ND)

Diamond nanoparticles (ND) or nanodiamonds can be found naturally and also produced in a laboratory. They are a 0-D allotrope of carbon which essentially means that the atoms in the material are quantised in all directions and do not have any degree of freedom. As the name suggests, NDs have dimensions in the nanometre scale. They have been synthesised by detonation techniques, laser ablation, high-energy ball milling of high-pressure high-temperature diamond micro-crystals, plasma-assisted chemical vapour deposition (CVD), autoclave synthesis from supercritical fluids, chlorination of carbides, ion irradiation of graphite, electron irradiation of carbon ‘onions’, and ultrasound cavitation with the first three of these methods being used commercially [36, 37].

NDs inherit most of the superior properties of bulk diamond in their nanoscale dimensions. These properties include superior hardness and Young’s modulus, bio-compatibility, optical properties and fluorescence, high thermal conductivity and electrical resistivity and chemical stability [36, 38]. Nanodiamonds have diameters of 4–5 nm, but they tend to aggregate and typical commercial suspensions of nanodiamonds contain larger aggregates [39]. De-aggregation of nanodiamond in suspensions by milling with ceramic micro beads has been developed, yielding colloidal solutions of individual nanodiamonds 4–5 nm in diameter [40]. In the field of tribology, it has been shown that purified nanodiamond, dispersed alone or with polytetrafluoroethylene (PTFE) or metal nanoparticles in greases or oils, provides enhanced tribological performance [39]. Macro-scale super-lubricity has been achieved with a combination of GO and ND [14]. The bio-compatible and chemically stable nature of the diamond core make nanodiamond polymer composites very well suited for biomedical

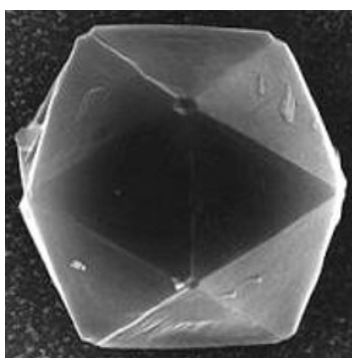


Fig. 1.4 A Nanodiamond [35]

applications. Research carried out has reported improvements in mechanical strength and wear resistance. Use of aggregated nanodiamonds will however lead to a degradation in properties [41, 42]. Many different functional groups can be attached to the surface of nanodiamonds without compromising its properties [39, 43].

1.3 Research gap

The development of nanocomposites, where at least one dimension of the filler phase is in nanoscale (<100 nm) has further propagated the research effort to manufacture nanocomposites using a variety of fillers like carbon black, layered silicates, and carbon nanotubes.

Recent and ongoing research at the Division of machine Elements at LTU has shown promising results in the form of reduction in wear up to 40% for polymer composite bearing applications under water lubrication [44]. The polymer used in this case was UHMWPE with size in the range of $140\text{ }\mu\text{m}$. GO and MWCNT, which can be categorised as nano fillers, were used as the fillers. It is to be noted that the fillers were used individually along with the polymer. Also, research has been carried out to study the performance of UHMWPE composites of ND. A 75% reduction of the specific wear rate was found for 1wt% ND in the composite, with no loss of the mechanical properties [45]. Therefore, as discussed in section 1.1, it remains to be seen how a hybrid composite containing both micro and nano sized reinforcements will perform under water lubrication.

Even though UHMWPE has a good wear resistance, wear particles can be generated with time. Therefore, there is a need to formulate UHMWPE based composites with better wear performance. This would prolong the component lifespan and minimise the harmful consequences of presence of wear particles in any tribological system. It can be hypothesised that a smaller polymer particle size used to make the composites can contribute to better performance of the composite. A smaller particle size will affect the manufacturing parameters and improve the dispersion of the reinforcements within the composite. Also, a higher surface to volume ratio will result in greater and better interactions. Consequently, the wear and friction characteristics could be positively influenced [18, 46].

It has been reported that SCFs were found to improve wear resistance of poly (ether ether ketone) (PEEK) based composites by carrying the main load between contact surfaces and protecting polymer matrices from severe abrasion [47]. Study of inclusion of SCF, a micro reinforcement, in UHMWPE polymer matrix and the subsequent performance of such composites under water lubricated contacts is scarce and has not been investigated thoroughly. The same applies for Nanodiamonds. Recent research has shown that using NDs in a tribological system can offer many advantages. The ability to functionalise NDs extensively

gives the added ability of tailoring properties for various applications. Incorporation of Graphene oxide in UHMWPE has been studied and the resulting composite has been shown to have impressive tribological behaviour. Although, these filler materials have been studied individually, little research has been undertaken in combining all these fillers to make a Hybrid material.

1.4 Objectives of the presented thesis

This master thesis project aims at experimentally investigating the influence and interaction of micro and nano carbon-based reinforcements on tribological behaviour of UHMWPE composites in water lubricated contacts and provide further understanding of the mechanisms involved. The objectives can be listed out as the following:

- Optimization of manufacturing parameters of the UHMWPE hybrid-composites at different reinforcement wt% and different polymer particle size.
- Study the effect of polymer particle size on the wear and friction in polymer composites.
- Study the effect of SCF, GO and ND fillers, both individually and in combinations on the thermal characteristics and bulk properties of the polymer composites.
- Study the influence of individual fillers both as single fillers or in a combined system on mechanical properties of the polymer composites
- Evaluation of frictional and wear behaviour of the composites
- Identification of the optimum loading of the filler material based on results obtained from frictional tests.

The process and methodology carried out to achieve the aforementioned objectives will be discussed in the following chapters. Chapter 2 describes the manufacturing of the composites and the different equipment used to carry out analyses and various measurements. The results of the analyses are discussed in chapter 3 and conclusions drawn from the various results are described in chapter 4. Chapter 5 briefly describes the research work that can be carried out in the future.

Chapter 2

Methodology

2.1 Preparing the composite

The work presented in this thesis involved manufacturing of various polymer composites which had different combinations in terms of the type of fillers and the quantity of polymer and fillers used. The manufacturing of the composites was carried out in four basic steps; 1) ultrasonication of nanofillers in ethanol, 2) ball milling of ultrasonicated nanofillers together with UHMWPE, 3) removal of excess ethanol, and finally 4) direct compression molding (DCM) of composite and UHMWPE. Manufacturing of composites with SCF as one of the fillers required a modified procedure. The manufacturing process will be described below and is shown as a flowchart in figure 2.1.

MIPELON™ UHMWPE XM-220 (Mitsui Chemicals, Japan) was used as the base polymer to manufacture the composites. The UHMWPE particles had an average size of $30\mu\text{m}$, a molecular weight of $2 \times 10^6 \text{g/mol}$ and a powder density of 0.4g/cm^3 . Table 2.1 shows the particle size distribution of UHMWPE particles in percentage of total composition.

Nanodiamond particles were obtained from *Adámas Nanotechnologies, USA* and had an average particle size of $4 - 5 \text{nm}$, an average agglomerate size of 30nm and a molecular weight of 12.01g/mol . Graphene Oxide nanosheets (*NanoInnova Technologies, Spain*) had a

Size	%
$20 \mu\text{m}$	10
$20 - 30 \mu\text{m}$	35
$30 - 40 \mu\text{m}$	35
$40 \mu\text{m}$	20

Table 2.1 Particle size distribution of UHMWPE particles

SI No	GO	ND	SCF
	wt%		
1	0	0	0
2	0.5	0	0
3	0	0.5	0
4	0	0	10
5	0.5	0.5	10
6	0.5	0.5	0
7	0.5	0	10
8	0	0.5	10
9	1	0	0
10	0	1	0

Table 2.2 List of composites prepared in terms of weight percentage of the constituent fillers

monolayer thickness of $0.7 - 1.2\text{nm}$ and an average lateral dimension of $3 - 7\mu\text{m}$. The SCFs (*Tenax®-A HT M100 100mu*) had an average length of $100\mu\text{m}$, diameter of $7\mu\text{m}$ diameter and bulk density of $1.82\text{g}/\text{cm}^3$.

The composites were prepared taking UHMWPE as the base polymer and with different combinations of the fillers. Table 2.2 lists out the various combination of composites prepared for the purpose of this work. For example, composite with serial number 9 in table 2.2 has 1 wt% ND and 99 wt% UHMWPE. The combinations of fillers and UHMWPE were decided on the basis of previous research and according to the points laid out in the concluding section of chapter 1. Composites from serial numbers 1-8 were prepared to study the influence of individual fillers both as single fillers and in a combined system on mechanical properties of the polymer composites. Manufacturing and testing of the composites with serial numbers 9 and 10 was carried out to ensure that the effect of the combined fillers in composite number 6 was not due to the increased amount of nano fillers in the polymer matrix.

2.1.1 Ultrasonication

Prior to wet milling, the filler particles were dispersed in ethanol using ultrasonication. Required amount of particles were weighed and transferred into a beaker containing ethanol. The beaker was then covered with plastic wrap and placed in the sonicator bath. Ultrasonication was carried out for about 3 hours. This step breaks down any agglomerates of the filler particles present resulting in a homogeneous solution. Ultrasonication using ethanol as a dispersing agent for the fillers prior to main mixing with UHMWPE has been reported already[48, 49]. Other solvents including water have also been used but not in this case. GO and ND particles were sonicated while SCFs were not. Due to the relatively higher

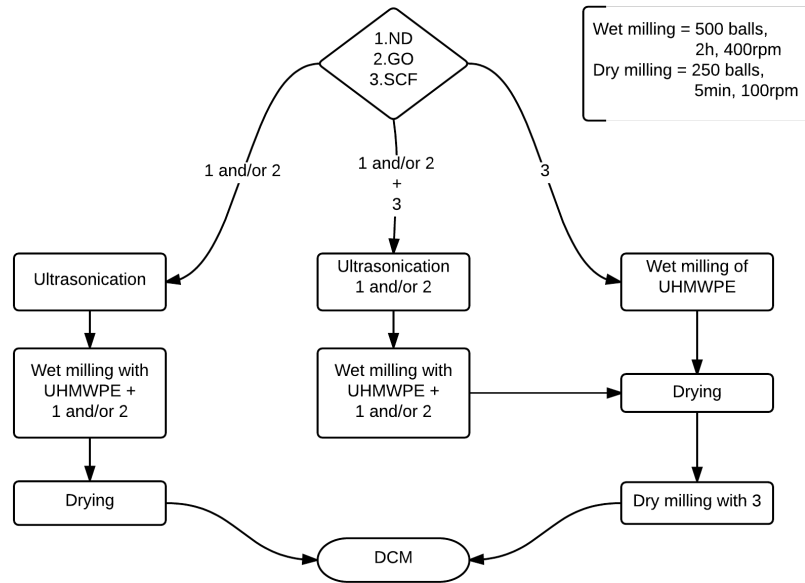


Fig. 2.1 Flowchart of the manufacturing process

size dimensions of the SCFs, dispersion in ethanol was not possible through ultrasonication. Also, ultrasonication would have resulted in the breakdown of SCFs into smaller fragments. Therefore, SCFs were not dispersed in a solvent before milling and remained dry.

2.1.2 Ball milling

To ensure that the manufactured composites have a homogeneous composition, it is necessary that the fillers are dispersed uniformly throughout. Melt mixing, a process commonly used for polymers cannot be used for UHMWPE composites in a straightforward manner as melt mixing of UHMWPE can only be done at temperatures significantly above the oxidation temperature of UHMWPE. Thus, it is only possible to carry out melt mixing without damaging the polymer if a lower molecular weight polymer or a solvent is added to the process. This consequently requires various solvent extracting steps which makes the whole process of making the composite tedious [50].

Ball milling is a common technique for grinding minerals, ceramics and paints into fine powder, as well as a technique for mechanical alloying. As it mixes the constituents in solid state, ball milling is a good alternative to melt mixing. A planetary ball mill consists of at least one grinding jar arranged eccentrically on a so-called sun wheel. The grinding jar is filled with the material to be milled plus the milling medium. Different materials are used as media, including ceramic balls, flint pebbles and stainless steel balls. The direction of movement

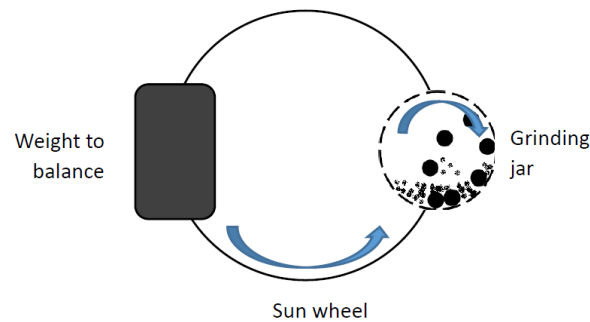


Fig. 2.2 Schematic representation of the ball-milling process [45]

of sun wheel is opposite to that of the grinding jars. The difference in speeds between the media and grinding jar produces an interplay between forces resulting in effective milling. The material to be milled is subjected to compressive loads from impact with the balls. A schematic representation of the ball-milling process is shown in figure 2.2. 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 jars) and even the atmosphere [51].

Research already carried out has found optimum values for the parameters mentioned above and has been adopted for the purpose of this work with minor modifications [44]. A *Retsch PM 100* ball mill and Zirconia balls of 5 mm diameter were used as the mill and milling media respectively. For composites involving ND and GO, only wet milling was carried out. For composite with UHMWPE and SCFs only, wet milling was carried out first with UHMWPE followed by drying process. Then SCF was added and dry milling was carried out. For composites involving SCF and GO and/or ND, wet milling was carried out with UHMWPE and GO and/or ND followed by drying. Then, SCF was added and dry milling was carried out. Flowchart in 2.1 shows the whole process in a simplified manner. Wet milling was carried out using 500 balls for 2 hours at 400 rpm while dry milling was carried out using 250 balls for 5 minutes at 100 rpm.

2.1.3 Drying

Once the required composition of the composite was milled, the slurry needed to be processed into fine powder so as to make it ready for moulding. The slurry straight out of the mill was dried inside a fume hood by transferring several times between two beakers. Between each transfer, as the ethanol evaporated, the powder left at the bottom of the beakers was collected. Care was taken to not leave any Zirconia balls in the collected powder. Once the material

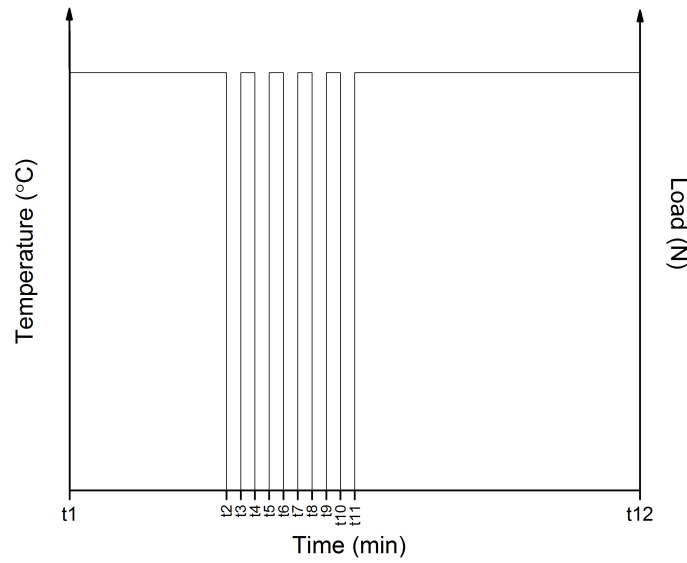


Fig. 2.3 DCM cycle

had been collected, it was left in an oven at 60°C for 24h to completely evaporate ethanol from the powder.

2.1.4 Direct Compression Moulding

As mentioned earlier, direct compression moulding is the most common process used to mould UHMWPE composites into required form and shape. Because of its ultrahigh molecular weight, the exceptionally high melt viscosity of UHMWPE leads to a gel state, making it nearly impossible to be processed by technologies such as screw extrusion, injection molding, etc.

For compression moulding of the composite materials in this work, a *Fontijne Presses LP 300 hot-press* was used. A 60mm × 60mm × 5mm mould, shown in figure 2.4a, was utilised to produce the samples in a cuboid form.

The mould was thoroughly cleaned off any residue from previous processes before being used. The amount of powder to be put into the mould was the volume of the mould plus 10% more to ensure that the mould was filled completely. This amounted to 18.6g of powder for each pressing step. 0.05mm thick Brass foil was placed between the mould base and top plates and the powder to prevent them from adhering to each other during moulding. The compression moulding was performed at 190°C for 70 minutes, under several short pressing cycles of 105 kN. The intervals of time in which the pressure was applied and removed is represented in figure 2.3.

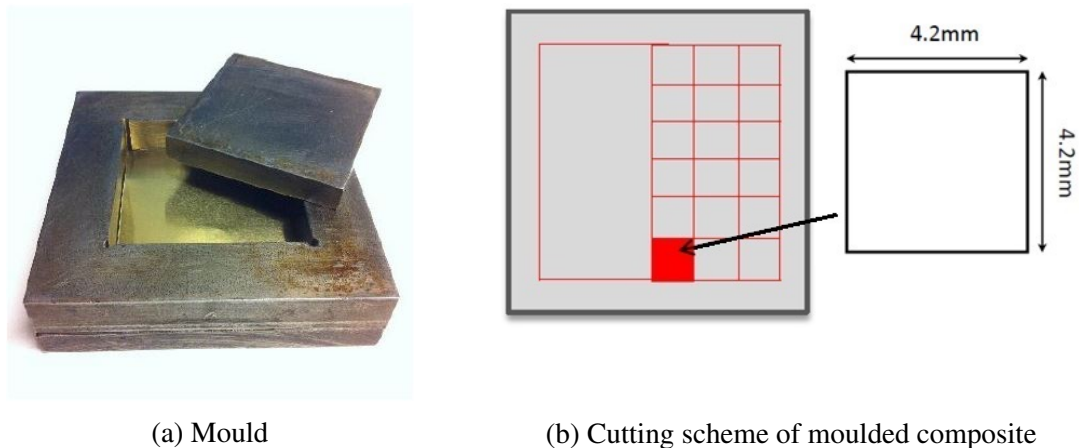


Fig. 2.4 Mould and Cutting scheme

2.2 Sample preparation

The moulded composites had to be prepared before being used in various analysis and tests. The composite blocks were cut into smaller pieces according to the scheme shown in figure 2.4b. The edges of the block had to be discarded as they had a slope and any measurement done on that part of the composite would not represent the true values. A large rectangular piece not exceeding a breadth of 15 mm was cut for use in contact angle and hardness measurements. The remaining block of the composite was cut into 30 pieces of $4.2 \times 4.2\text{mm}^2$. The edges of the cut pieces were ground using a manual grinding machine to make them suitable for use in analyses and tests.

2.3 Equipment and measurements

2.3.1 Pin-on-disc

A pin on disc tribometer (*TE67 Pin-on- Disc Tribometer, Phoenix Tribology, UK*) was used to investigate the frictional and wear behaviour of the composites. Inconel 625 discs were used as the counter surface as the material has excellent anti-corrosive properties. Before use in the tribometer, the discs were ground and rubbed against sandpaper in order to accelerate the tests. The grinding and sanding processes are thoroughly explained in appendix A. The choice of counter surface was made largely on the basis of its excellent anti corrosion properties. A simple schematic of the tribometer is shown in figure 2.5.

The tribometer was calibrated beforehand and the same calibration was used for all the tests. A load of 88N was applied on the composite specimens which measured $4.2 \times 4.2\text{mm}^2$

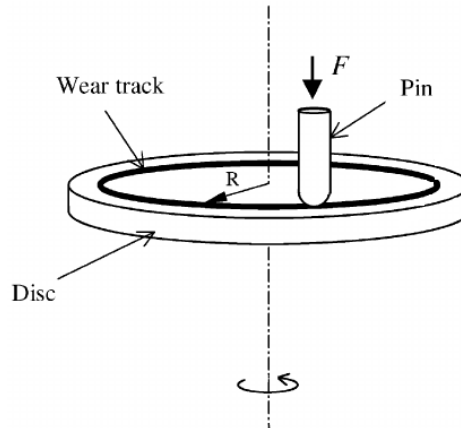


Fig. 2.5 Schematic of a pin-on-disc machine [52]

on the area of contact with the disc. The tests were ran for 20 hours each at a speed of 0.13 m/s. Each polymer composite was tested 4 times. A LVDT (linear variable differential transformer) sensor was used to measure the wear of the composites during the tests. During the tests, the contact surface of the polymer composites can experience wear or a transfer film can be formed on the counter surface causing minute changes in vertical position of the pin. These changes were recorded using the LVDT sensor. Friction and LVDT data was recorded every second for the whole test.

2.3.2 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry measurements were carried out using a *Mettler Toledo DSC* to analyse the crystallinity of the composites prepared. Samples for use in DSC measurements weighing approximately 10 mg were cut from the pre-cut pieces of the composites and loaded into non-hermetic aluminium pans. An initial heating and cooling cycle from 30°C to 200°C and back to 30°C was conducted to erase any thermal history. The heating and cooling rate was set at $10Kmin^{-1}$ and the samples were held at 200°C for 5 minutes. Once this had been done, the cycle was repeated with the same values to carry out the DSC measurement. The measurements were conducted under a continuous purge of Nitrogen while Liquid Nitrogen was used to accelerated the cooling process. The melting temperature could also be obtained from the measurements. The degree of crystallinity (X_c) of composites was calculated by using equation 2.1.

$$X_c = \frac{\Delta H}{\Delta H_{100}} \times 100\% \quad (2.1)$$

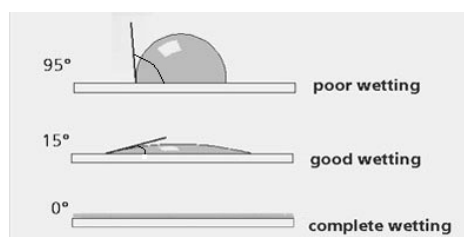


Fig. 2.6 Contact angles for hydrophobic and hydrophilic surfaces [53]

where, ΔH is the measured enthalpy of fusion of composites and ΔH_{100} is the enthalpy of fusion of 100 % crystalline PE which is estimated to 289 J/g. Each composite was measured thrice.

2.3.3 Wettability

Contact angle measurements were carried out to study the wettability of the composites. The water contact angles were determined using the sessile drop method in which 4 μL of distilled water was deposited on the surface of the samples and contact angle measurements were taken after one second. Each sample was measured at least 15 times.

2.3.4 Microhardness

Matsuzawa MXT- α microhardness tester was used to carry out measurements on the hardness of the composites prepared. Vickers method and indenter were used for the measurement. A load of 10g was applied for 15s and each composite was measured 10 times.



Fig. 2.7 Zygo NewView™ 7300

2.3.5 Optical profilometry

Zygo (NewView™ 7300, USA), a 3D optical surface profiler, shown in figure 2.7, was used to carry out topographic measurements on the Inconel discs. A 2.75x optical and an image zoom of 0.5x were used together with stitching application to analyse and image the topography of the discs. The scan length value was set at 150 μm . The analysis was carried both before and after the discs had been used in tribological tests. This helped study the wear track, transfer film and any other phenomena occurring during the tests.

2.3.6 SEM/EDS

The effect of the ball-milling process on the morphology of particles was investigated using a high resolution bench-top scanning electron microscope (JCM - 6000 Neoscope, Jeol).

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Results and discussions

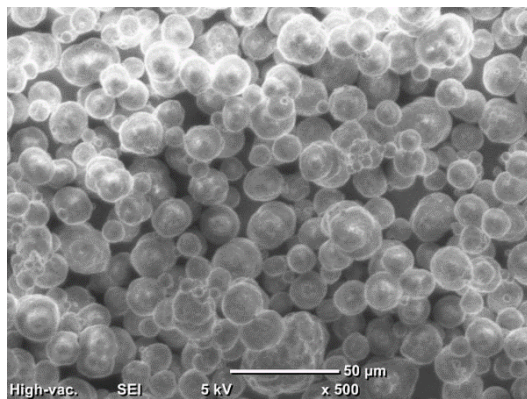
All the different results obtained from analyses and measurements are described in chapter 3. The primary aim was to investigate the tribological behaviour of the polymer composites prepared and correlate it with certain physical/material properties of the composites. The differences in these properties were the result of the different combinations of fillers used.

3.1 Morphology

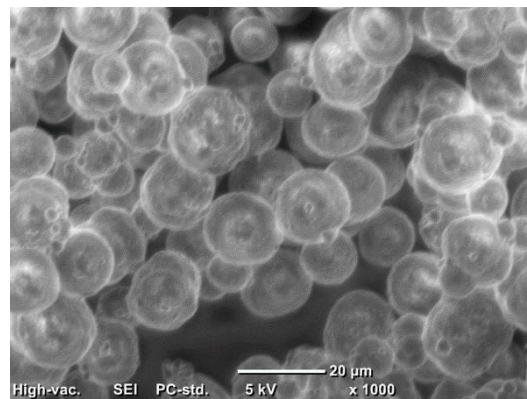
The virgin UHMWPE particles obtained had a diameter of approximately $30\mu\text{m}$. Figure 3.1 shows the SEM images obtained at different magnifications. The particles clearly have a spherical shape before being processed. The influence of using smaller UHMWPE particles (as compared to $140\mu\text{m}$ diameter sized particles used in other studies) will be discussed in further sections.

The processed particles shown in Figure 3.2 take a more disc like form. The particles have been flattened from their spherical shape which is evidence of plastic deformation occurring during processing. The ball milling process flattens the polymer particles. Although plastic deformation has occurred, the particles still hold together and have not been fragmented. In studies conducted on the influence of processing parameters on the UHMWPE particles, it has been shown that use of higher RPM results in fragmentation of the flattened particles [54–56]. The plastic deformation caused flattening also leads to an increase in the average size of the particles. The deformation may have an impact on the adhesion of UHMWPE particles with the fillers and consequently influence mechanical properties of the composites.

Processed composite powders containing the fillers had dimensions in between those of the particles shown in figure 3.1 and 3.2. While it was easier to image SCFs due to their relatively larger dimensions, comprehensible images of ND and GO could not be obtained. But, there is comprehensive research result available on the influence of processing

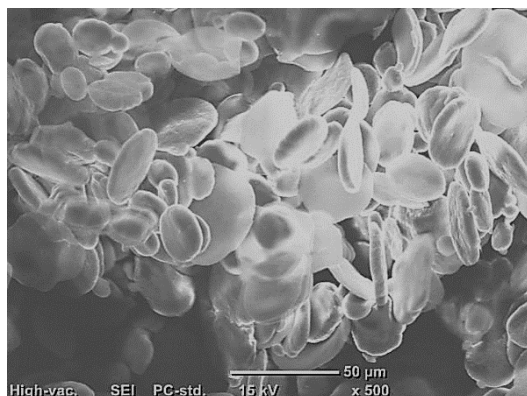


(a) 500x

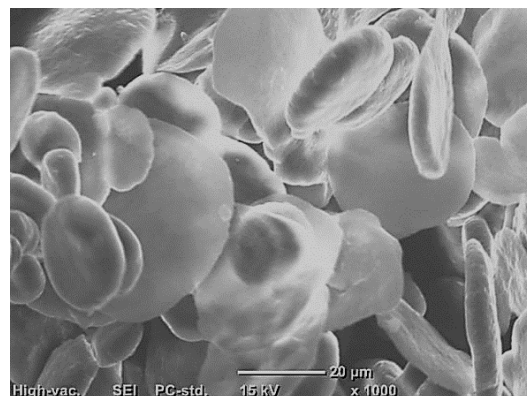


(b) 1000x

Fig. 3.1 SEM images of Pure UHMWPE powder (pre milling) at different magnifications

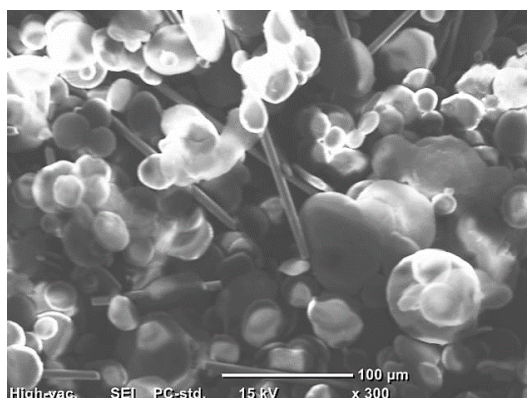


(a) 500x

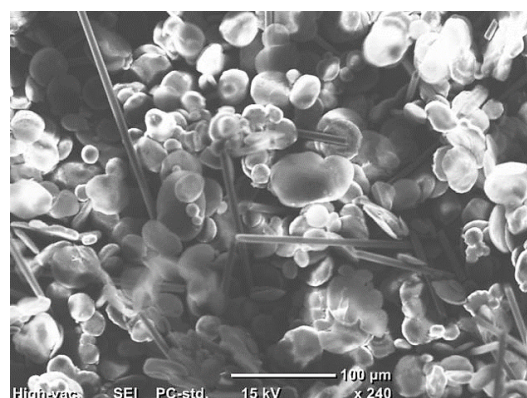


(b) 1000x

Fig. 3.2 SEM images of milled UHMWPE powder at different magnifications



(a) 10% SCF



(b) 0.5% GO + 0.5% ND + 10% SCF

Fig. 3.3 SEM images of (a) 10% SCF ; (b) GO + ND + SCF (both post milling)

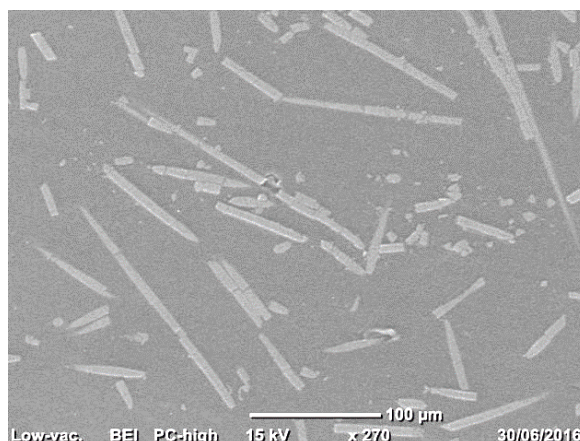


Fig. 3.4 10% SCF pin surface after pin on disc test (20 hours, water lubrication)

parameters on the dispersion of these fillers [50, 55]. We can assume with a measure of certainty that uniform dispersion of ND and GO in the polymer composite matrix has been obtained. Figure 3.3a shows a SEM image of 10% SCF composite powder while figure 3.3b shows the same for GO+ND+SCF composite. It can be noted that the dispersion of SCF is quite homogeneous. While it was feared that the SCFs may split into smaller pieces while undergoing milling, evidence from the SEM imaging points otherwise. The SCFs have held on to their shape and size. Therefore, from the evidence made available by SEM analysis and from research conducted, we can say that the correct processing parameters have been used for manufacturing the composites. The composites obtained have a good distribution of fillers in the matrix along with intact UHMWPE base polymer particles.

As mentioned, the polymer composite pin surfaces after pin on disc tests were also imaged. Figure 3.4 shows one such example. The 10% SCF pin surface clearly shows SCFs present on the surface, although split into smaller lengths when compared to SCFs in figure 3.3. Without a doubt, SCFs clearly take part in the tribological contact.

3.2 Tribological characterisation

3.2.1 Friction

Figure 3.5a shows the average friction coefficient values obtained for the polymer composites against Inconel surface under water lubrication (Pin on disc tests). The friction coefficient values for the last 5 hours of the 20 hour tests were averaged to obtain the values shown here. Each test run can be divided into two stages: a run-in and a steady state stage. The time taken by the tribological system to attain steady state could vary depending on various

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factors. Friction coefficient taken from the run-in stage is not a true representation of friction values as the contact has not yet achieved a stable state. As almost all the composites attain a steady state approximately 13 hours into the test, it was decided to use the values from the last 5 hours. The values show on the chart are the mean of the 4 tests carried out for each composite.

Taking the friction coefficient of virgin UHMWPE in figure 3.5a as the reference point, we can note that the use of smaller UHMWPE particles in this study has resulted in a lower friction coefficient. Research conducted earlier using composites of 140 μ m diameter UHMWPE particles and GO have given higher values of friction [45, 57]. Smaller particles translate to a better surface area to volume ratio which facilitates improved bonding between particles in the composites. Stronger bonds can enhance properties like hardness and crystallinity (as we will see in further sections). Although there is no straightforward relation between particle size and friction, we can say that the use of smaller particles improves various other properties of the material which in turn result in better tribological performance.

In general, addition of GO and/or ND seems to decrease the friction coefficient value. 0.5 wt% loading of these two fillers in the composite has been proven to be the optimal concentration [18, 45, 55, 58] in terms of wear rate and friction coefficient in water lubricated conditions. The improved tribological behaviour of UHMWPE upon incorporation of GO/NDs is mainly attributed to the lubricating action of the nano fillers in water lubricated sliding contacts. This is in accordance with the results obtained in several studies which attributed the friction reducing action of GO and NDs to their boundary lubricating characteristics. Inclusion has GO has shown to reduce the friction coefficient in tribological contacts [34, 57, 59, 60]. NDs on the other side, reduce friction by acting as nanoscale ball bearings between the two contacting surfaces. This transfers the sliding friction to rolling friction and prevents asperity to asperity contact [36, 39, 37]. By comparing 1%GO, 1%ND and GO+ND and the proximity of their friction coefficient values, we can conclude that the effect of the combination of these fillers at 0.5-0.5 wt% concentration is not due to the increased amount of nano fillers in the polymer matrix but solely due to their individual influence.

The composite combination of GO+ND+SCF shows the lowest friction coefficient value among all the composites tested. It can be proposed that a desired synergistic effect has occurred when using all the fillers together along with UHMWPE to form the composite. SCFs improve the mechanical properties of the composite while the nano fillers enhance the tribological performance. Also, all other composite combinations except 10%SCF and GO+SCF exhibit a lower friction coefficient value than virgin UHMWPE. The higher values for 10% SCF and GO+SCF can be attributed to the presence of SCFs on the pin surface and in the contact. The larger size of the SCFs may have a role to play in the increase of

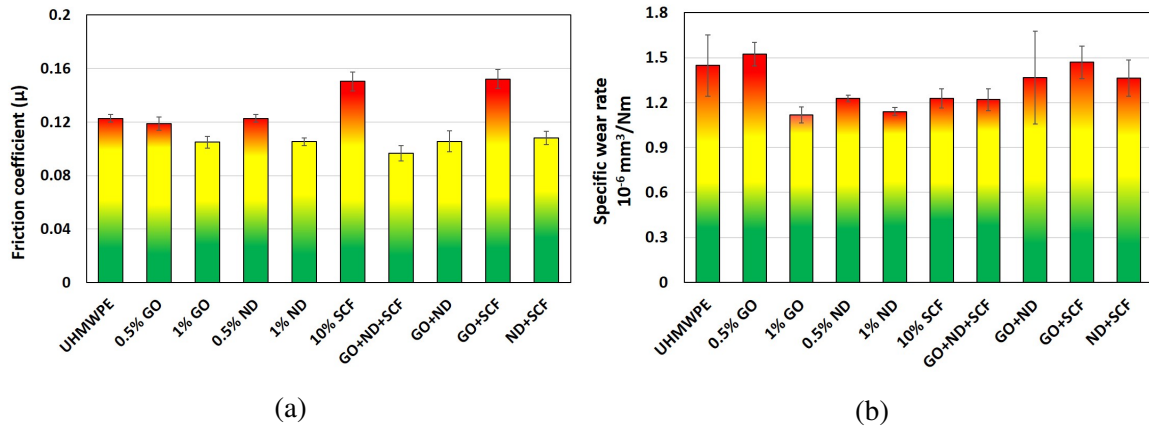


Fig. 3.5 (a) Friction coefficient and (b) Specific wear rate of the various polymer composites (colors indicate intensity gradient)

friction coefficient. SCFs present in the matrix protect the polymer surface but rub against the counter surface. Therefore, there is a trade-off in the mechanical and tribological properties of the composite when one uses SCFs as a filler. Although they may increase strength, they negatively influence friction values. One may argue that GO+SCF should have a lower value since GO has been used. But on closer inspection of the bar chart, it can be seen that the ND has a bigger positive influence on the friction coefficient than GO and SCF. While 10% SCF has a high value, composite ND+SCF has a value lower than even virgin UHMWPE.

3.2.2 Wear

The specific wear rate of the polymer composites was calculated using the data obtained from the LVDT sensor in the pin on disc tests. The wear volume per unit of load was plotted against distance for every data point. The slope of the resultant curve gave the specific wear rate of the polymer composite. The values shown on the chart in figure 3.5b are the mean of the 4 tests carried out for each composite.

Wear in a tribological contact is dependent on various factors. Much of these accountable for decrease in wear also help decrease friction in the contact. But, we should keep in mind that friction and wear do not always have a proportional relationship. In our results, all the composites exhibit a wear rate approximately similar to or less than virgin UHMWPE. The wear rates obtained from using $30 \mu\text{m}$ diameter UHMWPE particles in this work are less than the wear rates obtained when using bigger UHMWPE particles [57, 45]. The reasons for this are the same as the ones described in the preceding section for friction. A smaller particle size generally results in a material with better strength

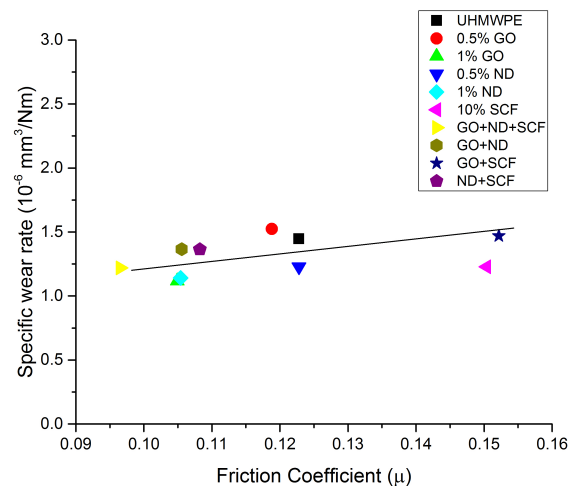


Fig. 3.6 Specific wear rate vs. μ for various composites

Inclusion of 1 wt% GO or ND into the composite has resulted in decreased wear rate compared to virgin UHMWPE. This is in accordance with results already obtained [31–34, 60, 61]. As mentioned in section 3.2.1, NDs are extremely hard particles and their presence in a contact prevents asperity to asperity contact. The extreme hardness of diamond allows it to have a very high wear resistance. Two-dimensional structure and good interfacial adhesion of GO to polymer particles enables a good stress transfer between GO sheets and the polymer matrix. Addition of anymore GO or ND has been proven to not improve the wear performance owing to aggregation of the filler material [44–46, 55]. Even though 10% SCF shows a high friction coefficient value in figure 3.5a, it's wear rate is relatively low. This is because SCFs in the matrix improve wear resistance by carrying the main load between contact surfaces while protecting the polymer surface from abrasion [23, 24, 26]. Composite GO+ND+SCF, which showed low friction coefficient value, again performs well, evident from its low specific wear rate value. All the three fillers have combined to improve the wear performance of the composite. They improve the material properties, enable better load distribution, prevent asperity to asperity contact and protect the polymer surface from abrasion. Crystallinity and wettability of the composites can also highly influence the wear rate. Influence of these two parameters will be discussed in further sections.

3.2.3 Relation between Specific wear rate and friction coefficient

Looking at the relation between friction coefficient and specific wear rate could shed a more clear light on the performance of the polymer composites. Figure 3.6 shows the relation

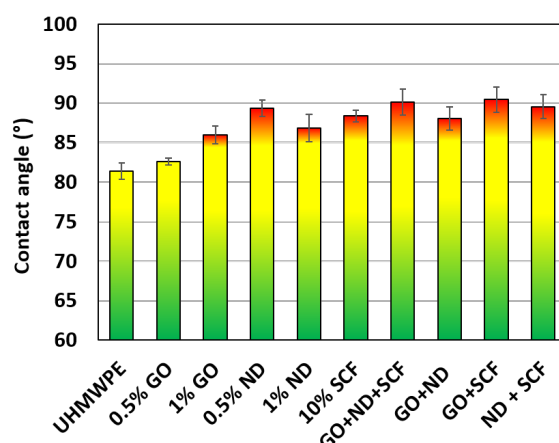


Fig. 3.7 Wettability of various composites

between the two. There is almost a linear correlation between the two parameters, indicated by the black line. While virgin UHMWPE has intermediate values, GO+ND+SCF, has both excellent wear rate and friction coefficient values. 1% ND and GO also exhibit good performance for both parameters. 0.5% GO has highest wear rate while having a moderate friction coefficient value. GO+SCF, whose wear rate is relatively moderate has high friction coefficient. As noted in earlier sections, 10% SCF has high friction coefficient but low wear rate values.

As we have pinned down the tribological performance of the composites, it is imperative that we take a closer look into the various properties responsible for such performance.

3.3 Wettability

The wettability of polymeric materials is one of the most important parameters affecting the tribological behaviour of polymer-metal material pairs in water lubricated contacts [15]. Increased hydrophobicity of the polymer can result in lower friction and wear. A hydrophobic character leads to the formation of a sufficient lubrication film as the lubricant tends to stay in the contact. A hydrophilic nature would mean affinity of water to the surface of the polymer causing it to spread out instead of forming a film in the contact. Hydrophobicity of UHMWPE is an important factor in low wear rate in metal-on-polymer and ceramic-on-polymer contacts. Thus, possible changes in wettability of the UHMWPE materials upon incorporation of the fillers were investigated.

We can observe from figure 3.7 that all composites show lower wettability i.e. higher contact angle values compared to virgin UHMWPE. Therefore, we can say that the addition

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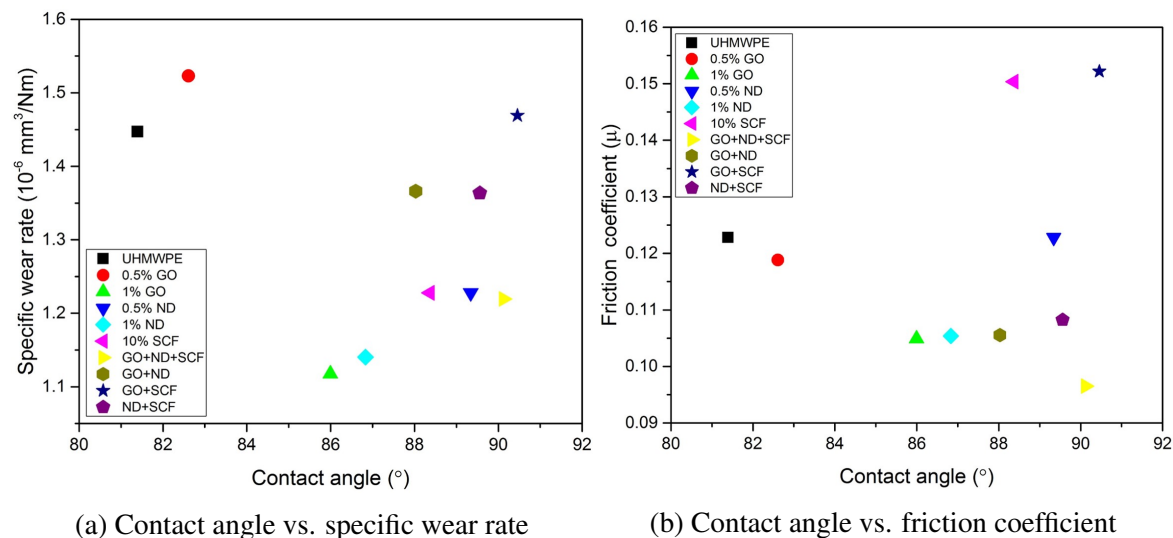


Fig. 3.8 Relation between contact angle, wear rate and friction coefficient

of fillers has caused the desired effect or at least has not increased wettability. An interesting point to be noted is that the use of smaller UHMWPE particles has enhanced the hydrophobic nature, unlike when 140 μ m was used. 140 μ m+GO resulted in improvement of wettability [55]. Composite with higher loading of GO has marginally higher hydrophobicity compared to 0.5 wt% GO in figure 3.7. This trend is reversed in the case of ND. The trend shown by GO agrees with results obtained in research already conducted[58]. GO+ND+SCF also exhibits good hydrophobic nature, evident from a 11% increase in contact angle values compared to virgin UHMWPE.

3.3.1 Relation between contact angle, wear rate and friction coefficient

Frictional behaviour of the polymers is determined by both their wettability and solubility in water, where generally an increased hydrophobicity and relative energy difference with regard to water results in lower friction. Therefore, it would be extremely useful to look at the correlation between wettability and tribological performance.

Figures 3.8a and 3.8b show the relationship between wettability of the polymer composites and specific wear rate and friction coefficient values respectively. In the former, most of the composites with high contact angle values have lower wear rates. GO+ND, GO+SCF and ND+SCF, which are the exceptions, still have a wear rate lower than that of virgin UHMWPE. 0.5% GO is the only composite with wear rate higher than virgin UHMWPE.

Although there is no clear trend in the relation between wettability and friction coefficient values, we can see that most of the composites show lower friction coefficient values than

virgin UHMWPE. The only exceptions are 10% SCF and GO+SCF. As discussed earlier, SCFs, due to their large size, rub against the contact surfaces, leading to a higher friction coefficient. GO+ND+SCF occupies a respectable position in both the charts. While having good hydrophobic nature, it exhibits the lowest friction coefficient and has low specific wear rate.

3.4 Crystallinity

The crystallinity of a semi-crystalline polymer is inversely related to the amount of amorphous regions available in the polymer matrix. Therefore an increased degree of crystallinity can potentially reduce the susceptibility of a polymer to water absorption and the consequent adverse effects. Also, improved crystallinity will result in a stronger material with better physical properties. Inclusion of fillers can have a mixed effect on crystallinity of the composite. If the filler content is not optimum, it can act as obstacles for crystallisation.

For the composites used in this work, while the change in crystallinity on the inclusion of fillers is not large, there are some interesting observations to be made. Use of larger $140\mu\text{m}$ diameter UHMWPE particles had resulted in lower crystallinity values than the ones seen here [45, 50, 57, 62]. Crystallinity was observed to improve with the addition of small loading (0.5 wt%) of GO and ND. The filler particles act as nucleation sites for crystallisation to occur. But, increasing the content of the fillers decreases the mobility of the polymeric chains resulting in a negative effect on crystallinity [31, 59]. The effect of addition of ND is less pronounced than that of GO or SCF. The tiny size of ND filler particles do not influence

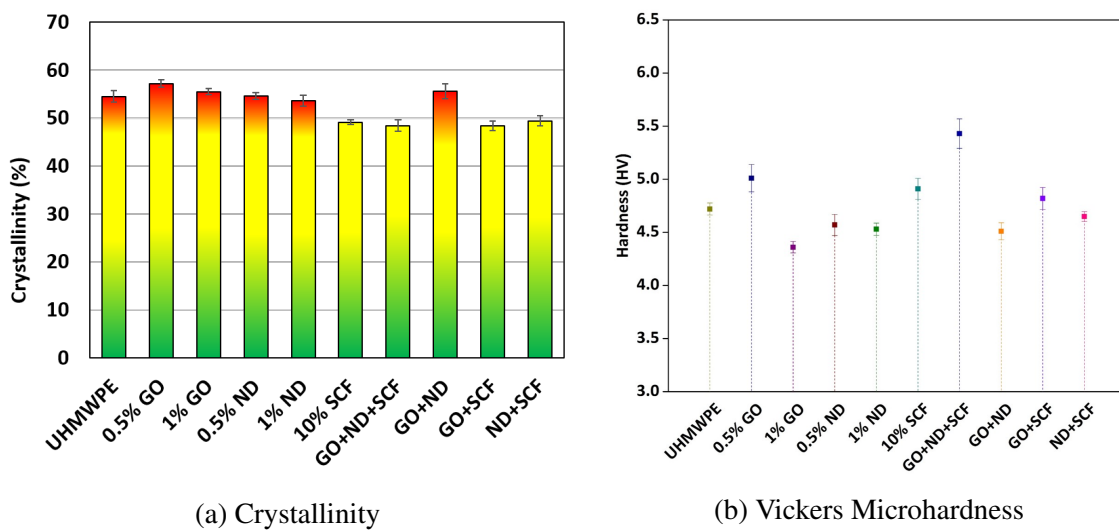


Fig. 3.9 Crystallinity and Microhardness of composites

the crystallisation process to a great extent. Composites having SCF as the only or one of the fillers exhibit a lower crystallinity value. This can be attributed to the fact that SCFs have a size in the micro-meter range and consequently hinder the formation of long chains of polymer in the composites. GO+ND+SCF, which has performed well in all other tests here, exhibits a crystallinity values less than that of virgin UHMWPE. This is mainly due to the presence of SCFs as composite GO+ND shows good crystallinity.

3.5 Microhardness

Figure 3.9b shows the Vickers microhardness values obtained for the polymer composites. GO+ND+SCF again performs well, having a 14% increase in hardness compared to virgin UHMWPE. While the addition of lower concentrations of GO and ND does not affect the crystallinity negatively, higher concentrations do. This may be due to the result of aggregation of filler materials, enough to affect the hardness of the composite. With increase in quantity, it progressively becomes harder to obtain a homogeneous solution during the fabrication process. Addition of SCFs seems to have a positive influence on the hardness of composites. On the other hand, NDs do not affect the hardness significantly just as they do not affect the crystallinity.

Chapter 4

Conclusion

In this study, newly developed composites with UHMWPE as base polymer were manufactured and their tribological performance in water lubricated tribological contact was investigated. Three different fillers, namely Graphene oxide, Nano-diamonds and Short carbon fibres were used and it was expected that composites with combinations of these fillers will exhibit improved tribological performance. Also, the effect of inclusion of fillers on the material properties of the composites was investigated. The conclusions drawn from this body of work are listed below.

- The manufacturing process for these composites were optimised. While a part of the process was adapted from an earlier research work, inclusions of SCFs posed a new challenge. Various manufacturing pathways were tried and tested before narrowing down on a particular process. The composites prepared did not show aggregates or clusters of fillers in the bulk.
- Friction and wear
 - 10% SCF+UHMWPE composite showed relatively higher friction coefficient values but not wear. Moreover, upon SEM analysis, SCFs were visible on the surface of the worn polymer pins. Therefore, we can conclude that the presence of SCFs protect the polymer from abrasion and consequent wear. The rubbing of the SCFs against the counter surface leads to increase in the friction but their presence protects the polymer pins from wear. Inclusion of SCFs leads to a trade-off in properties of the composite.
 - Addition of GO and ND had a positive influence on friction coefficient and specific wear rate of the composites. Inclusion of these fillers resulted in lower values for both parameters.

Conclusion

- The influence of NDs was found to be greater than that of GO and SCFs. It is hypothesised that NDs, once in the contact, can act as miniature ball bearings. As they are quite hard, they reduce wear and friction by preventing asperity to asperity contact. While GO and SCFs help in their own way, the influence of NDs is far greater
 - Composite GO+ND+SCF exhibited both low friction coefficient and specific wear rate. The inclusion of all three fillers has resulted in a synergistic effect causing improvement in the properties of the composite.
- Wettability
 - The addition of fillers has had the desired effect on the wettability of the composites. While there exist various opinions on the influence of wettability on tribological performance, we have chosen to follow the theory that a lower wettability would translate to a better lubrication film formation between the contact surfaces. A better film would mean reduction in friction coefficient or specific wear rate or both, All of the composites here displayed a more hydrophobic nature compared to virgin UHMWPE.
 - The loading of 1wt% ND resulted in a higher wettability compared to 0.5wt% ND. NDs used here have hydrophilic functional groups on their periphery. Therefore, addition of more ND would have resulted in increase in wettability and therefore is not recommended.
 - On looking at the relation between wettability and tribological performance, we could clearly conclude that composite GO+ND+SCF is one of the best performing composite having low wear and lowest friction coefficient with good hydrophobic nature.
 - Crystallinity
 - Lower loading of GO and ND did not seem to affect crystallinity negatively. At low concentrations, they act as nucleation sites for crystallisation from where the formation of polymer chains takes places. But, at higher concentrations, they act as barriers and hinder crystallisation.
 - The loading of SCFs used in this work affect crystallinity negatively. All the composites that include SCFs as one of the fillers have lower crystallinity than the rest of the composites. SCFs, due to their larger size, hinder the formation of long chains of polymer in the matrix.

- Microhardness

- While addition of SCF has a positive effect on the hardness of the composite, inclusion of ND does not seem to cause any difference. Owing to the hard nature of NDs, one may assume that their inclusion will lead to higher value of hardness. On the contrary, due to the extremely small size of the ND particles, they do not lead to an increase in hardness.
- Composite GO+ND+SCF shows a 14% increase in Hardness compared to virgin UHMWPE, highest among all the composites tested. This bodes well for the composite as it has performed well on other tests too.

In retrospect, the possibility of forming a hybrid composite to be used as tribological material in water loaded applications has been investigated. Composite GO+ND+SCF has performed exceedingly well in all the measurements and tests conducted and is an exciting prospect for further research. Nano sized fillers like GO and ND offer more surface area for interaction while SCFs strengthen the composite material. Therefore, a synergistic effect is obtained in the composite material. Also, the use of smaller polymer particles as the base material for the composite has led to material with better properties and tribological performance. The principle here is the same as that of nano fillers. All the fillers used combine well with the UHMWPE particles to form the composites. Their effect on properties of the composite and tribological performance both individually and in combinations have been studied.

Chapter 5

Future work

Although extensive study has been carried out on the composites in this study, there are still areas to which future work can be directed.

- Incorporation of carbon based nano particles in the polymer matrix can influence the thermal stability of the polymer matrices. Therefore in order to investigate the possible changes in the thermal stability of the UHMWPE matrix upon incorporation of the fillers, Thermo-Gravimetric Analysis (TGA) needs to be carried out.
- Physical and mechanical properties like Young's modulus and yield stress of the composites could help shed more light on their performance and help find ways to improve the materials. Therefore, these tests are recommended for the immediate future.
- Various other fillers can be considered to be included into the composites. Careful study and literature review needs to be carried out to determine the feasibility of including other fillers.
- The pin on disc tests for this work were limited to 20 hour durations. It would be interesting to conduct longer tests and evaluate the performance of the composites.
- Looking at the counter surface could prove very valuable. Information of what kind of mechanisms occur in the tribological contact can be obtained. Polymers tend to form transfer layers on the counter surface which help reduce friction and wear. Analysing the counter surface could help us form a more definite picture on the performance of the composites.

Future work

- Studies on the effect of ageing on the composites were not possible in this work due to the short time frame. Therefore, ageing studies on the composites are very much necessary.
- While the composites need to have good ageing characteristics, it is also necessary that they have a good shelf life. There are subtle differences between ageing of the composites and shelf life. While life span tests requires study of wear and tear on the component, shelf life test would depend on entirely different parameters.

References

- [1] E. Rabinowicz. *Friction and wear of materials*, 2nd ed. Wiley, New york, 1995.
- [2] M. Narkis W. Brostow, H.E. Hagg Lobland. Sliding wear, viscoelasticity, and brittleness of polymers. *J. Mater. Res*, 21(9):2422–2428, 2006.
- [3] S. R. Wisner W. Brostow, D. Pietkiewicz. Polymer tribology in safety medical devices: Retractable syringes. *Adv. Poly. Tech*, 26(1):56–64, 2007.
- [4] L.D.C. Georgescu. Water lubrication of ptfe composites. *Industrial Lubrication and Tribology*, 67(1):1–8, 2015.
- [5] J.K. Lancaster. Lubrication of carbon fiber-reinforce polymers. *Wear*, 20(3):315–333, 1972.
- [6] D. Tabor S.C. Cohen. The friction and lubrication of polymers. *Proc. Roy. Soc. A*, 291:186–207, 1966.
- [7] A.S. Cattaneo P. Mustarelli E. Quartarone S. Angioni, D.C. Villa. Influence of variously functionalized sba-15 fillers on conductivity and electrochemical properties of pbi composite membranes for high temperature polymer fuel cells. *Journal of Power Sources*, 294:347–353, 2015.
- [8] R. Salgado M.P. Balandin S. Ramirez M. Saadah F. Kargar A.A. Balandin J. Renteria, S. Legedza. Magnetically-functionalized self-aligning graphene fillers for high-efficiency thermal management applications. *Cornell Univeristy*, 2015.
- [9] Guido KICKELBICK. *Hybrid Materials. Synthesis, Characterization, and Applications : Introduction to Hybrid Materials*. Wiley, Weinheim, 2007.
- [10] K. Liao M. M. Thwe. Durability of bamboo-glass fiber reinforced polymer matrix hybrid composites. *Composites Science and Technology*, 63(3-4):375–387, 2003.
- [11] T. Nguen Suanb L. R. Ivanovaa M. A. Korchaginc S. V. Shilkod Yu. M. Pleskachevskiid S. V. Panina, L. A. Kornienkoa. Wear resistance of composites based on hybrid uhmwpe-ptfe matrix: Mechanical and tribotechnical properties of the matrix. *Journal of Friction and Wear*, 36(3):249–356, 2015.
- [12] M. N. Ramdziah Bt C. Boon Peng, M. A. Hazizan. The effect of zeolite on the crystallization behaviour and tribological properties of uhmwpe composite. *Adv. Mat. Res.*, 812:100–106, 2013.

References

- [13] C. Yang X. Kang, W. Zhang. Mechanical properties study of micro- and nano-hydroxyapatite reinforced ultrahigh molecular weight polyethylene composites. *J. of App. Poly. Sci.*, 133:1–9, 2016.
- [14] S. Sankaranarayanan A. Erdemir A. V. Sumant D. Berman, S.A. Deshmukh. Macroscale superlubricity enabled by graphene nanoscroll formation. *Science*, 348, 2015.
- [15] S. Glavatskih B. Prakash A. Golchin, G.F. Simmons. Tribological behaviour of polymeric materials in water-lubricated contacts. *Proceedings of the Institution of Mechanical Engineers Part J-Journal of Engineering Tribology*, 227:811–825, 2013.
- [16] M. Chanda. *Plastics technology handbook*. Taylor and Francis group, Florida, 2006.
- [17] S. Kurtz. *UHMWPE Biomaterials Handbook, 3rd Edition*. Academic press, 2009.
- [18] N. Gowland J. L. Tipper N. Emami S. Suñer, C. L. Bladen. Investigation of wear and wear particles from a uhmwpe/multi-walled carbon nanotube nanocomposite for total joint replacements. *Wear*, 317:163–169, 2014.
- [19] K. G. Plumlee C. J. Schwartz. Porous uhmwpe scaffolds impregnated with bio-derived materials: A new class of orthopaedic material. *Wear*, 267:710, 2009.
- [20] D. G. Li S. Y. Li. Bio-inspired polydopamine functionalization of carbon fiber for improving the interfacial adhesion of polypropylene composites. *Mater. lett.*, 134:99, 2014.
- [21] [Online] Polymer science learning center of University of southern Mississippi. Making carbon fibre, retrieved from <http://pslc.ws/macrog/carfsyn.htm>, 2005.
- [22] J. G. Morley. *High-Performance fibre composites*. Academic Press, 1987.
- [23] K. S. Novoselov. Electric field effect in atomically thin carbon films. *Science*, 306:666–669, 2004.
- [24] Q. Zhao R.K.K Yuen R.K.Y. Li H. Quan, B. Zhang. Facile preparation and thermal degradation studies of graphite nanoplatelets (gnps) filled thermoplastic polyurethane (tpu) nanocomposites. *Compos Part A*, 40:1506–1513, 2009.
- [25] Tony McNally, Peter Boyd, Caroline McClory, Daniel Bien, Ian Moore, Bronagh Millar, John Davidson, and Tony Carroll. Recycled carbon fiber filled polyethylene composites. *Journal of Applied Polymer Science*, 107(3):2015–2021, 2008.
- [26] D. I. Chukov. Investigation of structure, mechanical and tribological properties of short carbon fiber reinforced uhmwpe-matrix composites. *Composites Part B: Engineering*, 76:79–88, 2015.
- [27] A. Rusinek A. Arias D. Garcia-Gonzalez, M. Rodriguez-Millan. Investigation of mechanical impact behavior of short carbon-fiber-reinforced peek composites. *Composite Structures*, 133:1116–1126, 2015.
- [28] [Online] TCI chemicals. Graphene and graphene oxide (nanocarbon materials), retrieved from <http://www.tcichemicals.com>.

- [29] [Online] Jesus de La Fuente. Graphene oxide - what is it? retrieved from <http://www.graphenea.com/pages/graphene-oxide>, 2016.
- [30] C. W. Bielawski R. S. Ruoff D. R. Dreyer, S. Park. The chemistry of graphene oxide. *Chemical Society Reviews*, 39(1):228–240, 2010.
- [31] G. M. Chen G. D. Huang H. D. Huang Y. W. Zhao W. C. Pang, Z. F. Ni. Mechanical and thermal properties of graphene oxide/ultrahigh molecular weight polyethylene nanocomposites. *Rsc Advances*, 5:63063–63072, 2015.
- [32] S. Y. Fu K. Friedrich X. J. Shen, X. Q. Pei. Significantly modified tribological performance of epoxy nanocomposites at very low graphene oxide content. *Polymer*, 54(3):1234–1242, 2013.
- [33] S. Lee J. Jang K. Y. Shin, J. Y. Hong. Evaluation of anti- scratch properties of graphene oxide/polypropylene nanocomposites. *J. Mater. Chem.*, 22(16):7871–7879, 2012.
- [34] Y. F. An X. B. Yan Q. J. Xue Z. X. Tai, Y. F. Chen. Tribological behavior of uhmwpe reinforced with graphene oxide nanosheets. *Tribol. Lett.*, 46(1):55–63, 2012.
- [35] [Online] Robert A. Freitas Jr. How to make a nanodiamond: A simple tool for positional diamond mechanosynthesis, and its method of manufacture, retrieved from <http://www.kurzweilai.net/how-to-make-a-nanodiamond-a-simple-tool-for-positional-diamond-mechanosynthesis-and-its-method-of-manufacture>, 2006.
- [36] Y. Gogotsi V. N. Mochalin, O. Shenderova. The properties and applications of nanodiamonds. *Nature nanotechnology*, 7(1):11–23, 2012.
- [37] K. D. Behler. Nanodiamond–polymer composite fibers and coatings. *ACS Nano*, 3:363–369, 2009.
- [38] G. Galli. *Computer-Based Modelling of Novel Carbon Systems and Their Properties*. Springer, Florida, 2010.
- [39] D. Ivanov I. Petrov O. Shenderova M. G. Ivanov, S. V. Pavlyshko. Synergistic compositions of colloidal nanodiamond as lubricant-additive. *J Vac. Sci. Technol.*, 28:869–877, 2010.
- [40] M. Takahashi F. Kataoka A. Krueger E. Osawa M. Ozawa, M. Inaguma. Preparation and behavior of brownish, clear nanodiamond colloids. *Adv. Mater*, 19:1201–1206, 2007.
- [41] C. N. R. Rao. Mechanical properties of nanodiamond-reinforced polymer-matrix composites. *Solid State Commun*, 149:1693–1697, 2009.
- [42] D. S. Lim J. Y. Lee, D. P. Lim. Tribological behavior of ptfe nanocomposite films reinforced with carbon nanoparticles. *Composites B.*, 38:810–816, 2007.
- [43] H. Dillo A. Krueger T. Mainhardt, D. Lang. Pushing the functionality of diamond nanoparticles to new horizons: Orthogonally functionalized nanodiamond using click chemistry. *Adv. Funct. Mater.*, 21:494–500, 2011.

References

- [44] S. S. Moreno. *Nanodiamond/Ultra-High Molecular Weight Polyethylene Composites for Bearing Applications*. PhD thesis, Luleå University of Technology, 2014.
- [45] A. Villain. Nanodiamond/ultra-high molecular weight polyethylene composites for bearing applications. Project course, Division of Machine Elements, Luleå University of Technology, 2015.
- [46] N. Gowland J. L. Tipper N. Emami S. Suñer, C. L. Bladen. *Ultra high molecular weight polyethylene/graphene oxide nanocomposites: wear characterisation and biological response to wear particles*. PhD thesis, Luleå Technical University, 2014.
- [47] G.X. Sui R. Yang Y.J Zhong, G.Y. Xie. Poly(ether ether ketone) composites reinforced by short carbon fibers and zirconium dioxide nanoparticles: Mechanical properties and sliding wear behavior with water lubrication. *J Appl Poly Sci*, 119:1711–1720, 2011.
- [48] T. Yu S. Ruan, P. Gao. Ultra-strong gel-spun uhmwpe fibers reinforced using multi-walled carbon nanotubes. *Polymer*, 47(5):1604–1611, 2006.
- [49] S. Peng D.X. Yan J.F. Gao, Z.M. Li. Temperature-resistivity behaviour of cnts/uhmwpe composites with a two-dimensional conductive network. *Poly.-Plast. Tech. and Eng.*, 48(4):478–481, 2009.
- [50] E. Enqvist. *Carbon Nanofiller Reinforced UHMWPE for Orthopaedic Applications*. PhD thesis, Luleå University of Technology, 2013.
- [51] E. K. Goharshadi M. Abareshi, S. M. Zebarjad. Study of the morphology and granulometry of polyethylene – clay nanocomposite powders. *Journal of Vinyl and Additive Technology*, 16(1):90–97, 2010.
- [52] [Online] ResearchGate. Numerical study of sliding wear caused by a loaded pin on a rotating disc, retrieved from <https://www.researchgate.net/245110694>.
- [53] [Online] Teach Engineering. Contact angles for hydrophobic and hydrophilic surfaces, retrieved from <https://www.teachengineering.org>.
- [54] S. S. Moreno. *Carbon Reinforced UHMWPE Composites for Orthopaedic Applications*. PhD thesis, Luleå University of Technology, 2013.
- [55] N. Emami S. Suñer. Investigation of graphene oxide as reinforcement for orthopaedic applications. *Tribology-Materials, Surfaces Interfaces*, 8(1):1–6, 2012.
- [56] V. Martínez-Nogués M. J. Martínez-Morlanes, P. Castell. Effects of gamma-irradiation on uhmwpe/mwcnt nanocomposites. *Composites Sci Technol*, 71(3):282–288, 2011.
- [57] N. Emami A. Golchin, A. Wikner. An investigation into tribological behaviour of multi-walled carbon nanotube/graphene oxide reinforced uhmwpe in water lubricated contacts. *Tribology International*, 95:156–161, 2016.
- [58] V. Laporte. Go / uhmwpe nanocomposites for bearing applications: Preparation and characterization. Project course, Division of Machine Elements, Luleå University of Technology, 2015.

- [59] M. Shafiee-A. Kheradmand H. Bahrami, S. A. A. Ramazani. Preparation and investigation of tribological properties of ultra-high molecular weight polyethylene (uhmwpe)/graphene oxide. *Bull. London Math. Soc.*, 17:305–317, 1985.
- [60] Y. Qi X. Yan-B. Liu Q. Xue J. Pei Y. An, Z. Tai. Friction and wear properties of graphene oxide/ultrahigh-molecular-weight polyethylene composites under the lubrication of deionized water and normal saline solution. *Journal of Applied Polymer Science*, 131(1), 2014.
- [61] A. Kausar M. Ullah. Reinforcing effects of modified nanodiamonds on the physical properties of polymer-based nanocomposites: A review. *Polymer-Plastics Technology and Engineering*, 54(8):861–879, 2015.
- [62] J.L. Tipper N. Emami S. Suner, R. Joffe. Ultra high molecular weight polyethylene/graphene oxide nanocomposites: Thermal, mechanical and wettability characterisation. *Composites Part B Engineering*, 78(1):185–191, 2015.

Appendix A

Preparation of the Inconel discs

The Inconel discs were ground using P240 sand paper on a *Buehler MetaServ 250 twin grinder-polisher*(Figure A.1(a)) until a consistent homogeneous finish was obtained on the surface of the discs with the grinding marks pointing in a single direction . Subsequently, the discs were ground against P120 sand paper manually (Figure A.1(c)). A metal block was used to provide uniform load on the discs (Figure A.1(b)). Each disc was sanded 30 times on one half of the sand paper and 50 times on the other resulting in a total of 80 repetitions. The disc along with the metal block was rotated along the vertical axis between each move.

The logic behind this whole process was to obtain discs that had the approximately the same surface characteristics and had been aged in the same manner so as to accelerate the Pin-on-disc tests.

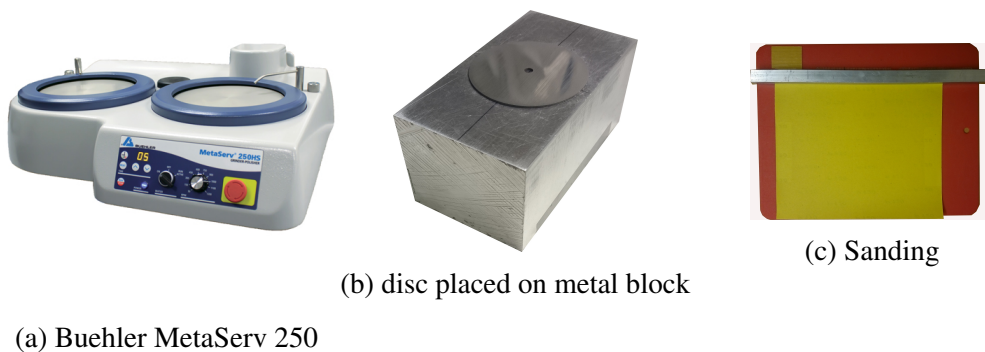


Fig. A.1 Preparation of Inconel Discs

