Towards faster skis:

The development of new surface modifications and treatments to reduce overall friction in alpine skiing.

A dissertation submitted to

The University of Sheffield

Department of Chemical and Biological Engineering

For the degree of

Doctor of Philosophy in Snowsports Engineering

Presented by

Richard C Coupe

October 2013

Abstract

Developments in sport technology have been driven by competition and skiing is no exception. Skiing has evolved over many years making use of new materials and post-treatments methods, but in recent years progress has been limited. The low friction exhibited when sliding over snow and ice is governed by the tribological interaction between ski base and snow and the subsequent accumulation of a thin melt water film. The properties of new, innovative, blended ski base materials and post-treatment methods have been investigated using a range of methodologies. The incorporation of fluorinated hydrophobic silica nanoparticles into current ski waxes has been achieved. These nanoparticles have also been used as nano-abrasives to modify the physical surface structure of a ski base composed of ultra-high-molecular-weight polyethylene (UHMW-PE). Such polyethylene samples were also subjected to other physical treatment methods including abrasion with 120 grit, 800 grit sandpapers and 10-15µm silica particles combined with surface planing. The resultant surfaces were examined under a scanning electron microscope, contact angle tested and friction tested. The surface treatments which tended to be both physically and chemically hydrophobic were found to be beneficial at reducing friction in warm and wet snow conditions (snow temperature above -2°C). The addition of carbon black to UHMW-PE was also found to be beneficial in reducing static friction on snow. This was an interesting finding as the unmodified UHMW-PE was shown to be slightly more hydrophobic than UHMW-PE with added carbon from the contact angle evidence. Additionally, the visibly finer surface refinements with micro-scale to nano-scale features were also found to be more beneficial at reducing friction. A hydrophobic fumed silica, polydimethylsiloxane (PDMS), and perfluoropolyether (PFPE) were both blended with UHMW-PE to chemically modify the bulk material in contrast to traditional surface modification with hydrocarbon wax. PFPE, in particular, has been successfully blended with UHMW-PE to produce a novel base material for a downhill ski. Subsequent glide testing of skis, manufactured with this base material, in a range of conditions, demonstrated that the blended white base material closely matched the performance of skis with the current downhill black base material. The new blends also matched a hydrocarbon-waxed surface for hydrophobicity and were also found to be resistance to carbon coating at 5% levels of loading. Combined with the surface planing and nano scale abrasive structuring methods previously described, this novel base material has the potential to either compete or be a compliment to current wax treatment methods in order to achieve the small reductions of friction required to be successful in an alpine race.

Table of contents

List of figures

List of tables

List of symbols

μ	Coefficient of friction
N	Normal force perpendicular to that of the plane
f	Frictional drag force
COF	Coefficient of friction (COF)
μ plow	COF snow compaction and plowing (ploughing)
μ dry	COF due to snow compaction
μ wet	COF due to the resistance of melt water
μ cap	COF due to capillary attraction
μ dirt	COF due to surface contamination
Ac	Actual contact area
ai	Individual contact area
FN	Normal force exerted by the skier
a	Air component
w	Water component
b	Ski base component
γ	Surface Tension
σ	Compressive strength
l	Length
Δz	Change in height
Fcomp	Force due to compaction
μc	COF due to the compaction of the snow
τ	Shear strength
Fdry	Dry frictional force
β	Coatings constant

H	Hardness
Fplow	Force due to plowing
w	Width
p	Density
v	Velocity
QDry	Heat effect in dry regime
Qwet	Heat effect in wet regime
t0	Starting temperature
ΔT	Change in temperature
λ	Thermal conductivity
Cp	Specific heat capacity
Λ	Non-dimensional film parameter
Rqbs	Root mean square roughness of the ski base
Rqsn	Root mean square roughness of the snow surface
hwf	Height of water film
D	Contact sport Diameter
t	Time
η	Viscosity
AW	Wetted film contact area
Re	Reynolds number

Acknowledgements

I would like to express my gratitude to my main supervisor Professor Peter Styring for providing me with the opportunity to continue to follow my passion for snowsports and directing it towards scientific research. I must thank you for the guidance, belief and support which has allowed me to write this thesis as well as for the enthusiastic and interesting discussions about skiing and snowsports. In addition, I would like to thank Dr Jon Howse, my second supervisor, for his valuable suggestions and for always keeping me on my toes.

I would not have developed such a passion for snowsports were it not for my parents, Chris and Alan Coupe. They got me in to skiing at such a young age, and I thank them for having the patience and commitment to guide me from my first snow ploughs at the age of age three, though to racing and competing at an international level. This dedication has continued throughout my university life with the provision of much advice and financial support, as well as many long, patient phone calls, discussions and proof readings. In addition to this they pushed me to gaining my instructor and race coaching qualifications, which has provided me with such a valuable insight into the snowsports industry. I dedicate this thesis to both of you, for having complete, unconditional faith in me from the moment you brought me into this world.

I wish to thank our industrial partner Atomic, Austria GmbH of the Amer Sports Group, for the interesting collaboration. Special thanks are due to Peter Pechhacker for showing us how manufacturers test and rate World-Cup Skis using a glide testing method and for including our treatments in this program. Sharing our ski base treatments with you has been a pleasure in the pursuit to discover the new ‘World-Cup secrets’.

Acknowledgements and thanks are also given to the technicians at Sheffield University Chemical and Biological Engineering Department for their advice and guidance, but also their patience when a 1.5 ton steel ski press was constructed practically in their doorway. Special thanks must also to go to my to all my university housemates, throughout this PhD course, for putting up with all the skis, equipment and my eccentricities, and for allowing me to convert a whole cellar into a ski workshop- with all the late night construction, dust and noise associated with routing over 200 individual pieces of wood for this project. Thank you for the cups of tea, the interesting scientific and mechanical engineering discussions, the enforced breaks and the banter. I’ll never forget it!

Thanks must also go the many companies who have also supported this research with materials and advice. These include Ticona for the UHMW-PE, Evonik for the Aerosil nanoparticles, Creative plastic solutions (CPS) for the ski base and top sheet materials, Formax for the Carbon fibre reinforcements, Dow Corning for the PDMS and 3M for the polyurethane adhesive.

Without all the people and friends I’ve met along the way and many more I haven’t mentioned, such an undertaking would not have to been possible. I express my gratitude and thanks to you all.

“Glory lies in the attempt to reach one's goal and not in reaching it”

Mahatma Gandhi

Chapter [1]   Introduction

The primary aim of this thesis is to explore new approaches which may allow skis to go faster. Ever since competitive skiing began over 90 years ago this has been a driving force for athletes, designers, scientists, engineers and manufacturers. Whilst there have been significant advances over this time, particularly in ski design, some of the current practice in ski base preparation and treatment is in need of re -appraisal.

The fundamental starting point of any approach to improve the performance of skis in an alpine environment must be the treatment of the sliding friction of a ski base surface on snow as a tribological interface. This interface is a complex system not least because snow varies and metamorphoses over time, depending on a variety of environmental conditions. Critical to an understanding of sliding friction on ice or snow is an understanding of the development of a water film which acts as a 'natural' lubricant at the interface. The development of this water film is characterised by the classical 'Stribeck' curve which demonstrates the importance of the actual contact area between the ski base material and the asperities of the snow. Kinetic friction will therefore change during a ski run and using these tribological principles, a model has been created which is based on the tendency of the water film thickness in different frictional regimes. This model is used to critically consider the effectiveness of current and newly devised base treatments and modifications.

Waxes and other more unusual treatments have been applied to the base of the ski ever since the era of wooden bases. The primary purpose of their use was to apply a waterproof layer to the wooden surface. Modern skis now use polyethylene as a running surface as industry standard. Over the years, the polyethylene used has increased in molecular weight to provide superior wear resistance properties when sliding over snow and ice. However, only recently has the practice of waxing polymer-based skis been critically questioned. It is suggested that traditional waxing may not always be beneficial and that the focus should be on the physical structure as well as the chemical disposition of the sliding surface. This is explored in this thesis using micro and nanoscale texturing together with traditionally adopted macroscopic texturing applied to skis using a stone grinding method. Waxes tend to cover up and fill in the nanoscale cavities and features created by this process, thereby obscuring the any positive or negative effect of the underlying base structure. The act of treating a pair of skis with wax may be an influential process in ski base sliding friction by changing the physical structure to a more beneficial configuration. Certainly treatments including stone grinding and physical structuring, hot-waxing and subsequent scraping and brushing require further investigation as they will each influence the physical structure. It is still unclear which type of physical structure is appropriate for particular environmental conditions as there are contradictions evident in the in the limited number of investigations conducted by other authors in this area.

The base of a ski preferably has a hydrophobic disposition. However this is determined by both the physical and chemical structure of the surface. This is also evident from studies of naturally super-hydrophobic surfaces in nature. Waxes seek to improve the hydrophobicity of the surface by the additional of a chemical coating on the surface. The act of treatment to improve the physical structure is sometimes neglected. A number of new micro and nanoscale base modifications and treatments are investigated in this thesis. Such treatments particularly focus on the use of fumed silica nanoparticles and perfluorocarbons. Perhaps the ultimate goal is to obtain a sliding surface which does not require post-treatments. To this end polymer blending has been investigated and new blends containing nanoparticles have been tested. Testing methods include contact angle testing; friction ramp testing; glide testing in real alpine environments and scanning electron microscopy. These investigative techniques were employed for both surface treatments and bulk modifying the base material.

The practical realisation of new modifications and treatments is seen as a major goal for this study. This is partly achieved through the development new polymer blends, new surface preparations and new tools and methodologies for ski preparation. This goal has been enhanced through the support from the snowsports manufacturing industry. This is especially so through collaboration with *Atomic* who are one of the major international manufacturers of snowsports equipment. In addition, a wide range of other manufacturers have generously provided information and raw materials for this project.

The aims and objectives of the thesis are identified in the proceeding chapter and this is followed by a Chapter [3] on the evolution of the modern alpine ski and how this has been driven through competition in the sport. Chapter [4] contains a detailed review of the sliding interface and hydrophobicity influenced by both chemical and physical factors. The methodology is included in Chapter [5], and results and discussion are contained in Chapter [6]. Overall conclusions and future directions are discussed in Chapter [7] and Chapter [8]. Whilst this thesis focuses on sliding on snow and ice as it applies to alpine skiing, it is recognised that research in this area has much wider applications.

Chapter [2] Aims and objectives

The overall aim of this thesis is to develop and investigate new surface treatments and modifications for ski bases, informed by tribological principles, which reduce overall sliding friction.

The broad objectives of this thesis are to:

- Critically review current knowledge of the nature of the sliding interface between ski and snow and factors influencing hydrophobicity.

- Develop new ski wax formulations containing hydrophobic fumed silica nanoparticles and compare with traditional hydrocarbon and fluorocarbon waxes using contact angle testing, friction testing and glide testing in a real alpine environment.

- Explore the effect of a range of surface treatments which modify the ski base at micro/nano-scale levels using contact angle testing, friction testing and scanning electron microscopy.

- Develop new polymer blends which bulk modify Ultra High Molecular Weight Polyethylene and investigate their properties using contact angle testing, friction testing, scanning electron microscopy and glide testing in a real alpine environment.

Chapter [3] Evolution of the modern alpine ski

The development of the modern ski has been driven by the need to go higher, faster and to explore new territory or navigate the mountain with finer control. Contemporary alpine downhill events held in the modern era, such as those held at Kitzbühel, see athletes travelling at 100 kmh^{-1} on average over a 3km course with a top speed of 145 kmh^{-1}, and negotiating jumps of over 80 metres and a maximum gradient of 85% (Kitzbühel Tourismus, 2013). An estimated 2949 million media viewers watch international alpine skiing events (FIS, 2012). Advancements in materials, tuning, construction and geometry have given skis their modern performance characteristics, with athletes constantly pushing the limits of their skis. In an alpine race, a one hundredth of a second can be the difference between victory or defeat and, as such, each small innovation in design can provide a significant advantage. As in most sports, developments first made for elite competition usually become incorporated in skis manufactured for the mass leisure market.

The competitive nature of the sport has developed over time since skis were first used as far back as 5000 BC. Skis were primarily used as an important means of transportation in snow locked areas, as evidenced in early rock paintings, for example at those seen at Rødøy in Norway. The subsequent adoption of skis by armies to gain a military advantage may have contributed to the wide-spread use of skis but also stimulated early signs of competition. During the 15th century the entire Swedish army was equipped with skis and competitions started to take place between the soldiers. The first known civilian-organised competition took place in 1843 at Tromsø, Norway, and thus a means of transport started to be turned into a sport. However, skis of this period were still essentially lengths of wood or bone of varyingly thickness, with straps to bind them to the toe of the skier which facilitated travel (Fry, 2006).

The need to travel faster down the a mountainside is evidenced as far back as the 1850s when miners used skis to descend down the steep slopes from mines in the mountains, reaching speeds of nearly 90 kmh^{-1} on 3.6m lengths of wood. The first significant degree of ski control probably originated in the Telemark region of Norway where skiers experimented with new methods to control the speed and direction of the downhill decent, developing into the Stem Christie and Telemark turns, techniques which are still used today (Lovett, 2006).

All types of skiing increased in popularity throughout the 20th century with the first winter Olympic Games held in 1924 in Chamonix, France, featuring Nordic Combined and Ski Jumping. Subsequently, in 1932, Cross-Country Skiing also became an Olympic Sport. Downhill skiing was less popular at this time until mechanical assistance, up the steep mountain slopes, became more widespread after it first appeared in the Jungfrau area in Switzerland and in America in the early part of the 20th century.

British tourists formed the vast majority of visitors to the Alps in the late 1800’s /early 1900's. They organised the first Downhill and Slalom national championships which were held on the Lauberhorn in January 1921. These are generally acknowledged as the first ever National Ski Championships (DHO, 2012). Sir Arnold Lunn and 15 members of the Kandahar Ski Club, which was founded in 1924, organised the first downhill race in 1928 using hickory skis with seal-skins to 'skin' up the Schilthorn to the starting point, staying the night up the mountain, then returning to the valley the following day. Downhill racing featured eight years later as an Olympic event in 1936 and the original Kandahar 'Inferno' downhill race is still held today (Morgan 2009).

Competition has continued to influence the technique of skiing and the design of the equipment to the present day. Alpine skiing has diversified into many different facets testing a skier's skill and technique in imaginative ways. The FIS Alpine World Cup, founded in 1966, is the pinnacle of these races and is staged throughout the winter season. It is considered as the foremost competition in alpine skiing, even more so than the Olympic Games, because it requires athletes to ski at an extremely high level over several competitions types or disciplines to take the title (Fry, 2006). The Governing Body, *Fédération Internationale de Ski* (FIS), sets the rules and regulations for the majority of skiing events. This includes the equipment restrictions, the sizing and type of the marked course, safety features and homologation of the ski run or slope for competition use (FIS, 2012). In order to define Alpine skiing, and set it apart from Nordic, Telemark or Ski Jumping, the ski bindings in the Alpine discipline must have a fixed heal binding.

The structure of the modern alpine ski consists of many laminate layers glued together with a waterproof adhesive. In the early 1900’s ski makers, such has HM Christiansen in Norway, started experimenting by combining the properties of two types of wood; using a lighter body of spruce, combined with a hard base of hickory or ash (Masia, 2004). Waterproof adhesives improved the adhesion between the laminates, and innovative new materials, reinforcements, and construction methods gave the modern alpine ski its characteristics.

The modern ski can made up several different layers of composite materials which are bonded together by a resin based adhesive to provide the required engineering and performance properties. Given the right combination of core, composite layers, and adhesive a high stiffness, low weight, durable ski can be produced. The motive for producing a composite structure is to create a material with a profile of properties not offered by a single material (Ashby, 1993). Older, more traditional skis are essentially planks of wood in comparison which have been developed, over time, into the complex laminate structures of the modern ski. The aerospace industry was one of the first to adopt the use of laminate structures in design. When the merits of these new materials were confirmed, they later spread across a broad range of industrial sectors (Black, 2003).

The composite layers primarily found in skis are as follows:

- Core layer - This provides the primary structural element to the ski and distribution of flex.
- Base layer – This is a low friction, abrasion resistant, running surface with metal edges to aid grip to snow and ice.
- Laminate layers – These reinforce the core material both above and below the core. They improve torsional and longitudinal stiffness, durability and load transfer.
- Adhesive – This is a polymeric resin which bonds and secures all the layers together and sets the shape of the ski during manufacture.

The construction of skis has been described in brief outline only as the focus of this thesis is on the treatment and modification of the base layer with the aim of reducing friction. Base treatment methods and their tribological properties will be reviewed in detail in the next section. However, it should be recognised that there are many different disciplines in alpine skiing and a wide range of ski deigns for each purpose and also for levels of ability. A common feature all of these designs is, however, the UHMW-PE running surface.

Chapter [4] Tribology- the physics of sliding friction

The sliding interface between ski base and snow is a complex system. The sliding surface (snow) is difficult to categorise into specific types as every individual snow flake is effectively unique. When the snow accumulates into a covering it can metamorphose into many different forms dependent on numerous diverse variables. The ski base can have a variety of different surface treatments and structures. The effectiveness claimed for these surfaces is often dependent on stated snow and air temperatures. On closer examination of the frictional process involved in skis sliding over snow, it quickly becomes apparent that there are a host of additional variables that should be taken into account. Relatively few authors have contributed to a theoretical model of ski base sliding although all those who have, have used classical tribological principles and methods of investigation in an attempt to characterise and comprehend the process involved.

Tribology is the science or practice of lubrication or wear applied to engineering surfaces in relative motion (Moore, 1975) and is derived from the Greek word *tribos* meaning rubbing. Tribology also encompasses other related disciplines associated with wear and lubrication. Treating the sliding friction of a ski base surface on snow as a tribological interface can elucidate the frictional mechanisms involved and has the potential to lead to base modifications and treatments designed to optimise friction which are based on sound scientific principles. The tribological system in ski base sliding friction is made up of the following four tribo-elements. Firstly, the ski base which is the element in motion where structure, hardness and material properties all have an influence on friction. Secondly, the snow, which is the quasi-stationary element of which metamorphism, type and structure have an influence. Thirdly, the interface, which is the area of interaction between the ski base and snow; and finally the atmosphere, which is the supplier of external energy and a medium of energy exchange.

The tribological interactions between the exposed surface of a solid and interfacing materials in the environment may result in a bulk loss of material from the surface, more commonly described as 'wear'. The resultant wear is dependent on the properties of the interacting materials. Czichos (1978) has suggested a methodology to minimize the wear of components involving the comparison of material properties against tribological requirements under the normal operating conditions. UHMW-PE has been found to be an effective slider which has led to it currently being the sole choice of material for manufacturers who produce skis. The first step towards reducing the friction and wear of UHMW-PE is to understand the tribological mechanisms at the interface. This is, however, complicated by the complex nature of snow and the number of other associated variables. Nevertheless, in spite of this, a logical approach would be to review the detailed properties of both snow and UHMW-PE and then investigate the tribological interaction between them.

The development of a methodology to test materials under normal operating conditions can prove challenging. A tribometer or tribotester is a commonly used type of instrument in the field of tribology to measure quantities such as the resistive force and coefficient of friction as well as wear and rates of abrasion of interacting materials. The aim of these instruments is to replicate the motions and forces that occur in the normal operating environment of the selected interacting materials. A limited number of scientific investigations have used this approach whilst attempting to replicate ski/snow sliding interactions present in an alpine environment. Such studies include those by Bowden (1953); Ericksson (1955); Kuroiwa (1977); Shimbo (1971); Lehtovaara (1985): Pihkala and Spring (1986); Sturesson (2005); Baurle et al (2007) and Theile et al, (2009). However, the changing consistency of natural of snow once a slider is passed over the surface is a challenge which has yet to be replicated in laboratory conditions. To replicate sliding, either a linear or a rotational motion must be employed at varying velocities. However, as skiers can easily reach speeds of 100 kmh^{-1}, thereby covering 26.6 m in one second, this seriously limits the use of such tribotesting machines from fully replicating the conditions at the interface. During skiing, the snow interacting with the base has not been repeatedly subjected to a sliding motion, which causes shearing of the crystals or grains. Whilst it is recognised that in the natural environment of the mountain, on-piste snow may have been slid over many times, it has also had the opportunity to metamorphose between slides. Tribotesting has sought to overcome this problem by using slower sliding speeds and varying the atmospheric conditions surrounding the snow. Although, this may give an insight into the sliding mechanism, repeated sliding over the same area of snow prevents this method from fully replicating the interface. This introduces additional variables as a result of the inevitable deformation of the snow crystals during repeated passes, over the same area with the slider.

Similar challenges to tribotesting also exist with in situ glide tests where skier, ski and snow interact in a natural mountain environment. However, at least the velocity, applied force and snow conditions are all variables which replicate normal skiing practice. The introduction of human element, however, introduces new challenges for any experimental methodology. The actions of skiers during glide testing can significantly affect the results (Federolf et al 2008). Additionally, the natural environment introduces changeable conditions, bringing in additional variables such as wind, sunlight, humidity and temperature changes. Again, relatively few authors have developed a systematic methodology which overcomes or minimises the impact of external variables in glide testing.

Friction is a force that resists the motion of two bodies in contact with each other. This frictional force is relatively low between a ski base and snow and ice when compared with other interacting materials. This low coefficient of friction is part of the enjoyment of skiing, allowing skiers to accelerate quickly up to considerable velocities and glide over long distances. However, the impact of friction can be found in every aspect of technology and everyday life, as well as in nature. Since the early beginnings of skiing, skiers have sort to reduce friction with the application of lubricants. This began with the application of waxes and oils derived from natural sources and progressed to synthetic modern-day treatments. Most of the early remedies for this particular tribological challenge were derived from everyday experiences and observations. As explained in section 3, competition seems to be the driving force behind development of further treatments and technology. High level international sport has certainly driven the development of treatments but this has not always been backed by in-depth scientific investigation. One of the reasons for such a lack of understanding, despite continued interest in the subject may be the fact that tribological interactions tend to be extremely sensitive to the conditions under which the investigation takes place. Hence, the repeatability and validity of the results are sometimes questionable and challenged and the observed differences in friction are very small.

Modern-day hydrocarbon waxes have been adopted by the ski industry to reduce friction and wear by introducing a lubricant (wax) into the interface as described previously. Despite this, it is very interesting to note that no substantial evidence has become apparent to advocate widespread use of wax in the limited number of scientific investigations which have been conducted in this area (Shimbo, 1960 and 1971; Mathia et al, 1992; Slotfeldt-Ellingsen and Torgersen, 1983). How can one be sure of the efficacy of any treatment when the resulting effect is so small and the number of variables is so considerable? Skiers, technicians, athletes and manufacturers qualitatively describe a positive effect after treatment with glide wax. On the other hand, polymer tribologists discourage the use of lubricants, wherever possible, as this can increase dirt accumulation leading to higher observed coefficients of friction (Briscoe and Sinha, 2002). Many of the published scientific investigations comparing waxed versus non-waxed (untreated) skis have failed to provide details of surface properties of the non-waxed ski. The act of stone grinding or normal sliding wear/abrasion or the application of the wax with post scraping and brushing will inevitably change the surface properties. The effect of different treatments was demonstrated by Sturesson (2005) who utilised scanning electron microscopy and optical profilomentry to illustrate the differences in the surface structure after varying treatments; as shown in Figure 1 and Figure 2. Approaches adopted by the ski industry focus more on the selection of an appropriate glide wax, rather than on the preparation of the base as a significant factor in gaining a performance increase. This issue also seems to be neglected from scientific investigations on the subject of anti-friction coatings on skis where the untreated model is not described in any great detail (Ambach and Mayr 1981; Kuroiwa 1977; Fauve, 2005).

Recent advances in polymer science and nano-technologies may offer suitable material alternatives to UHMW-PE. Furthermore, surface or bulk modification of polyethylene to promote desirable physicochemical properties may also be more dimensionally suited to the field of nano-science and technology. Certainly, micro- and nano-tribology have made significant advances. Frictional interactions in microscopically small components are becoming increasingly important for the development of new products in many sectors of industry. Although many experimental and analytical studies have been reported, a clear understanding of the mechanism of friction and wear at the nanoscale has yet to be achieved. Would any of these methods, modifications or new materials be suitable for increasing the performance of the ski base? This question should certainly feature as a subject for further exploration.

It is clear, on closer inspection, that there is little evidence of a structured, logical, theoretical or practical approach to the effectiveness of treatments. A structured analysis follows of the tribological mechanism based upon the interaction of the ski base (Section 4.1), the snow (section 4.2) and the interface between them (section 4.3). There are also new and emerging technologies in polymer science and nano science which require experimental investigation to ascertain if they have the potential to increase the performance of skis; discussed in section 4.4. A consideration of the physics underpinning the sliding mechanism can facilitate exploration of new treatments and modifications with optimal frictional properties. This is critically reviewed and discussed with the aim of applying this knowledge to advance the performance of snowsports equipment.

4.1. The sliding surface (base)

The base or running surface of the ski is the material which is primarily in contact with the snow. It has to demonstrate effective sliding properties over snow and ice as well as handle the abrasive properties of the snow. It must show good adhesion to the subsequent overlying laminate layers and have the ability to be treated or modified for varying environmental conditions. The Austrian firm *Kofler* introduced the first extruded polyethylene ski base in 1953, followed two years later by *Inter Montana Sport (IMS)* who introduced the P-tex brand. This polyethylene material was a great improvement over other plastics because of its low friction and durability. Over time, even more durable versions were created by increasing the molecular mass of the polyethylene. A sintering process was first introduced in 1962 which could produce ultra-high molecular weight polyethylene (UHMW-PE). This has been the material of choice since that time and possesses the desirable properties referred to above (Lund and Masia, 2003 and Frederolf, 2005).

UHMW-PE is a type of polymer. A polymer is basically a chain of many (poly) smaller repeating units (mers) linked together with covalent bonds; in the case of UHMW-PE of ethylene (ethene), $C_2H_{4,}$ units. UHMW-PE is a linear homopolymer made up of purely ethylene units: $(C_2H_4)^n$. It has extremely long chains where n= 100,000 to 250,000 and has a molecular mass of around 9 million g/mol. The chains intertwine forming a semi amorphous/ semi crystalline structure. The longer chains transfer loads more effectively to the polymer backbone, resulting in superior abrasion resistance and desirable mechanical properties (Stein, 1998). The abrasion resistance is generally superior to that of carbon steel using a water-sand slurry test (Tong et al, 2005). The coefficient of friction, when sliding over snow or ice is also comparable to polytetrafluoroethylene (Teflon) and significantly lower than polyamides (nylon) or polyoxymethylene (acetal). It has an extremely low water absorption of 0.01% and a contact angle of approximately 80° indicating that it is highly resistant to water or hydrophobic in nature. Polyethylene also has no polarity apart from at the ends of the molecular chains. The friction of a material when sliding over snow and ice is understood to be related to the relative permittivity of the sliding material or the degree it concentrates electrostatic lines of flux (Colbeck, 1994). It follows that in order to reduce friction it is beneficial to have an inert, non-charging, sliding material. UHMW-PE has a very low relative permittivity- for example *Ticona GUR 4150 PE-UHMW, Unfilled* has a permittivity of 3.0 @ 1.00e+6Hz ASTM D150 (Matweb 2012).

There are many different types of polyethylene, of varying molecular weights and structures. These include: Low Density Polyethylene (LDPE), Linear Low Density Polyethylene (LLDPE) which has a branched structure, High Density Polyethylene (HDPE), and UHMW-PE which has the longest molecular chains and is, as stated above, the material of choice for ski bases. UHMW-PE has many other applications including medical, automotive, defence, industrial and sports.

An effective slider over snow and ice would possess the following: low frictional properties against snow; resistance to ice abrasion (hardness and water resistance), low thermal conductivity, good adhesion to the underlying ski construction material, and be hydrophobic in order to resist water adhesion.

UHMW-PE is a visco-elastic material and consequently has a time-depended hardness (Suwanprateb, 1998). The time dependent property of the material implies that during short loading periods, hardness will significantly increase. The production of higher molecular weights of polyethylene through a sintering process has led to increases in the hardness of PE over time (Bowden, 1953; Liu et al 1999). Hardness has been estimated in the range of 30 -90 MPa at room temperature and is greater at lower temperatures (Sturesson et al, 2008). Hardness and wear resistance can be increased by the addition of particle fillers to the UHMW-PE matrix; however, such modification may reduce the sliding performance of the material (Khedkar et al, 2002).

Carbon black is generally added to UHMW-PE as a polymer additive to reduce antistatic effects. However, Colbeck (1995) and Petrenko (1996) investigated the charging effects of skis and could not find a relationship between the electrical conductance of the skis base and the static electric field strength. It is suggested, therefore, that that the main reason for any beneficial effect of adding carbon black to the UHMW-PE is the increase abortion of solar radiation provided by the resultant black colour. Colbeck and Perovich (2004) demonstrated that a black ski bases absorb about 45 times more heat than white bases. He goes onto suggest that black bases may be more beneficial in colder temperatures where more energy is required to melt the snow/ice to produce a lubricating layer. Although by adding carbon black to UHMW-PE, a reduction in wettability and degradation of wear resistance is evident (Werder et al 2003).

The amount of adhesion between the water film and ski base is an important factor in the reduction of friction. If the ski base is hydrophobic (water resistant), adhesion is reduced (Saito et al, 1997). Thus the utilisation of materials with hydrophobic properties is beneficial. UHMW-PE has a contact angle of around 80° indicating adequate hydrophobic properties. Further post-treatments can increase the contact angle to a maximum of around 120° with perfluoro additives. Whilst it may be beneficial to have a highly hydrophobic material in warmer wetter conditions, colder conditions, where melt water production is limited may require a slightly less hydrophobic material to achieve ideal low frictional sliding properties. The modification by post-treatment seeks to tailor the surface properties to that of the sliding conditions.

Ticona GUR 4150 is a linear polyolefin resin in powder form with a molecular weight of approximately 9.2 g/mol calculated using Margolie's equation. *Ticona* claim that this displays superior abrasion and impact strength compared with other available grades of UHMW-PE. *Ticona* report that it is used by several large manufacturers to produce their ski bases seen on many models of skis. The data sheet for which is included in the appendix. There are several different commercially available grades and brands of ski base or soles. Major manufacturers offering such products include *Creative Plastic Solutions CPS* (see Table 3)*, GmbH*, *Crown Plastics* and *Okulen*. Most companies offer a range from the less expensive ram-extruded and compression moulded grades up to the more expensive sintered grades. Because of the high melt viscosity of UHMW-PE, it is a difficult material to extrude unless a high pressure ram extruder pushes the material through a die (Stein, 1998). Consequently a slightly lower molecular weight UHMW-PE is utilised, reducing the viscosity, which enables this process to become viable. The sintering process is an alternative, more complex and expensive method to ram extrusion. This involves filling the sintering mould with fine UHMW-PE powder, then exerting heat and pressure on the material for an extended period of time. After this, the heat is increased and the pressure is reduced, then finally, during cooling period, the pressure is again increased. The whole cycle takes several hours to complete (Sloetfeldt-Ellingsen and Torgersen, 1982; Karloff et al, 2005). Once the UHMW-PE plastic is released from the mould, it is turned into a long sheet by planing or skiving a thin layer off the moulded block. This process enables the highest molecular weights of polyethylene to be manufactured into sheets and, as previously mentioned, these higher molecular weight polymers have more suitable mechanical and dielectric properties for sliding over snow and ice.

Table 1: Various types of P-tex ski base running surfaces and their corresponding mechanical properties reported by CPS, (2012)

P-tex® type	**Extruded**	**Press sintered**	**Black**	**Clear**	**Coloured**	**Molecular Weight g/mol**	**Density g/cm3**	**Modulus of elasticity MPa**	**Abrasion resistance sand slurry steel 37=100**	**Wax absorption mg/cm2 bei 110C**
P-tex 2000 clear		•		•		5,000,000	0.940	500	20	1,9
P-tex 2922 w HTR		•		•		3,600,000	0.927	361	20	2,0
P-tex 2000 coloured		•			•	5,000,000	0.940	500	20	1,9
P-tex 2500 w black		•	•			5,000,000	0.960	488		
P-tex 4000 clear		•		•		9,200,000	0.930	300	15	2,2
P-tex 4500 black		•	•			9,200,000	0.930	300	20	1,9
P-tex 800	•		•	•	•	215,000	0.934	362		
P-tex 1820	•		•	•		600,000	0.964	600		
P-tex XC	•		•	•		600,000	0.964	600		

To achieve a flat, uniform surface of polyethylene on the base of the ski, which is level with the edges, a grinding or sanding process is utilised. Due to the high molecular weight of PE used, this grinding process can cause the development of tiny hairs on the surface which inevitably reduces sliding performance. Stone and belt grinding techniques and methods of increasing the roughness of the base by grinding a structure or pattern into the surface are discussed in the following sections. One finding considered in some detail is that a rougher or structured surface has been shown to promote better sliding over snow and ice compared to a smooth surface.

In 1955, Ericksson suggested that the surface roughness of the sliding material had a significant effect on friction. His experiments demonstrated that runners with smooth surface treatments exhibited a higher coefficient of friction when compared with rougher surface treatments. This was later confirmed by Shimbo (1971), Moldestad (1999), Kietzig et al (2009).These studies suggested that the size of the apparent contact area is a principal factor which is altered when the surface structure is applied. The apparent contact area implies that sliding friction only occurs over a limited number of contact spots. The diameter of these spots has been investigated in various studies and has been found to be in the order of 100 to 200µm (Baurle 2007, Kuroiwa 1977, Theile et al 2009). Many contact points of 100-200µm support the load of the skier which is on a different scale altogether than that of snow ground structures.

Moldestad (1999), who sought to explore the optimum surface structures of Nordic ski bases for varying snow conditions, observed that rougher sliding surfaces were particularly beneficial when the humidity and temperature were higher. He suggested that this effect might be related to the thickness of the water film underneath the ski's base, which is generated by frictional heat. The water film, of varying thicknesses, has been investigated in a number of different studies, each yielding conflicting results of magnitude (Colbeck, 1988, Baurle 2006, Strausky et al 1998, and Ambach, 1981). Thickening water films can be attributed to higher apparent contact areas as more free water leads to a greater wetting of the surface; this is discussed in further detail in section 4.4.1. Moldestad (1999), who experimented with a range of surface roughnesses (2.5 to 12 µm), reported that the coarser structures exhibited lower friction at higher speeds (for cross country skis) and warmer temperatures, whilst fine and medium structures created optimally low friction in lower temperatures and humidities.

Shimbo (1971) reported that friction on a smooth surface was considerably higher, slightly decreasing with increased feature heights of asperities between 15 and 35µm. Kietzig et al (2009) (2008) confirmed the higher friction for very smooth surfaces these results, but also indicated that a coarse structure of 1.2 µm increased friction at lower sliding velocities when compared to structures of 0.6 µm, although they reported that this trend was completely reversed for higher sliding velocities.

There appears to be a consensus in the literature that a textured surface helps to reduce friction in sliding. This type of surface contributes to reducing the wetted contact spots, reducing capillary drag. Finer structures are more beneficial at lower sliding velocities and in colder conditions. Coarse structures may act like a tyre tread, breaking up the water film, which is thicker at higher sliding velocities and warmer conditions, into smaller contact spots. The appropriate size, orientation and pattern of such structures, however, still require further investigation.

Overall, there is limited scientific evidence as to which type and orientation of structure offers superior sliding properties for a particular discipline or in specific snow conditions. However, it does appear that there may be a tentative link between the depth of the structure and optimum performance in different environmental conditions.

After grinding and structuring the UHMW-PE in an attempt to minimise sliding friction, the base is prepared for further friction-reducing treatments. The ski base material under general use, but particularly when sliding over abrasive snow or following grinding and structuring, will inevitably have deteriorated. The wearing mechanism, particularly on hard abrasive snow, dislodges tiny hairs of UHMW-PE from the bulk, which can have a detrimental effect on friction. The hairs can be easily seen and felt on poorly conditioned skis, also known as 'hairy' base. To prevent this skis are regularly tuned for performance by structuring and waxing methods.

In order to promote sliding, abrasive and chemical treatments are utilised before applying a wax coating. The wax coatings are considered by the majority of those in the ski industry to be the most appropriate method of tailoring the surface properties of the base to promote sliding. This view will be critically reviewed in section 4. The application methods, composition of wax treatments and subsequent selection of these products for specific snow conditions are discussed in section 5.1.

Waxing is the industry standard surface modification for tuning ski bases to specific environmental conditions. Even in the early beginnings of skiing, products such as tar/ pine pitch, vegetable/animal oils, rosin and paraffin wax were used to improve the glide of skis. As these early ski bases were constructed out of wood, these treatments also acted as a chemical sealant as well as a glide promoter. In the early days of wax treatment (1900-1940), beeswax was the most commonly used type of wax (Karloff et al, 2005).

Wax is a generic term for a group of natural or synthetic substances which have a tendency to have the following attributes:

- Solid at room temperature but the consistency can vary between be soft and malleable to hard and brittle
- Structure contains coarse to fine crystalline regions
- Low viscosity at temperatures just above its melting point
- Insoluble in water
- May be polished into a glossy surface by rubbing using light pressure
- Melt and re-solidify without decomposition.

(Karloff et al, 2005)

The manufacture of ski waxes has since developed into a large commercial industry, with its advancement attributed to competitive events. There are many companies dedicated to producing ski wax to suit every environmental condition. Tailoring a wax to specific conditions is still an estimate based on a mixture of guesswork and calculation. However, some principles derived from investigations into the tribology of the interface between the ski base and snow has informed this process. Key points are summarised in this section and 5.1 in order to explain the wax selection process.

All wax manufacturers have similarities product lines for particular environmental conditions. Harder waxes are recommended colder temperatures and softer waxes are for warm temperatures. Additionally, additives such as fluorocarbons, which are more water repellent, are used in warmer temperatures or higher speeds. Frictional heating which is further discussed in section 4.3.3 as the primary element responsible for the formation of the melt water film, although in some environmental conditions, solar radiation can also have a significant effect (Colbeck et al, 2003). The melt/free water is the lubricant in the interface and waxes only attempt to tailor the surface properties of the base to that of the sliding conditions. The velocity of the skier and environmental conditions are the largest influences in frictional heat generation and, subsequently, the water film thickness. Solar radiation, ambient temperature and humidity, free water content, and crystal structure of the snow all affect the potential thickness of any given film. At the beginning of a ski run the skier has first to overcome static friction and may continue in a predominately dry friction regime in cold conditions. However, may quickly reach a wet friction regime in warmer conditions. The faster the skier travels, the more frictional heat is generated and the ski base becomes increasingly supported by the water film. This reduces the amount of solid-solid interactions (dry friction) and eventually becomes a purely wet friction regime. The water film height, in this wet friction regime, can continue to respond to frictional heat, increasing in thickness. However, the thicker the water film becomes the greater the wetted contact area and this has a detrimental effect on the coefficient of friction. Also, if the water film becomes too thick, suction will occur when the water film shears (the capillary drag). A phase of mixed lubrication where some solid-solid interactions take place, lubricated by a thin layer of water, has been demonstrated to produce the lowest coefficients of friction of approximately 0.02/0.03. The evidence for this is discussed in detail in section 4.

The UHMW-PE ski base contains both crystalline and amorphous regions and the relative percentage of each depends on the grade of material and manufacturing process. Karloff et al (2002) argue that the wax diffuses into the amorphous regions of the base. The driving force for this diffusion process is heat. However, there is some disagreement as to whether the wax does actually penetrate these amorphous regions. Kuzmin and Tinnesten (2008) argue that a pure dilution process is a more appropriate explanation and that the wax does not impregnate the crystalline regions of the base, although it may act as surface filler.

The basic makeup of most modern-day waxes are either mineral, saturated hydrocarbons refined from crude oil such as petroleum/paraffin, or synthetic, longer straight chain saturated hydrocarbons. Other hydrocarbon structures can include branched chain or microcrystalline cycloalkanes. To adjust the specific hardness of the wax, the length of the carbon chains are adjusted. Longer hydrocarbon chains produce harder waxes whilst the shorter chains decrease both the resulting hardness and the melting point. Branched chain and microcrystalline structures also produce very soft waxes. Combinations of these various components will change the overall hardness of the wax to tailor it to the specific snow conditions.

Other additives are also incorporated into waxes to decrease water adhesion or improve the glide properties. These can include fluorocarbons, Teflon™ (PTFE), silicone, graphite, nano-particles, molybdenum disulphide and gallium. Each of these additives has its own specific properties but they can also affect the resulting hardness of the basic hydrocarbon wax.

The use of fluorocarbon additives and perfluorocarbons were hailed as a turning point in waxing technology because of their high hydrophobicity. These expensive formulations are commonly found in waxes used for competition as they have been found to be very effective. In fluorocarbon waxes, some of the hydrogen atoms have been replaced with fluorine. The name ‘perfluorocarbon’ implies that all the hydrogen atoms have been replaced with fluorine atoms; however, many of these derivatives contain atoms other than carbon and fluorine and other specific functional groups. Fluorocarbons are most effective in warmer, wetter conditions because of the higher liquid water content in the snow. Waxes with a high contact angle, or low surface tension compared to water are preferred, fluorocarbons fulfil this requirement with measured contact angles of around 120°. Jobwerx (2007) has argued that fluorocarbons have reached their maximum hydrophobic potential because they are not soluble within the wax matrix. *Toko*, a wax manufacturer, offers a dibloc copolymer, an intermediary containing both hydrogen and fluorine groups on one carbon backbone. This may allow the fluorine side of the copolymer to orientate to the surface, increasing hydrophobicity, whilst the miscible hydrocarbon side merges with the base wax.

Molybdenum disulphide is similar to graphite in appearance and properties. Indeed, like graphite, it is widely used as a solid lubricant because of its low frictional properties. However, unlike graphite it does not rely on absorbed water vapour or moisture to maintain its properties. It is used in ski wax to prevent static build-up in dry, fine grained, cold snow conditions and for its dirt repellent properties (Engineers Edge, 2012). Graphitised carbon or carbon black has excellent conduction and anti-static properties. It is already added to black ski bases for the improvement of anti-static properties. However, due to the abrasion by snow and ice crystals, some of the graphite and the UHMW-PE base are inevitably abraded away. Therefore, it is suggested that it is sometimes beneficial, under certain snow conditions, to use a wax with a graphite additive to redistribute the graphite layer and further enhance the anti-static properties of the original ski base (Tognar Toolworks, 2011).

The companies, teams and athletes do not usually reveal what mixtures or additives they are using in their high performance wax as they seek to maintain their competitive advantage. Testing and application are performed in secret, and legal action can sometimes be threatened or even taken if such information is made known (Scheve, 2011). Therefore although basic guidance on the wax selection process can be provided, reliance usually has to be placed on experience, personal or team experimentation and expert knowledge of specific snow conditions.

A wax is usually selected based upon the snow and air temperatures, relative humidly, and snow type. Wax manufacturers usually publish charts using temperature ranges to guide users to the optimum wax for the conditions, although an educated guess may still be required. Additionally, the following criteria offer some insight into factors which guide this decision:

- With fresh, well defined snow, move colder because the crystals are very abrasive.
- With older, granulated or high density machine groomed snow pack, move warmer because the crystals are more rounded giving a larger contact area.
- With a high humidity or foggy conditions, move warmer or use higher fluorocarbon content due to additional free water content.
- With a lower humidity or windy conditions, move colder or use a lower fluorocarbon containing wax due to the snow drying out giving a smaller degree of free water content.
- With sharp, granular, crystal-like snow, move colder to overcome the additional abrasiveness
- Dry, cold conditions or dirty conditions where there is high degree of static friction use a molybdenum additive
- If the critical glide sections of the course are in the sun, wax warmer or alternatively if they are in the shade, wax colder.

Skiwax.ca (2012); Tognar Toolworks, (2011); Harvey, (2000)

Once an appropriate selection has been made for the forthcoming expected conditions, the wax needs to be applied to the base of the ski. The most common method is hot-waxing followed by scraping and brushing which leaves behind a thin surface layer of wax. Further explanation of the methods for or hot-waxing and base preparation is contained in the method section 5.1. The process of ski tuning and maintenance imparts a physical structure to the surface in addition to any impact the chemical properties of the wax may have. Various scraping materials such as are Plexiglas or metal as well as different types of brush material will impart various structures on the base. These physical structures may not be visible to the naked eye but can be observed at high levels of magnification. The difference between plastic and metal scraping for example is shown in Figure 1 and Figure 2 below.

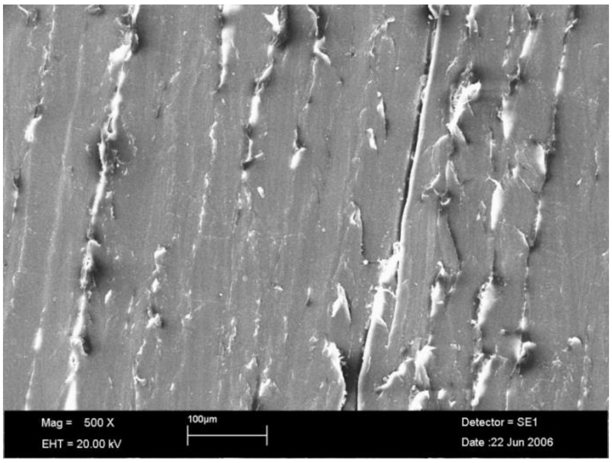


Figure 1: SEM image of a base scraped with a metal scraper (Ski, builders, 2012)

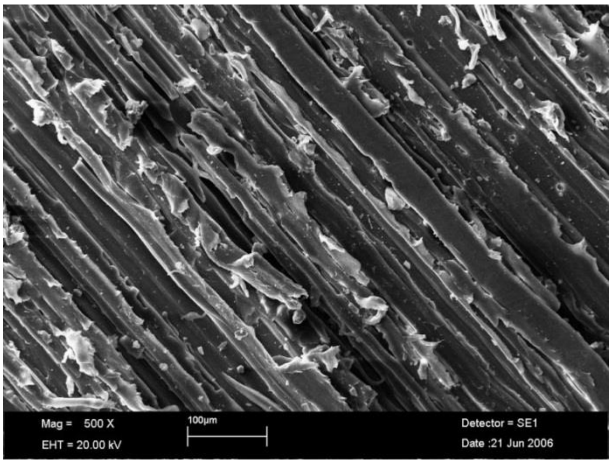


Figure 2: SEM image of a base scraped with a plastic scraper (Ski, builders, 2012)

Hot waxing is considered to be the standard treatment for improving the running surface of skis. Skis can be further modified using a variety of finishing products which usually containing a high or pure fluorocarbon content. Perfluoro powders are not miscible with the wax matrix but can be 'buffed' or polished into the wax with cork or felt. These are used to increase the hydrophobicity of the wax in warmer, wetter conditions. In racing, they are usually applied between the first and second runs after the weather has warmed up during the course of the day. There are a multitude of finishing products available including perfluoro liquids, powders, and rub-on wax. During use, the ski is exposed to variety of snow conditions which can be highly abrasive causing deterioration of the running surface and edges. Post-treatments and servicing are therefore required to keep the desirable properties of low friction sliding and edge grip. Modification of the sliding interface seems to be the most widely accepted method of increasing the glide performance of skis and tailor them to the corresponding environmental conditions.

Understanding the practical process of preparing skis is crucial to any scientific testing of surface properties or a ski’s frictional properties. Whilst some scientific papers have investigated the effects of base tuning, they have neglected to detail the process of preparation which has been used. When investigating small changes in velocity of different treatments to evaluate the differences in treatments, even small variations in the tuning process could significantly affect the results. Certainly the wearing and contamination during normal skiing can influence friction, causing detrimental damage to the UHWM-PE, particularly in abrasive conditions. Waxing and other physical treatment methods, such a grinding, seek to remove or restore the surface and also attempt to impart beneficial chemical and physical properties to the surface to reduce sliding friction. The waxing method itself could be described as both physical and chemical with the scraping and brushing of the surface.

4.2.The sliding substrate (snow)

Snow is initially formed by water vapour in atmospheric clouds condensing upon condensation nuclei (dust and salt particles) when the air temperature is below 0°C. At lower temperatures, the number of suitable freezing nuclei increases until, at -40°C, the freezing nuclei are no longer needed to form ice crystals. The growth of the ice crystals is determined by two processes: firstly by the diffusion of water molecules towards the ice crystals, driven by pressure differences and secondly as a result of collisions with other particles in the cloud causing the ice-crystals to gain in mass. Once a critical mass is reached, the particle is then pulled to earth by gravity. The subsequent shape of the crystal is dependent on the temperature and humidity of the atmosphere it descends through.

After the snow reaches the ground the crystals quickly lose their original atmospheric shape when they accumulate in a covering and sinter together. The snow cover is an aggregate of ice crystals and its texture is polycrystalline. The individual crystals are called grains and are separated by grain boundaries which can bond together to form a polycrystalline structure. The structure of the crystals and grains change due to the effects of temperature and pressure; this process is called metamorphism. The density and strength of the snow pack changes as the bonding of snow grains progresses. Metamorphism can occur in a number of different ways described by the following terms: equi-temperature metamorphism; temperature gradient metamorphism; melt-freeze metamorphism and pressure metamorphism.

Equi-temperature metamorphism occurs when unstable crystals with high surface to volume ratios, for example those with dendrites; seek to change their form to a near spherical equilibrium state. The driving force for this process is the slow diffusion of water vapour between different sized crystal grains. Small particles have a high radius of curvature and therefore exhibit a higher water vapour pressure than larger particles which leads the latter to grow in size at the expense of smaller particles. The rounding of grains eventually will lead to a more unstable snow pack; however, during this process, the contact points between the grains become stronger. The rate of redistribution of mass by this vapour diffusion process is driven by, and dependent on, the amount of available heat energy. It follows that the rate of metamorphism is a function of temperature although it should be noted that this process of isothermal metamorphism is very slow when not subjected to large temperature and pressure gradients experienced in deep snow cover. When a large difference in temperature and pressure are present within the snow pack, temperature and pressure gradient metamorphism occurs. The mass transfer of water vapour from the warmer areas towards the colder areas causes an increase in the size of the crystals. This effect occurs mostly on the top of high density layers due to the higher thermal conductivity of denser layers with reduced air. Solar heating will additionally cause the top layer of snow to undergo a cycle of melting then re-freezing. Gravity pulls the water through the snow pack releasing latent heat as it re-freezes, this process strengthens the snow pack, rounding the gains and causing stronger boundaries to form. Natural snow cover often develops patterns of layering specific to each climate zone (Strum et al 1995).

Sintering occurs over time, aided by pressure, and snow grains bond together to form a polycrystalline structure. The metamorphosis of the initial dendritic forms into rounder or more faceted forms which bond and grow in size eventually leads to a breakup of the snow pack. Snow crystals with the highest surface to volume ratios will disappear first, gradually becoming more rounded overtime. However during this process, the contact points which form between grains greatly increase the strength and density of the snow pack.

Schulson (1999) has described a number of different forms of ice, including stable and open cellular forms. The stable from of ice formed when ice freezes at low pressure is termed ice I and has two forms; hexagonal (Ih) and cuboidal (Ic). Both states are formed by vapour deposition at low temperatures. Snow is made of crystalline grains of ice and is therefore regarded as an open cellular form of ice, in which grains are bonded together. Petrovic (2003), using a range of established methods, suggests that the tensile strength of ice is between 0.7-3.1 MPa over a temperature range of -10 °C to -20°C. The compressive strength ranges between 5-25 MPa over the same temperature range.

A liquid-like layer forming on the surface of ice grains during sliding was first proposed by Fletcher (1970) and a clearer understanding of the unique surface properties of ice has emerged from this period. Surface melting of the ice begins below the bulk transition temperature and the water layer gradually thickens with rising temperatures (Wettlaufe, 1999). The liquid-like layer is between 3 and 50 monomolecular layers thick at -10 and 0°C respectively (Karloff et al 2005). Oxtoby (1999) suggests that such characteristics are explained by the fact that ice has no nucleation barrier for melting. The most common and simplest means to describe the manner by which water transforms between solid, liquid, and gas is through a phase diagram as shown in Figure 3, below.

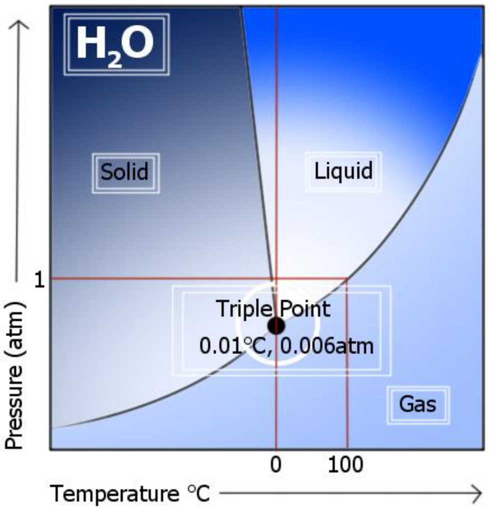


Figure 3: Representative phase diagram for water with pressure on the vertical axis and temperature on the horizontal.

Most skiing occurs around the triple point, which is the point at which the three phases of water coexist and water can exist as at solid, liquid, or gas. This explains how small variations in temperature and pressure can cause a liquid layer to form below the bulk freezing temperature and also the tendency of the transference of mass between phases during snow metamorphism. It should be recognised that there are many diverse snow conditions and many authors have found great difficulty in classifying snow in types due to their sheer diversity. The International Classification of Snow developed by Colbeck el al (1990) gives an overview of snow conditions and types. However, the most important factor when considering the friction of ski base is the tendency of the water to change state with small pressure and temperature changes at the sliding interface.

When the ski is in relative motion over the surface, even a small temperature variation can cause a liquid layer to form or an existing one thicken. Reynolds (1899 and 1901) suggested that this melt water film originated as a result of pressure; however, this notion has subsequently been largely rejected in favour of frictional heating (Bowden and Hughes, 1939). Pressure melting as a cause of the melt water was rejected because of the high pressures that would be needed to lower the melting point significantly. At temperatures close to 0˚C, pressure melting could have a small effect; however, Colbeck (1994a) estimated that, in order to reach melting temperature at an ambient temperature of -20˚C, a pressure of 2.7×10^{8} Pa would have to be applied. This would imply a contact area of 2.3 mm^2 which is much lower than observed values detailed in section 4.4.1. It is therefore unlikely that a pressure melting theory is principally responsible for the formation of a water film but it could be considered as a contributing factor in warmer conditions, close to 0˚C, although, even then, the increased contact area may dissipate the force, lowering the contact pressure.

The theory of frictional melting was first suggested by Bowden and Hughes (1939) and has been supported experimentally by several different authors. For example; Evans et al (1976) used an apparatus based on a pendulum hanging around a of ice to measure the kinetic friction between a slider and an ice surface under conditions commonly experienced in ice skating (temperatures from -15 to -1 °C and velocities from 0.2 to 10 ms^{-1}). They demonstrated that that the heat, produced by frictional heating at the contact areas, flows into the slider and into the ice. This supported the frictional heating theory of Bowden and Hughes and demonstrated that the heat produced by friction is significant enough to raise the surface temperature of the snow/ice to become liquid and aid sliding. Ambach and Mayr (1981), based on a thesis written by Mayr (1979), demonstrated, by the use of glide testing and dielectric capacitor measurements, that water film thickness was depended on both ambient temperature and sliding velocity. Colbeck and Warren (1991) installed thermocouples in a ski to measure the heat generation associated with the sliding of skis on snow. They found the ski bases reached a steady-state temperature below the melting temperature of the snow and the bases exhibited a larger thermal response at lower ambient temperatures due to lower melt-water production and higher friction. The temperature rise was also shown to increase with load, possible because of the increased contact areas. Colbeck (1994) also found that the greatest temperature response was from just behind the foot, on a skating ski, where the ski is most heavily loaded.

Measuring the water film thickness has been attempted by many authors. Golecki and Jaccard (1978) reported a temperature-dependent quasi-liquid layer on the surface of ice as thick as 100nm at 1˚C. Ambach and Mayr (1981) were the first to measure the thickness of the water film underneath a moving ski. They utilized a comb-shaped capacitor installed on the running surface of a ski. The capacitor measured the relative permittivity between the snow and the ski during sliding. The measurement frequency was 100 kHz, which was then compared to the known relative permittivity of water. Since the relative permittivity of water is known to be significant higher than snow and ice, high permittivity values denote the existence of thick water films. A calibration procedure was employed to relate the measured voltage from the capacitor to the water film height. They concluded that water film thickness was in the range of 5.0µm to 13.5µm at temperatures of -4 and 0°C respectively. Colbeck (1988) commented that these values were of the right magnitude but not necessary exact: his own mathematical estimation of water film height was in the order of 1.5 µm. More recent investigations by Strausky et al (1998), Bäurle et al (2006) and Bäurle et al (2007) concluded that water film thickness is more likely to be in the region of 0-1µm. Strausky used a fluoroescent spectroscopic method, flash freezing an aqueous solution of coumarin dye in ice and measuring the intensity at a defined wavelength which corresponded to the liquid phase and thickness of the water film. Baurle et al, using modelling and analytical methods derived from experimental data, confirmed Strausky's orders of magnitude for film thickness and subsequently dismissed Ambach and Mayr's earlier results. Based on this review it is probable that the water film thickness is in the order of 0 to 1 µm and that frictional heating is primarily responsible for the thickening of this film underneath the skis.

4.3. Interactions at the interface

Where the ski base and snow interact is called the interface. At the interface a number processes govern the resistance experienced by the slider (the ski base). These can consist of the collision of dry solid-solid contacts which can then progress to a lubricated regime. As previously mentioned in section 4.2, snow and ice can change state into liquid below its bulk transition temperature. The pre-existence of a melt layer, even at lower temperatures of -10°C, can, in part, explain the low coefficient of friction exhibited when sliding. The thickness of this film has a direct influence on the coefficient of friction (Glenne, 1987 and Colbeck 1992). During sliding, the energy corresponding to the sliding motion is dissipated into irrevocable compression and shearing of the snow or ice crystals. This energy can be converted into heat at the interface which causes local, discontinuous melting at the contact areas and subsequent thin water film creation (Colbeck, 1988).

The frictional resistance is greatest when large numbers of solid-solid interactions take place during a dry friction regime. Although, as previously mentioned, tiny amounts of additional water lubrication would be more common in alpine skiing due to a combination of surface melting of ice (Wettlaufer 1999), the interstitial snow moisture (liquid-water content) and the percolation of snow liquid-water to the sliding interface due to snow compaction (Glenne, 1987). An absolute dry friction regime, which only exists at extremely low temperatures, is unlikely to exist in the conditions experienced in normal skiing. The friction in a regime with a layer of lubrication only a few molecules thick can be described as boundary friction. However, in the literature associated with skiing on snow or ice, boundary and dry friction are often not distinguished for the reasons described above (Evans et al., 1976; Glenne, 1987; Colbeck, 1992)

The introduction of a lubricating layer between the interface lowers the coefficient of friction as a result of a reduction in the amount of solid-solid interactions that take place. A regime when both liquid and solid-solid interactions take place is described as a mixed lubrication regime. The least resistance has been shown to exist in such a mixed lubrication regime, where coefficients of friction have been found to be as low as 0.02 (Buhl et al, 2001). As the film thickens, and fully supports the load of the skier, friction becomes dependent on the viscosity of the lubricating fluid, water in this case, and this can then be described as a wet (hydrodynamic) friction regime. Hydrodynamic drag is experienced when the water film shears under relative motion. Colbeck (1988) argues that the explanation for the frictional increase at large water film thickness is capillary attraction between ice grains and the slider. Liquid bridging occurs to ice grains which are not carrying any load and this exerts a drag force on the slider. This idea was further developed by Lind and Sanders (2006) who proposed that the porousness of the snow gave space for capillary bridges to form. The melt-water connects to the sliding base then elongates producing a drag effect (capillary drag).

These broadly categorised frictional regimes are based on the classic 'Stribeck' curve as shown in Figure 4 after Czichos and Habig (2003). This type of curve clearly shows the minimum value of friction to be at the demarcation between full fluid-film lubrication and some solid asperity interactions.

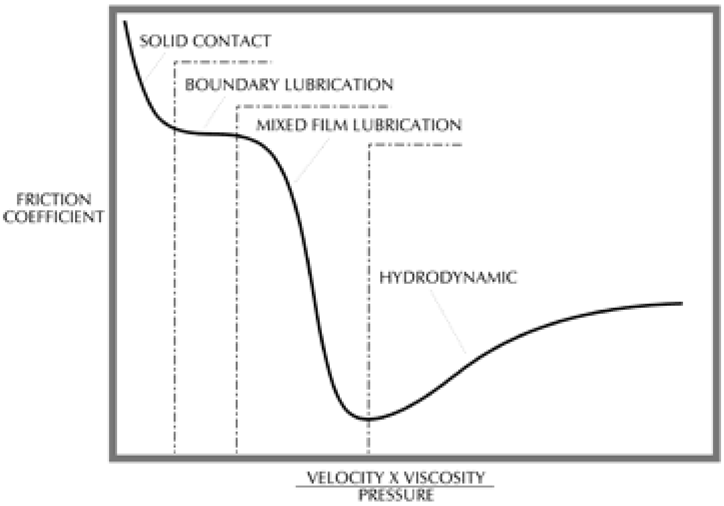


Figure 4: Stribeck curve detailing the different regimens of friction (Czichos and Habig, 2003).

A more detailed examination of the processes which govern sliding friction may offer insight to how proposed treatments, described in methods section 5.1, may influence sliding friction. In general, the term friction is used to classify all of the effects that taken collectively resist the motion of the skier, including air resistance. However, for the purposes of this review the focus will remain on sliding friction. The fundamentals of Newtonian mechanics of motion and the classic laws of friction shape this understanding. The laws of Newtonian mechanics are summarised below to aid clarity.

Vector diagram of a skier is detailed in Figure 5 where the G is the force of gravity acting upon the skiers centre of mass (CM). The centrifugal force (Fc) is the apparent force pulling the skier away from the centre of rotation as they turn. Whilst $F_{Athlete}$ is the force that the athlete exerts on the snow, which must provide and equal and opposite force to support the load of the skier.

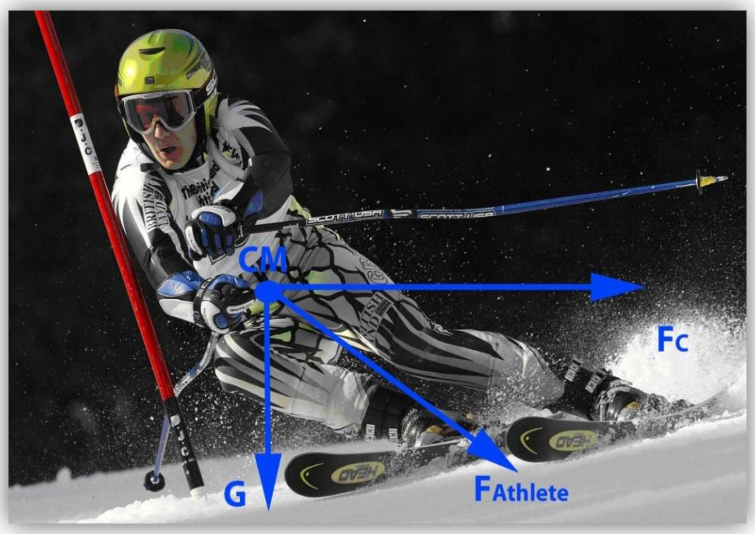


Figure 5: Vector diagram of a skier, Richard Coupe©

The empirical laws of friction, first enunciated by Leonardo da Vinci imply that:

1. The magnitude of the force of friction between un-lubricated, dry surfaces sliding one over the other is proportional to the normal force pressing the surfaces together and that
2. This frictional force is independent of the (macroscopic) area of contact and relative speed (Karloff et al ,2005)

Amonton (1663-1705) in 1699 continued to develop Leonardo's unpublished work and formulated two basic laws of friction. He stated that friction was predominately the result of the work done to lift one surface over the roughness of the other or cause the deformation or wear of the surfaces.

Coulomb (1736-1806) was the first to express frictional force as an equation showing that the frictional drag force (*f)* experienced by the slider can be expressed by:

$$f = \mu N$$

Equation 4:1

Where μ is the coefficient of friction (COF) and *N* is the Normal force perpendicular to that of the plane. This is often referred to as the third law of friction.

These laws imply that that the force of friction is independent of apparent area of contact. However, Moore (1975) and Czichos, (1978) more recently argued that these laws have several shortcomings. They suggested that the first law is correct except at high pressures when the true area of contact approaches the apparent area of contact. Additionally, the second law in not valid for elastic or visco-elastic materials but holds for materials with a defined yield point. Bowden and Tabor (1950) also previously determined that the true area of contact between ski base and snow is actually only a very small percentage state of that of the apparent contact area. The surface asperities of the interacting material were established to be responsible for this finding as the load of the slider is supported upon them. As the load on the slider increases more asperities come into contact causing the average area of contact to increase. Leonardo's principles, therefore, still hold true, however, it is the microscopic not the macroscopic area of contact which determines the amount of adhesion.

Colbeck, (1992) identifies a number of elements which contribute towards the total friction force (μ) experienced between ski base and snow. These are shown in equation 7:2 below.

$$Total\ COF\ friction\ (\mu) = \mu_{plow} + \mu_{dry} + \mu_{wet} + \mu_{cap} + \mu_{dirt}$$

Equation 4:2

Where μ *plow* represents COF due to snow compaction and plowing (ploughing); μ *dry* represents COF due to solid contact*;* μ *wet* represents the COF due to the resistance of melt water; μ *cap* represents the COF due to capillary attraction and μ *dirt* represents COF due to surface contamination.

These elements can act dependently or independently from one another. Whilst there are other, less significant, contributing components to overall friction which could be included, Equation 4:1 is sufficient to formulate an understanding of the major processes which govern the mechanism of sliding on snow. These components, however, are dependent on several variables, some of which can be influenced by engineering design or modification, such as the methods discussed in section 4.1; others are considered beyond human control and due to the naturally changeable environmental conditions.

4.3.1. Contact area

When a skier stands on the snow, their mass exerts a force distributed along the length of the ski on to the snow. The snow has to exert an equal and opposite force in order to support the load of the skier. The granular polycrystalline snow supports this load at many individual points of contact collectively with a given area of a_i. When the load of the skier is applied to any given contact point (spot), the contact spots will have to increase in number in order to support the load of the skier. This area of contact is far smaller than nominal base surface area of the ski. Pikhala and Spring (1986) found this to be as low as 5 to 15% of the surface area of the ski's base at -5°C. Baurle (2006) and Kuroiwa (1977) have shown that contact spots between base and snow grain to have an average radius of 100-200µm.

Actual contact area (A_c) can be defined as the sum of the areas of all the contact spot interactions.

$$A_c = \sum_{i=1}^{n} a_i$$

Equation 4:3

When a load (*N*) is placed upon the individual contact area (a_i) the sum of these interactions will constitute the normal force (F_N) exerted by the skier.

$$F_N = \sum_{i=1}^{n} N$$

Equation 4:4

When liquid water is present at the interface, the contact area is dependent on the physico-chemical interaction between the ski base and the snow. When two components (air, *a* and water, *w*) are in contact with a solid surface (Ski base, *b*), the fluids seek an equilibrium state dependent on the relative values of surface tension (γ) between each pair of the three part interface. The wetting (or dihedral) angle θ at which a droplet of water will rest on the surface of a ski base can be described by Equation 4:5.

$$\gamma_{wa} \cos\theta = \gamma_{ba} - \gamma_{bw}$$

Equation 4:5

It follows that when a force (F_N) is placed upon the water droplet it will spread out, further increasing its area of contact with the ski base. When this force is released the water will seek to return to an equilibrium state. Pikhala and Spring (1986) found that snow with densities of around 600kg/m^3 and 12% free water content gave rise to 45-50% contact; furthermore, 90-100% contact was seen with 28% free water content. This increase in area of contact has a direct bearing on further frictional heat generation and the resulting coefficient of friction.

4.3.2. Solid contact

When load is applied to a point of contact (a_i) between ski base and snow, the softer of the two materials will yield, increasing the area of contact to support the load (Bowden and Tabor 1964). The relative hardness of the slider (UHMWPE) and the snow/ice is therefore an important issue. The hardness of snow can vary enormously depending on its structure, loading times and ambient environmental conditions. The International Classification for Seasonal Snow on the Ground prepared by Fierz et al (2009) uses a quasi-objective, ram resistance, measure of snow hardness expressed in newtons. De Quervain (1950) cited in Fierz er al (2009) provides a range of experimental in-situ approximations of snow hardness. Whilst the precision of the methodology can be questioned, the ram resistance data clearly demonstrates the variation in hardness of snow and ice from 20N for very soft snow to >1200N for ice.

Kovak et al (1971) suggested the ideal hardness of snow in a giant slalom and slalom race should be in the order of between 7 and 10 kg/cm^2 density which approximates to 0.7 to 1.05 MPa. Studies using cross country tracks such as Sturesson et al, (2008) reported lower hardness values than this in 90 % of cases. The generally softer snow conditions and the decreased speeds of descent in cross country skiing prevent direct comparison with alpine skiing.

According to Petrovic (2003), polycrystalline ice can have a typical compressive strength at low temperatures of 5-25MPa from -10°C to -20°C. Ice, however, is far less elastic than UHMWPE. The Young's modulus for ice is approximately 9GPa (Gammon et al 1983). The modulus for UHMW-PE GUR 4150 is reported to be 0.6GPa by Laurian and Tudor (2003) and MatWeb (2013). Consequently it is far more likely that ice would experience plastic deformation and inevitably fracture. UHMW-PE, as previously mentioned, is visco-elastic and is therefore load-time dependent. If the impact occurs rapidly (>0.01sec) then the hardness of the UHMW-PE severely increases. Typical values for hardness are in the region of 30-90MPa but this can be expected to be reduced at lower temperatures (Sturesson et al, 2008) and also dependent on molecular weight. High local contact pressures over short load times will therefore fracture the asperities of the snow/ice which, in turn, will actuate a larger area of bulk material to support the load. Whereas, the base may respond, in the most part, elastically, some plastic deformation may also occur. Under most conditions it is likely that the base material is the hardest solid in the interface, the contact area can be defined as the normal force over the compressive strength of the snow pack. The unconfined compressive strength of snow(σ) is assumed to be a function of snow density, snow temperature and structure/size of the snow grains

(Mellor, 1964). When the snow is gradually compressed, it will yield until the snow stress equals the normal stress (Glenne, 1987).

$$A_C = \frac{F_N}{\sigma}$$ Equation 4:6

In soft snow conditions the friction caused by the compaction of the snow under the normal force of the skier's weight (F_N) is a significant factor. The skier will sink into the snow by the height (Δz) over a forward distance of one ski length (l). The work done by the component force necessary to propel the skier through the snow over a distance is the compaction force (F_{comp}) and can be expressed by:

$$Fcomp = \frac{\Delta z}{l} F_N$$ Equation 4:7

Dependent on the composition of the snowpack and pressure distribution of the ski, the exact compaction force (F_{comp}) would be difficult to calculate, however, in every case the compaction force required will be proportional to $F_N\Delta z$. Thus the coefficient of friction caused by the compaction of the snow (μc) can be expressed as:

$$\mu c = \frac{Fcomp}{F_N} = \frac{\Delta z}{l}$$ Equation 4:8

For sliding to occur, the surfaces must totally, or partially, deform elastically or plastically and in some interactions, must fracture the asperities (Kuroiwa 1977). Dry friction (μ *dry*) occurs when there is no lubricating layer present in the interface. If snow is assumed to be the softer material it may compress then shear due to the relative motion. This is dependent on the compressive strength (σ) and shear strength (τ) of the softest material Therefore, the deformation resistance, or dry frictional force (F_{dry}) will equal the sum of the shear stresses at every contact point (A_c) of the softest material; ice, ski base or wax treatment.

$$\boldsymbol{F_{dry} = A_{c\,\tau} = \frac{F_N}{\sigma}\tau}$$

$$\rightarrow$$

$$\frac{F_{dry}}{F_N} = \mu_{dry}$$ Equation 4:9

$$\rightarrow$$

$$\mu_{Dry} = \frac{\tau}{\sigma}$$

To reduce the coefficient of friction due to solid-solid contact, either between the UHMWPE base and ice/ snow or the wax coating and the ice, the materials in contact should be of similar hardness to prevent one from ploughing into the other. However, there are some discrepancies in the literature as to whether a hard wax coating can actually increase the surface hardness of the base. Kuzmin and Tinnsten, (2008) tested the Shore D hardness of a wax-treated UHMW-PE base with a cold temperature (-8 to -20°C) hard wax and with a warm temperature (0 to -4°C) soft wax. They reported that the Shore D hardness of the un-waxed base was 23% and 80% higher for hard and soft wax coatings respectively. Karloff (2005) affirms that ice is harder than PE in most situations. Whilst acknowledging this, Sturesson (2008) argues that both hardness and wear properties should be taken into consideration. He goes on to add that the elastic response from the base and time dependent hardness may be a prominent factor determining which material primarily yields in the interface. In very cold conditions (<15°C) a smooth hydrophobic slider may be more beneficial in reducing dry friction. Such a reduction of the roughness of the slider may minimise the amount of solid-solid interactions while allowing any available water to shear and elongate across the smooth surface. Cann et al (1994) claimed that smooth surfaces need proportionally thinner water films for good lubrication and Colbeck (1992) suggests that melt films can slide more easily over a smooth hydrophobic slider. Certainly SEM pictures in Figure 1 and Figure 2 show that a metal scraped surface would be beneficial in these circumstances. Also, cold temperature waxes may also reduce the surface roughness and shear stress experienced at the interface. The friction coefficient with a dry lubricated coating (μ_{Wax}) can be expressed as the share between the shear stress of the coating and how resistant the snow is to fracture or permanent plastic deformation. Where β is a particular wax coatings constant and H is the hardness of that coating.

$$\mu_{Wax} = \frac{\tau}{\sigma}\left(1 + \beta\frac{\tau}{H}\right)^{\frac{1}{2}}$$

Equation 4:10

The dynamic ploughing of the snow as it impacts the tip of the ski also creates a resistive force. The ploughing force (plowing, F_{plow}), unlike the compaction force is not dependent upon the skier's weight but upon the frontal area of the ski (width of the tip (w) x Δz), the initial density of the snow (p) and the speed of the skier (v). This is negligible in hard, compacted or well sintered snow as the change the change in height (Δz) is very small.

$$F_{plow} = \rho w \Delta z v^2$$

Equation 4:11

4.3.3. Heat generation

As previously mentioned, the dominant mechanism for the progression from a dry to a wet friction regime is the momentary generation of frictional heat during solid-solid contact. The number of these interactions increases with velocity, generating enough heat to cause the surface of the snow to change state into a liquid. The effect (Q) in a dry friction regime leading to a wet friction regime is detailed in Equation 4:12 below.

$$Q_{Dry} = v\mu F_N \rightarrow Q_{Wet} = \frac{\eta v^2}{h_{wf}}$$

Equation 4:12

Heat flow is a function of velocity; pressure; and the friction coefficient as shown in Equation 4:12. Where, q- heat flux (W/m^2), σ- max pressure (psi), μ- friction coefficient and v – velocity (ms^{-1}) (Sturesson 2008).

$$q = v\sigma\mu$$

Equation 4:13

The amount of heat flowing into the slider and snow is governed by the thermal conductivity of the respective materials (Kuroiwa, 1977). The temperature rise of a material above its initial value can be described by Equation 4:14 where t_0 is the initial starting temperature, ρ is the density, λ is the thermal conductivity and C_p is the specific heat capacity.

$$\Delta T = 2q\left(\frac{t_o}{\pi\rho\lambda c_p}\right)^{\frac{1}{2}}$$

Equation 4:14

As the skier's velocity increases so does the heat flow into the base, this causes further thickening of the water film enough to cause fewer solid-solid interactions to take place. Even at cold temperatures (-15°C) friction has been shown by Oksanen and Keinonen (1982) to decrease with increased speed where velocity is greater than 0.5ms^{-1} but less than 3.0ms^{-1}. The water layer is capable of supporting the load of the skier because the total time taken for each interaction is very small. The water film wets the base causing increase contact, which will, in turn, increase the thickness of the water film as a result of further heating at the interface. When the film height becomes greater than the average height of the asperities on both the snow and the ski base, the topography of both surfaces will have a less influential effect on friction.

This interaction has been fully described by Moldestad (1999) based on work conducted by Hamrock and Dowson (1981) using a non-dimensional film parameter (Λ) based on the height of the water film and mean roughness's of both surfaces. This threshold can be used to differentiate between dry and wet regimes. Where h_{wf} min = the minimum water film thickness (µm): R_{qbs} = the root mean square roughness of the ski base structure (µm): R_{qsn} = the root mean square roughness of the snow surface (µm) and Λ is the water film parameter.

$$\Lambda = \frac{h_{wf} min}{\sqrt{R_{qbs}^2 + R_{qsn}^2}} \qquad \text{Equation 4:15}$$

This film parameter has been criticised by Cann et al (1994) for not considering the collapse of the water film during loading and also because the film is dependent on surface structure of the sliding surface, not just its roughness. However, the water film can only be assumed to carry the load of the skier for a certain time (*t*) before collapsing into the snow's matrix. Practically if liquid water is poured onto snow, the height of the resulting puddle will reduce until the snow becomes saturated. This mechanism, detailed in Equation 4:16, allows for the reduction in the height of the water film over time as it squeezed out between the grains of the snow. Of course, it depends on the area (D) and time (t) of contact, as well as the max pressure exerted σ_0 and η is the viscosity of water as shown in Equation 4:16 below.

$$\Delta h_{wf} = \frac{16t\sigma_0}{3\eta D^2} \qquad \text{Equation 4:16}$$

Bäurle (2006) estimates the resulting thickness change due to the collapse of the film; with a velocity of 1 ms^{-1}, an assumed contact of 100µm with a load time of 10^{-4}s to be from 100nm reducing to 80nm. It should be noted that skiers generally travel at far greater speeds therefore, reducing the load time and subsequently reducing this squeeze out effect. Bäurle (2006) and Kaempfer et al. (2007) both suggest that the increase in the coefficient of friction experienced in a wet friction regime is most likely due to increased contact area and the additional generation of frictional heat. The viscosity of water is temperature dependent with typical values of 1.76 $\times 10^{-3}$, 1.5 $\times 10^{-3}$and 1.3×10^{-3} at 0°C, 5°C and 10°C respectively.

4.3.4. Water lubrication

The wet friction regime arises when there is excess water at the interface supporting the load of the skier above the height of the asperities separating the snow and base. Relatively few grains develop a pressurised water film that resists the shearing motion caused by movement. However, the reduction of dry friction through the lubrication of the water is observable in the reduction of the overall coefficient of friction. Resistance in the wet friction regime is attributed to both the viscosity of water, which is greater at lower temperatures and higher pressures, and the relative shearing motion of the water film between base and snow (Colbeck, 1996). Water is a Newtonian fluid and, as such, its viscosity is independent from load. When the fluid has zero velocity relative to that of the ski, friction is attributed to the velocity gradient and the viscosity in a non-slip condition (Day, 1990). This can simply be described as the resistance of the water to shear (viscosity η) multiplied by velocity over water film height (h_{wf}). The shearing motion is similar to that of the dry friction condition; however, the contact area is attributed to the wetted film area (A_W) rather than the sum of the contact spots (A_c).

$$F_{wet} = \tau\, A_w = \frac{\eta v}{h_{wf}} = \frac{\eta V A_W}{h_{wf}}$$

Equation 4:17

The behaviour of the water sliding over the interface can be turbulent or laminar. Consider a no-slip condition as defined by Day (1990), between the lubricating water film and the snow. The use of a theoretical no-slip condition can be used to idealise a model of ski base /snow interface which is separated by a very thin water film only few micrometres thick and predict the flow of that water over the ski. In this situation the resistance of the film to shear against the momentum of the slider is due to the viscous resistance of the water. Using the following values typical of alpine skis and skiing: $v=25ms^{-1}$ $\eta=10^{-3}$ and $h=10^{-6}$: then Re=0.025. The nature of the flow of the water film over the ski base is lamina rather than turbulent, characterised by the Reynolds number of less than 1. The relevant equation is detailed below.

$$Re = \frac{vh}{\eta}$$

Equation 4:18

Colbeck (1994) suggests that the dominant mechanism for the removal of water is actually the shearing motion and he mathematically explained the relationship between change in water film height and time. This mechanism is approximated to be half the volume of the film for a displacement equal to the average contact spot diameter of the water on the base. This is shown in

Equation 4:19 (Bäurle *et al*, 2007) where *D* is the contact spot diameter (m), *h*wf is the height of water film (m) and t = time (s).

$$\frac{\partial hwf}{\partial t} = \frac{h_{wf} v}{2\,D} \qquad \text{Equation 4:19}$$

Colbeck (1996) further suggests that the relatively high increase in the coefficient of friction experienced in the wet regime is due to the formation of capillary attachments. This process has the potential to explain the high friction exhibited when the water film is relatively thick in particularly warm and wet conditions. These bridges are believed to form between the base and snow; they elongate and then shear, exerting a force opposite to that of the sliding direction. There is currently no scientific model to quantify the effect of such attachments and their effect would only be relevant in the wettest of snow conditions with proportionally thick water films or at higher sliding velocities with increased frictional heat production. However, the increased contact area, up to 100% of ski base area, may also be a significant factor for such an increase in friction (Pikhala and Spring, 1986).

The relationship between frictional force, velocity and water film production has been investigated by Baurle et al (2006) using a tribometer at velocities in the range of 0-10ms^{-1} on ice. They concluded that in cold conditions (-10°C) only a thin water film develops, compared to warmer conditions closer to the melting point (1°C), where a thicker film develops. Lines of best fit calculated from the tribometer results show the variation in the coefficient of friction in relation to velocity at both temperatures; shown in Figure 6.

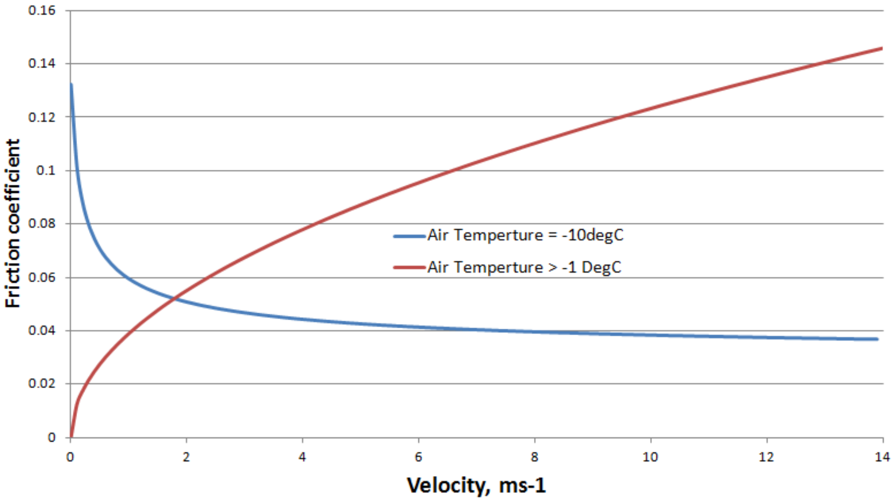


Figure 6: Gradients of best fit taken from the results of Baurle et al 2006 using a tribometer at temperatures of -10 and >-1°C

At higher sliding velocities, such as those in the range associated with alpine downhill ski racing (approximately 25-40 ms^{-1}), the development of thick water films and resultant shearing is a significant limiting factor. Whilst snow and environmental conditions would certainly influence the initial water film height and how quickly it develops, in the majority of day time conditions (snow temperature > -10°C), the skier would quickly reach a mixed or wet friction regime. Practical glide testing results by Buhl and Fauve (2001) also confirm that friction is lowest at -4°C to -3°C and that increasing dry friction by increasing contact pressure at lower temperatures reduces run times. Interestingly, a small increase in load did not affect glide times in these warmer temperatures, suggesting that a water film does support the load of the skier. The timescale of the development of a mixed regime would be dependent on a number of factors, most significantly the snow, speed and surrounding environmental conditions.

4.3.5. Ideal predisposition of the water film

In 'optimal', low friction, conditions a balance can be found between dry and wet friction, where a small number of solid-solid interactions take place but the water film generated is not significantly thick enough to shear. The friction coefficient in this mixed regime has been found to be as low as 0.05 by Barnes et al (1971); 0.03 (Shimbo1971) and 0.02 by Buhl et al (2001).

The dependence between the overall coefficient of friction and water film parameter Λ is characterised by Figure 7 based on Hamrock and Dowson (1981). Snow compaction (delta Z) would be likely to approach zero on prepared racing pistes at lower temperatures but this would not be the case in where fresh snow had fallen. The coefficient of friction values therefore assume there are negligible contributions from impact and compaction of the snow from a hard snow surface.

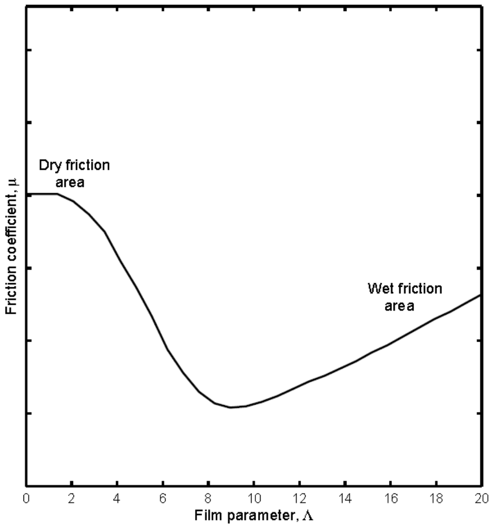


Figure 7: Relationship between the overall coefficient of friction and water film parameter Λ (Hamrock and Dowson, 1981).

Colbeck (1994b) recorded increasing temperatures from tip to tail of a ski during sliding, indicating that the water film increases in thickness along the slider’s length. Moore (1975) also suggests that the friction at the tip of the skis is probably due to dry friction at the front progressing to mixed and wet friction regimes towards the tail. Moldestad (1999) argues that it is still very difficult to predict water film development along the skis in all snow, skiing and weather conditions. The formation of the film, however, is strongly dependent on real contact area and velocity which can be modelled using the equations in this section and is summarised in Figure 8. Reducing the friction of skis can be informed by a thorough understanding of the elements governing the production of this film. The goal should be to achieve a 'perfect balance' by manipulating the water film height to support the load of the skier but at the same time, to avoid inducing shearing of the film Buhl et al (2001) demonstrated that at lower temperatures (below -6C) increase loading can actually reduce practical glide times. They suggested that, in this predominantly dry friction regime, load would contribute to this system, increasing frictional heating and shifting the regime more to a lubricated one. By influencing the formation or a water film in a variety of snow conditions, friction can be reduced and the water film used to lubricate the skis in a variety of snow conditions. This is dependent on a large number of variables which have been discussed. If the water film is to be influenced however, we may be able to learn from how a range of animals and plants resist wetting. This discussed in the next section, along with a critical review of current methods of adapting the running surface of the ski to snow conditions.

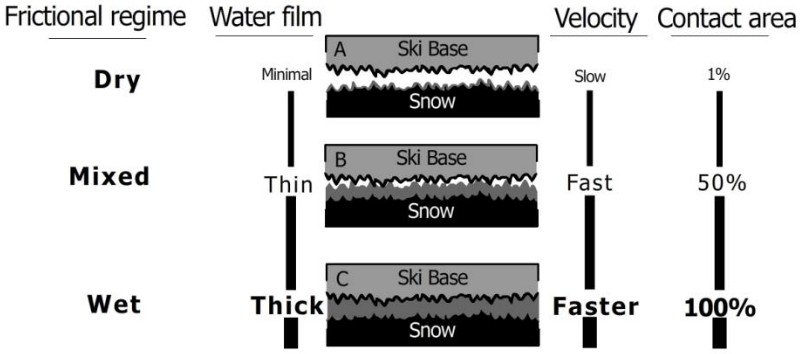


Figure 8: Diagram illustrating the relationship between the frictional regimes; water film thickness; velocity and real contact area.

Current surface modifications and post-treatments to the base material are described in section 5.1. These include the application of waxes for specific environmental conditions. The trend, in the product lines of most manufacturers, is that the softer and more hydrophobic the wax, the more suited it is said to be to warmer and wetter snow conditions. The practice of blending and mixing different waxes with the aim of achieving the largest performance increase is still considered more of an 'art' than a ‘science’. So how effective are these products at providing a performance increase? Furthermore, how does one measure this increase in performance? Given the enormity of different snow conditions, described in section 4.2, any treatment selection clearly still amounts to an educated guess. In addition, establishing the relative efficacy of different treatments is only as proficient as the test method(s) used. Test methodology for assessing the efficacy of waxes will be discussed in section 5.2.3. These methods include in-situ glide testing, and ex-situ tribometer or friction testing.

Testing which takes place in environments without natural snow clearly cannot compare waxes in different snow conditions. Even when testing the tribological interface in-situ, using natural snow, the snow type can be difficult to describe. Measured values such as temperature, humidity and hardness and crystal and grain type/size can only provide a guide. It is unlikely that the specific snow conditions during testing are replicated exactly on the day of a competition, where any performance enhancing ski treatment will be most beneficial. A suggested approach to the development of a methodology to match ski treatments to specific snow conditions would be to focus on the governing element responsible for transition between the varying regimes of friction (Dry→Boundary→Mixed→Wet→Capillary). The water film, or the tendency for the water film to increase in magnitude, could be used as the primary indicator of the effectiveness of any given treatment. Snow and Ice have a tendency to become liquid water and the temperature and pressure ice does so can be shown in a simple phase diagram. It follows, therefore, that the tendency for the water film to become larger in magnitude could be predicted with some degree of precision. Of course, an alternative, more direct approach would be to attempt to measure the water film in various snow conditions. However, an accurate methodology for such measurements has yet to be found, as small contact times and small contact areas make such an approach particularly difficult. At best, the results reported by Ambach and Mayr (1981) only show the order of magnitude of the water film thickness.

In transitioning between all the regimes from Dry→Capillary, velocity and pressure are the main governing elements. Frictional heat is generated in the Dry regime and the amount of heat generated not only depends on the coefficient of dry friction but also on both velocity and pressure. An increase in the water film occurs when the interface temperature and pressure are significant enough to phase change the snow pack. When a water film is already inherently present, the load of the skier is supported by the water film. An increase in velocity and the resulting shearing of the film generates further frictional heat which also increases the magnitude of the film up to the Capillary regime. Any subsequent reduction of film height in then governed by pressure as a result of the squeeze out effect of the water film penetrating between the grains of the snow.

As previously described and experimentally demonstrated by Colbeck (1994), a ski base increases in temperature during the course of a run. The rate of increase in the temperature of the ski base will depend on how thermally conductive the base material is, it's initial starting temperature and the proportion of dry + wet frictional heat produced by certain snow conditions. The heat flux is dependent on velocity, pressure and the coefficient of friction as evidenced in Equation 4:13. Unlike, glide testing, which is described in detail throughtout; skiers do not normally ski in a straight line down the hill; they turn. The act of turning introduces dynamic and cyclic velocity and pressure variations of different orders of magnitude, depending on the type of competition or event. Therefore, the amount of heat produced will vary and subsequently so will the resultant height of the water film.

When a skier, overcomes static friction and starts to slide on snow conditions with a certain tendency to produce a water film. As the ski is put on edge to turn, less contact area and higher resulting contact pressures are also magnified from the centripetal forces generated during the turn. Due to these factors, there is strong possibility of the film height increasing as greater heat flux is produced at the interface. As the pressure is released, at the end of the turn, less heat flux is produced subsequently lowering the amount heat flowing into the snow and base. Although, over the total time of the ski run, the starting temperature for every turn will be slightly higher from heat flux into the base experienced from previous turns, resulting in a net temperature rise of the base.

It is known from the Stribeck curve what order of magnitude of the overall coefficient of friction can be apportioned to each regime and that a mixed regime demonstrates the lowest coefficient of friction of all the regimes. Therefore, it can be presumed that any treatment should aim to seek this equilibrium between dry-wet regimes. However, any treatment aiming for this equilibrium must not only consider the snow conditions at the start but also cyclic film development generated during turning and the change in the temperature of the base over the course of a ski run.

In order to take account of these factors in any prediction of water film thickness and the effects of possible treatments, it is suggested that four starting conditions be defined, based upon the predisposition of the water film. These starting conditions are described below and their approximate position on the Stribeck curve is shown in Figure 9.

Condition I : Predisposition of water film : Very thin

The regime proportion could be described as the transition between Dry → Boundary. This occurs in very dry, very cold conditions; humidity <10% and very low snow temperatures of -25 to -15°C. Therefore, minimising dry friction with a view to initialising the production of a supporting water film would be most beneficial. The real contact experienced in this condition would be less than 10%.

Condition II : Predisposition of water film : Thin

The regime proportion could be described as the transition between Boundary → Mixed. This occurs in dry, cold conditions; humidity <50% and low snow temperatures of -15 to -5°C. Therefore, minimising both dry and wet friction with a view to maintaining the production of the water film and resulting film parameter would be most beneficial. The real contact experienced in this condition would be approximately 10% rising to 50% upon generation of thin water film.

Condition III : Predisposition of water film : Thick

The regime proportion could be described as the transition between Mixed → Wet. This occurs in humid, warm conditions; humidity >50% and snow temperatures of -10 to 0°C. Therefore, minimising wet friction with a view to minimising the production of the water film and resulting film parameter would be most beneficial. The real contact experienced in this condition would be around 50% rising to 80% upon generation of a thick water film.

Condition IV : Predisposition of water film : Very thick

The regime proportion could be described as the transition between Wet → Capillary. This occurs in humid, very warm conditions; humidity >80% and high snow temperatures of -5 to 0°C with even higher air temperatures. Therefore, minimising both wet and capillary friction with a view to minimising the production of the water film and resulting film parameter would be most beneficial. The real contact experienced in this condition would be around 80% rising to 100% upon generation of a very thick water film.

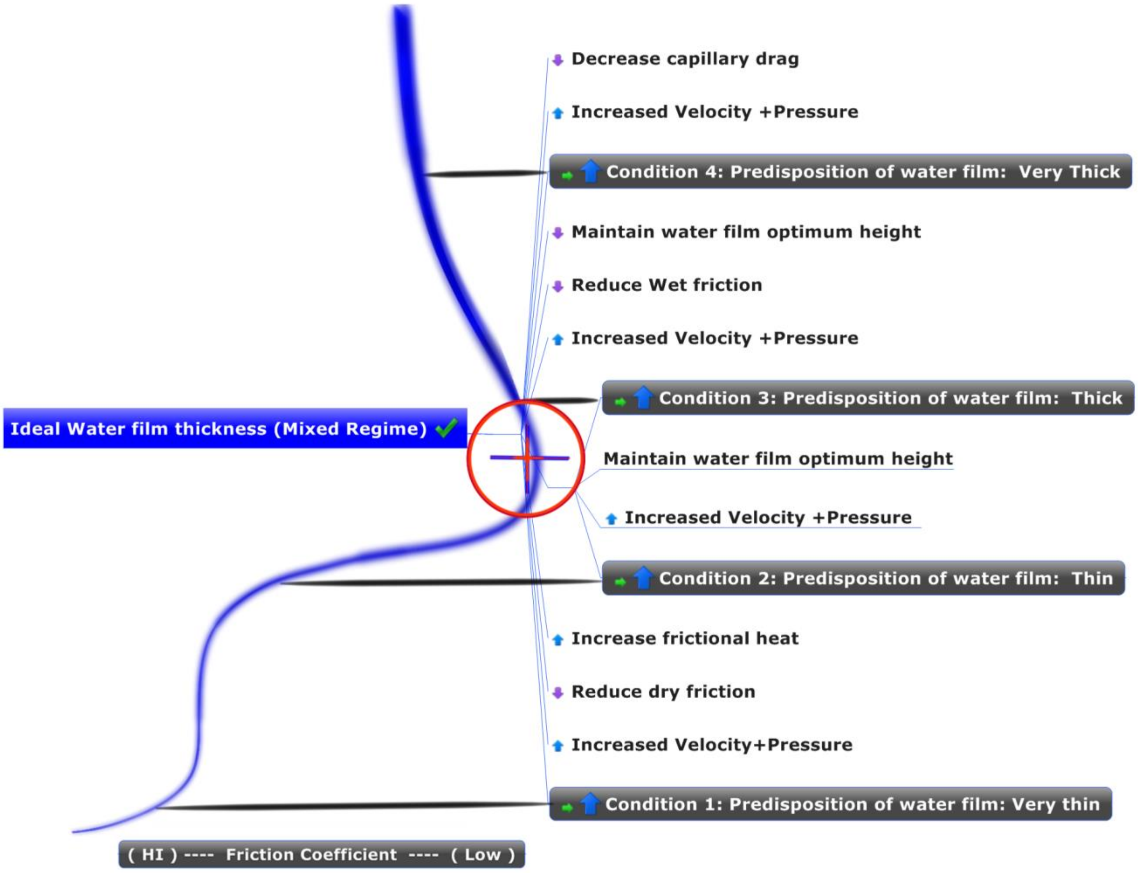


Figure 9: Starting conditions depending of water film height in Stribeck curve

The next section will focus on each starting condition in more detail and discusses current treatments and their effect on minimising friction. Such an approach will also be used to suggest possible new treatments or enhancements with the potential to enhance performance. This method of approach does not ignore snow conditions but it focuses on the tendency of those conditions to produce and thicken a water film. The frictional type which has the greatest proportion in that specific regime should be minimised in order to lower the overall coefficient of friction and subsequently achieve a performance increase. The temperature rise in the base material is only ever going to increase the film height during the course of a run. Therefore will a view to obtaining an ideal low, mixed friction regime and remaining in that theoretical window for as long as possible, it may be beneficial in condition I to increase frictional heating or start with a higher initial temperature. In condition II it may be beneficial to reduce dry friction at the front of the ski and wet friction towards the rear. In condition III it may be appropriate to focus more on reducing wet friction rather than dry. In condition IV it may be beneficial to focus on decreasing capillary drag and wet friction. This was summarised in Figure 9, where each of the starting conditions are indicated with a green arrow, subsequent film growth in blue and friction reduction in purple.

4.4.Hydrophobicity: chemical and physical

As previously described, the base of a ski preferably has a hydrophobic disposition. However, Wenzel (1936) and Cassie and Baxter (1944) established that wettability is determined by roughness as well as surface energy. Therefore, both the physical and chemical structure of the surface is responsible for the hydrophobic effect. Current chemical modifications with wax treatments have a hydrophobic potential of around 120° for highly fluorinated waxes (Jobwerx, 2007; Shafrin and Zisman, 1964; and Blossey, 2003). Even regularly aligned closely packed CF_2 hexagonal structures such as polytetrafluoroethylene (PTFE) only have a similar contact angle potential. Therefore, to increase the hydrophobicity of the ski base to above that of the chemical potential of the surface (120°) , appropriated optimisation of the structure has to be employed (Miwa et al, 2000; Bhushan, 2002; Blossey, 2003). Although, the interaction of the water molecules on a structured surface may demonstrate extremely high contact angles, it is unknown how this will change when subjected to the tribological conditions of the ski base sliding interface.

There are many examples in natural world of water repellent surfaces exhibiting contact angles of 150-165°. According to Quere (2005) in a major review of natural hydrophobic surfaces, over 200 plants and insects exhibit these highly hydrophobic surfaces; with familiar examples including: eucalyptus leaves, lotus leaves, duck features and butterfly wings. These natural surfaces generally have three common attributes: namely a dual-scaled roughness surface with texture or bumps, typically 10µm and a with smaller second texture (often micro hairs) typically in the scale of 1µm and additionally; this dual-scaled surface is then coated with a thin film of wax or wax crystalloids. These combined physical and chemical attributes are responsible for the high contact angles exhibited and are considered an essential factor for the development of super-hydrophobic surfaces. Wang and Liang (2007) offer a definition of super-hydrophobicity as a surface which has a contact angle of greater than 150° and a roll off angle of less than 10°.

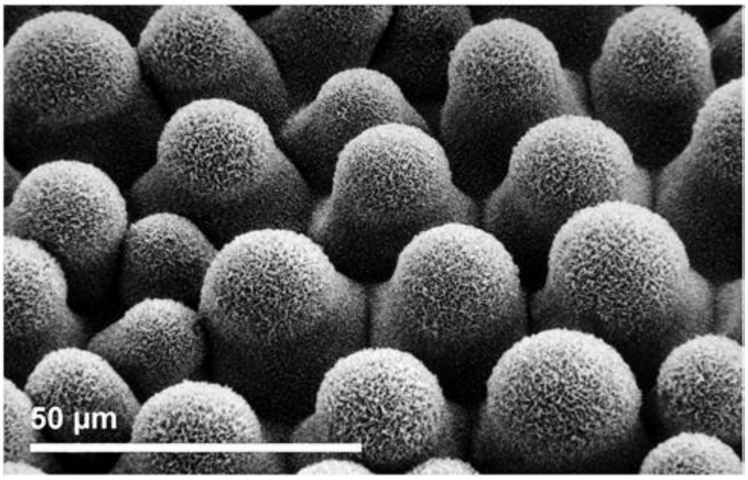


Figure 10: Image of super-hydrophobic plant, the common Taro (Colocasia *esulenta*) structured at two levels at scales of 20µm and hairs at a scale of 1µm (Quéré 2005)

Figure 11: Images of three different plants captured after the rain in a UK garden which illustrate the characteristic hydrophobicity of many species of plants. Richard Coupe©

Water can behave in two different ways on the surface either assuming the Wenzel and Cassie states as shown in Figure 12. The resulting contact angle is governed by forces acting at the interface where the water droplet meets the substrate. The interaction between solid/liquid; liquid/gas and solid/gas stipulates the water droplet's surface tension (Blossey, 2003). Within the Cassie state, the water droplet sits on top of the asperities leaving air below. The Wenzel state occurs when the surface tension of the water droplet is broken by the surface asperities. This leads to a lower contact angle and reduced water repellency and is induced by external pressure or by lowering the surface tension of the water. Due to the small, high pressure contact areas between a ski base and snow the mass of the skier would inevitably easily overcome the tension of the water droplet/film. However, wetting behaviour of a water droplet on the surface is purely thermodynamic. Consequently, it has no direct influence on the nature of fluid flow past the interface (Cottin-Bizonne et al, 2003). The water film in the sliding interface has been shown to be in the order of 1-1.5µm therefore, only the smaller magnitude of structures, both spacing and depth, may be appropriate. This is supported by Torris et al (2003) and Wier and McCarty (2006) that a smoother surface refinement, than currently applied to skis, would be more advantageous in increasing hydrophobicity but also assisting to reduce friction in certain snow conditions.

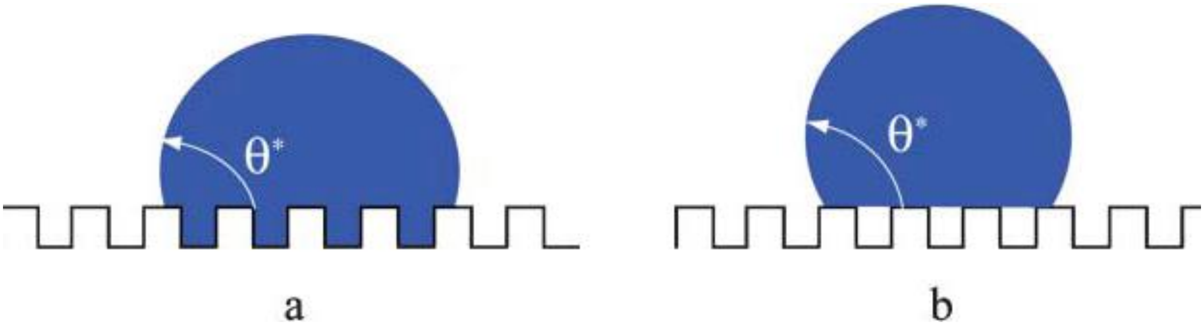


Figure 12: Two hydrophobic states: a) Wenzel b) Cassie (Quéré, 2005)

Synthetic examples often mimic the natural examples found in the nature with hierarchically ordered nano and micro roughness and an inherently low-surface energy coating material. They can be imparted onto different substrates by a variety of methods, significantly increasing the resultant contact angle. Commonly, a directed beam of electrons, ions or photons are used in nano-lithography to impart a structure onto the chosen substrate. However, polyethylene is not suitable substrate for this method. These synthetic surfaces are simplified versions of the dual-roughness of plant structures with geometrically designed asperities spaced between 100µm and 100nm. Unordered fractal surfaces have also been shown to increase hydrophobicity (Onda et al, 1996). However, such surface modifications are very susceptible to damage (Blossey, 2003). When considering the application of hierarchical or fractal surface modification to the sliding surface of a ski, it quickly becomes apparent that these type of structures may not be appropriate unless the wear resistance is improved and nano-lithography can be applied to the UHMW-PE substrate.

The contact angle is a valuable parameter to measure the wettability and spreadability of a droplet, and it is independent of the droplet volume on a homogeneous solid surface (Zisman, 1964). Several experimental treatments, described later in this section, require a measurement of the wettability of the surface. A non-wetting drop would form a prefect sphere on the surface of the substrates with a contact angle of 180° which represents the theoretical maximum. However, the surface tension of the water droplet interacting with the atmosphere and substrate causes the droplet to relax into an equilibrium state. Thus a contact angle of 180° or above cannot be achieved under normal atmospheric conditions (Zisman, 1964). Equation 4:5 listed in section 4.4.2 details this interaction between substrate, atmosphere and liquid. Any substrate with a liquid droplet forming a contact angle of greater than 90° can be considered hydrophobic; less than 90°, hydrophilic. Figure 13 below illustrates increasing contact angles with the crossover at 90° where the Interfacial energy of the solid and liquid interface equals the Interfacial energy of the solid and vapour interface.

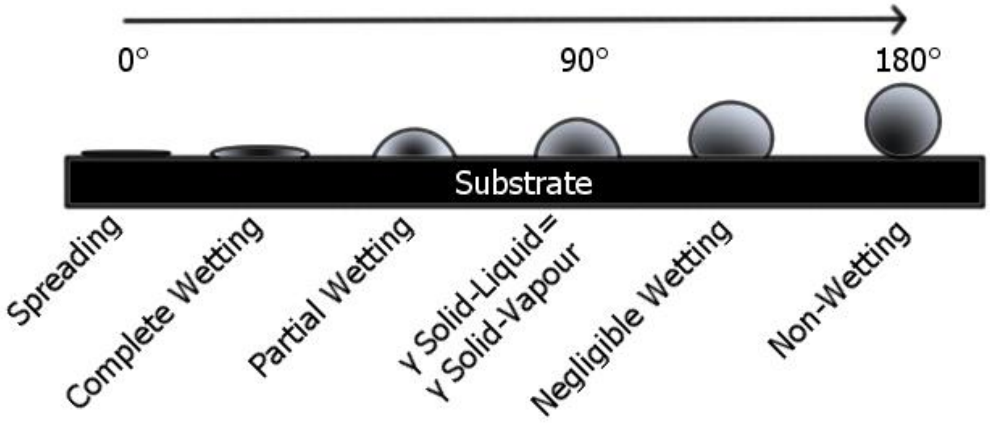


Figure 13: Illustration of varying contact angles on a substrate

According to Jobwerx (2007), fluorocarbon waxes have already reached the maximum chemical hydrophobic potential of around 120°. Additionally, waxes attract dirt, wear and consequently need reapplication. Pure fluorocarbons are also utilised as a finishing treatment in traditional ski waxing methods discussed in section 5.1. These are imparted on the surface by frictional heat encapsulating them into the surface layer of the underlying wax. Without a wax layer present they would not adhere to the surface of the UHMW-PE without some form of bonding mechanism.

If we continue to use wax as a bonding mechanism for hydrophobic chemicals then it would seem a natural evolutionary step to add a structural element into the wax matrix to improve hydrophobicity. This is based on examples of natural hydrophobicity where a chemical and physical structural element is present to improve water repellency. This notion is also reinforced by the finding that a structure or roughness in more beneficial in breaking up and reducing the water film height in starting conditions III and IV. The water film height in a boundary regime is presumed to be of nanometre scale therefore any such structure would also logically have to be of this magnitude. One area of interest for a wax additive to provide a structural element is hydrophobic fumed silica which has an average particulate size of approximately 10nm. Another current industry use of for these nanoparticles is as polymer fillers. Could these nanoparticles be incorporated into a UHMW-PE ski base material? This is investigated in section 6.3.2 .

Polydimethylsiloxane (PDMS) should be a polymer of interest to the ski industry as it demonstrates some beneficial properties. Owing to its highly flexible silicone/oxygen backbone it belongs to the family of silicones. The flexible backbone provides virtually unhindered rotation about the siloxane bonds. It had favourable wetting properties with methyl groups extending from the backbone, giving contact angle of 90-120° and a low surface tension of 24 dynes/cm (McDonald, 2000), which is comparable to current ski waxes. At low molecular weights it is utilised as a lubricating oil, but is also used in shampoos and food as an antifoaming agent due to its non-toxic properties. It's visco-elastic properties, like polyethylene, bestow a time dependent hardness. The tensile strength is 2.24 MPa with a resulting Young's modulus of 360-870 kPa (Mark, 1999). When blended with other polymers, such as polyethylene, polyurethane or polystyrene, the resulting blends demonstrated a lower coefficient of friction (Ryan et al, 2000 and *Dow Corning*, 2012). Additionally, Khorasani et al (2005) have investigated blended PDMS and UHMW-PE for improving wear in artificial hip joint acetabular cups, although, this study found difficulty obtaining a uniform matrix, due to the processing difficulties with UHMW-PE. They used a hot mixing (100 rpm at 180°C) and compression moulding method to produce samples, shown in Figure 14.

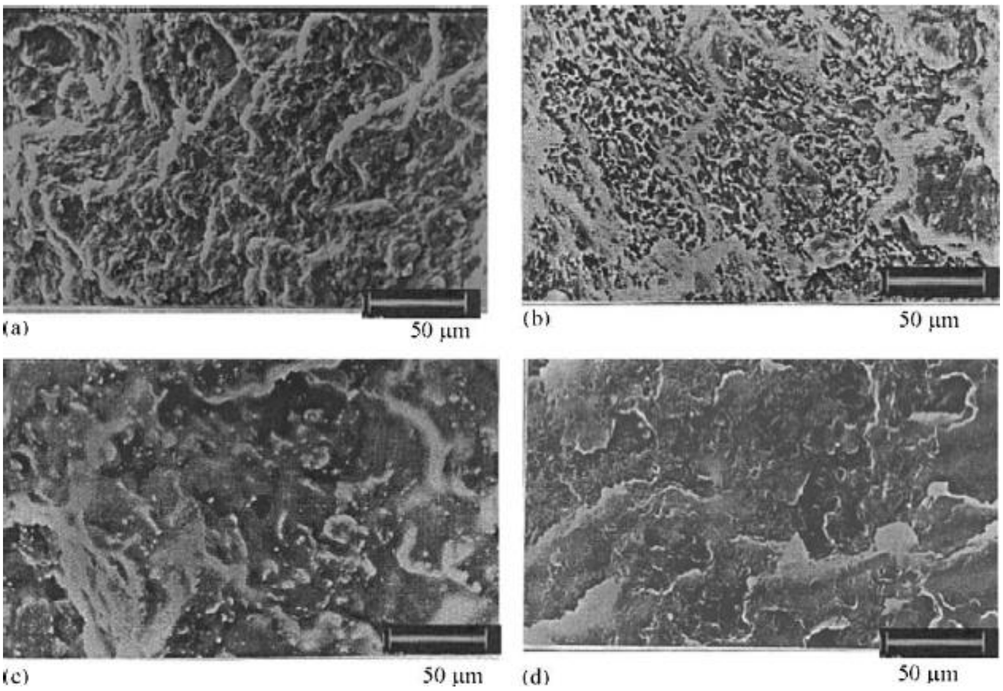


Figure 14: SEM images of UHMW-PE/PDMS blends: (a) 80% UHMWPE; (b) 70% UHMWPE; (c) 50% UHMWPE; (d) 90% UHMWPE. (Khorasani, et al. 2005)

In summary the advantages of using PDMS are:

- Hydrophobic 90-120°.
- Young modulus of 360-870 KPa
- Tensile or fracture strength 2.24 MPa
- Good adhesion properties
- Flows through the amorphous regions of plastics through to the surface.
- Reduces friction at the surface
- Improves melt flow properties
- Improved impact, tensile and abrasion resistance when mixed with polyolefins at 1%

Perfluoropolyether (PFPE) should be another polymer of interest to the ski industry. With a carbon oxygen backbone populated with highly hydrophobic fluorinated groups it has a resulting surface tension of 22 dynes/cm. (MATWEB, 2012) Compared with the C-H bond found in polyethylene, the C-F bond is more stable because of the higher bond energy (C-F: 485kJ/mol and C-H 414kJ/mol), higher electronegativity and a smaller diameter. These factors result in low intermolecular cohesion which reduces the surface energy of the polymers containing a high component of the C-F radical (Fried, 2003). Fluorocarbon polymers such as PFPE have splendid oxidative stability, chemical inertness, low refractive index and thermal insulation (Gnanappa, et al, 2008). PFPE is widely used in the magnetic disk drive industry as a lubricant to reduce the coefficient of friction on the head-disk interface (Gnanappa, et al, 2008). Due to the beneficial lubrication properties, as previously discussed, it has already been used as a lubricant for skis by a company named *Zardox* in a product called *Notwax*. One of the manufacturer's recommended methods for application of this product is to combine it with a hard hydrocarbon wax; named the 'Felix method'. Glide testing conducted in an indoor snowdome by Coupe (2008) demonstrated that this type of perfluoropolyether lubricant showed a positive effect in the reduction of snow friction once the element of dry friction was overcome in the first 10m of the run. Both the *Notwax* and the 'Felix method' were investigated, however, no distinction between these two methods could be found. Because *Notwax* is miscible with a hydrocarbon matrix it suggests that it could also demonstrate these properties when used as an additive to the base material.

One area of particular interest has been the research into man-made surfaces mimicking a natural phenomenon found in nature, known as the *lotus effect*. The chemical resistance of a surface to water can be complemented by a structure at the nano or micro scale. Any surface which is initially hydrophobic can be made superhydrophobic by modifying its structure (Quere, 2005; Cheng et al, 2006). Mimicking the lotus leaf with its dual scale roughness of micro structures together with nanoscale features on the surface, has led to the production man-made surfaces with advancing contact angles of 160-180° (Quere, 2005). Wetting of these rough surfaces can assume either an homogenous state, where the water completely penetrates the rough surface asperities or an heterogeneous state, where air is trapped underneath the water (Marmur, 2004). Micro and nanostructures on ski bases would probably exist in a homogenous state due to high local contact pressures overcoming water tension. In this state, the increased contact area and the decreased mobility of the water droplets might have a negative effect on friction. However, very few scientific investigations have been conducted involving these types of structures across all frictional regimes, especially with forces and velocities with the values associated with skiing.

A study by Lorusso et al (2008) irradiated UHMW-PE samples in an attempt to produce a hydrophobic surface. They found that the contact angle linearly decreased with the number of laser pulses. This was attributed to the formation of oxidised groups rendering the surface more hydrophilic. This reduction of the PE's chemical resistance to water may have counteracted the hydrophobic effect of the changes in nanostructure. However, polyethylene surface modification can be achieved in several different ways, for example through acid treatment, chemical grafting and radiation treatments. The effects and methods of these different treatments developed for polyethylene have been comprehensively reviewed by Desai and Singh (2004). A rare investigation by Kietzig et al (2009) into how roughness at a nanoscale influenced friction across all the friction regimes showed that friction could be reduced in a wet friction regime by nano structuring. Steel alloys with different surface preparations were used as sliders. The samples of interest had a dual scale roughness of 500nm spacing with micro bumps of 9µm and were compared with samples which were polished which had a 600µm roughness in concentrically and randomly grooved patterns. As expected, this investigation revealed that initial dry friction was increased for the dual scale roughness compared to a smooth polished slider. However, at warmer temperatures and higher sliding speeds the dual scale roughness reduced friction. The force (3N) and small contact area was not significant enough to cause a contact pressure comparable to alpine skiing. Comparisons, therefore, cannot be drawn between this investigation's findings and the effect micro /nanostructures would have if utilised on a ski base. Further investigation at higher contact pressures might reveal whether friction can be reduced in these conditions with such dual scale structuring.

Nanoimprint lithography (NIL) has recently emerged has a promising technology for nano-patterning the surface of UHMW-Polyethylene. Micro-scaled patterns of 50-200µm have successfully been applied to UHMW-PE by the use of hot press moulding with a nano/micro textured mould (Zang et al 2012; Kustandi et al 2009). In both studies the resulting samples show a significant reduction of friction. Kustandi (2009) reported a 35% reduction in the coefficient of friction compared to that of an un-textured polyethylene surface in dry sliding at 3mN loading whilst interesting, Zang et al (2012) reported an approximately 70% reduction in lubricated friction with a 50µm pattern lubricated with 15µm of distilled water with 700N loading @ 200rpm. This technology shows significant promise as both studies reported increase wear resistance (35.5% by KustandHabi et al, 2009) which is an important factor when dry sliding over hard ice crystals. In most situations, the sliding surface has to pass through a dry friction regime to reach a lubricated, wet friction regime, although this may happen almost immediately during skiing. The solid-solid interactions in a dry friction regime are responsible for the bulk of the wear exhibited on a ski’s base. Therefore, both dry and wet/lubricated regimes have to be considered. These studies suggest nano-imprint lithography as a possible avenue for further exploration which has not currently been applied to ski base sliding friction. This technology is in the very early stages of commercialisation and the high temperatures required, near the melting temperature of UHMW-PE, could affect other laminate layers in a ski and this could provide a major challenge to its successful application.

Current structuring methods reduce friction in the wet regime (starting condition III and IV) by appropriately matching the coarseness of the base to the level of the water film, as previously described in section 4.4.5. However, there is some evidence that the water film becomes thicker towards the tail of the ski (Colbeck 1992). Current base treatments incorporate the same patterning of structuring along the whole length of the ski which, at best, represents a compromise. A structure increasing in coarseness down the length of the ski, in commensurate with water film height, may be more effective at reducing friction. However, further investigation is clearly needed to quantify the variation in film thickness when sliding so that optimum structure coarseness can be developed.

In colder, dryer, snow conditions (starting condition I and II), dry friction can be reduced by decreasing the surface roughness of the base allowing proportionally thinner films to lubricate the interface. Stimulating the onset of early water film creation has never been explored although it would involve increasing dry friction in order to achieve a rapid transition to a mixed friction regime. In a mixed lubricated regime, friction is around 10% lower than in dry solid-solid contact. Increasing or decreasing the real contact area would control the coefficient of friction and subsequent heat flux into the interface. This could be achieved chemically; by altering hydrophobicity, or physically; by adjusting roughness. Therefore, in starting condition I or II an increase in roughness at the front of the ski would increase dry friction and decrease the time taken to reach mixed lubrication, whilst at the tail of the ski the proportionally thinner film would slide more easily over the smoother surface. In starting condition III, dry friction and wet contact should to be reduced at the tip of the ski to minimise the tendency to increase the magnitude of the water film. Towards the tail of the ski, friction will be balanced towards a wet friction regime and therefore, an application of an appropriate magnitude of macroscopic structure and microscopic roughness could be applied to reduce the water film parameter. In starting condition IV, the whole length of the ski should seek to control the water film height by increasing the macroscopic and microscope roughness along its length. In summary; once a film lubricates the interface a controlled increased in roughness or hydrophobicity along the length of the ski would seek to keep the ski in a mixed regime for the majority of the skis length.

Investigation of nano /micro structures across the frictional regimes would be beneficial in the future of base structure designs. Current methods of either indirectly or directly imparting a defined roughness on a UHMW-PE are discussed in section 4.5.1. These include stone grinding for macro structures; additionally Plexiglas and metal scraping have been shown by Sturesson (2005) to indirectly impart a roughness to UHMW-PE. Waxing seems to complicate the interface by imparting a smoother surface layer on top of an already roughened surface. However, it is tentatively suggested that ski preparation should focus on ski base roughness rather than covering any rough surface over and filling it in with softer wax. As the wax layer wears off it will inevitably expose the underlying roughness of the base anyway. Sturesson (2005) tested a variety of traditional treatments with optical profilometry providing values of arithmetic mean roughness (Ra) and (R_T) maximum peak to valley height listed in Table 11 below.

Table 2: Results by Sturesson (2005) of the indirectly imparted mean (Ra) and peak to valley (Rt) roughnesses indirectly imparted on a UHMW-PE substrate.

Treatment	(Ra) µm	(R_T) µm
Stone ground	5.7	25
Steel Brushed Surface	5.4	30
CH4 waxed surface	3.37	22
Nylon brushed surface	3.1	23
Metal cutting edge scraped surface	0.2	1.2

As previously stated, Bäurle et al (2006) argues that the current range of surface roughness (10-150µm) imparted by modern stone grinding techniques is too course for the effective control of the water film. It seems, from Sturesson's (2005) results, that a metal scraped surface provides a similar peak to valley (R_T) roughness to that of the water film height. This would certainly be beneficial in starting conditions I and II when very little melt water is present. Starting at conditions III or IV may require an additional macroscopic structure, of the magnitude of that provided by a stone grinding technique. Giesbrecht et al (2010) created a range of sliders with different grain patterns and sizes which were then observed using optical profilimetry to determine mean roughness and peak to valley roughness. They investigated their sliding properties on snow at relatively warm snow temperatures between -2 and -4°C and at slow speeds (maximum average speed 5.8ms^{-1}). They suggested an optimum surface roughness in the range 0.2 - 1.0 µm when friction was at its lowest. When either the roughness was reduced or increased beyond this optimum range, the time of descent increased. It is suggested that a dual scale roughness could be imparted between a stone ground macroscopic structure and a metal scraped surface. However, are there other methods to impart a microscopically smooth surface between macroscopic structures: ceramic or glass scraping for example? Could the previously mentioned nanoparticles be used as a micro abrasive to control the roughness of the surface? Certainly diamond lapping pastes are used for polishing metal surfaces to specified roughnesses, as they contain diamond particles of specified nanoscale sizes. However, it is reasoned that any surface treatment should not leave any trace after application otherwise it might affect the resulting coefficient of friction. Any treatment applied may not ever be totally removed and may increase friction due to dirt/contamination. A treatment could be removed with a solvent and a micro abrasive, but this action may damage or alter the roughness imparted. However, any treatment which aided ski base sliding friction by increasing hydrophobicity and which also encapsulated the removed UHMW-PE and dirt, may be beneficial.

Polytetrafluoroethylene (PTFE) could be considered a first-priority candidate for an alternative base material as it possesses ideal hydrophobic low friction properties. This would be very advantageous because post-treatments would not be required to increase the hydrophobicity of the surface. However, the wear resistance of this polymer is not ideal. The use of PTFE as a base material was considered back in the 1950's (Bowden, 1953), however manufacturers rejected the idea due to the high material cost and adhesion difficulties. If we take cost out of the equation; adhesion problems have been solved by modern surface refinements (Bradey, 1996) and wear resistance has been increased with the addition of a crosslinking process by irradiation (Oshima, 1995). Nevertheless, the mechanical properties of PTFE may still only be acceptable for use in softer, less abrasive snow conditions. Tang el al (2010) measured the tribological and wear properties of cross-linked PTFE. The results showed that although the Young's modulus and wear resistance of the material increase significantly when irradiated with highest doses of radiation. Tang et al reported a Young's Modulus of 375MPa for irradiated PFPE and 107MPa for non-irradiated. The coefficient of friction actually increased by 0.05-0.1 when irradiated. The absorbed radiation doses were shown to be related to friction coefficient, which only slightly increased at lower absorbed doses. However, the coefficient of friction increased after the more highly cross-linked surface layer was abraded. In summary, it would appear that the low wear resistance and deficient mechanical properties of PTFE prevent it from being generally used as a bulk ski base material, although it may prove useful as a polymer modifier.

There is one company, *FX-smart base,* which has developed a polypropylene-copolymer blend with added percentages of lubricants, hardeners and straighteners, antistatic elements and fillers to tailor the mechanical properties of the resulting material. *Fx-smart base* utilises a blend of two propylene-alkene based co-polymers (propylene-ethylene, the other propylene-(C_4-C_{12}). The ASTM D2240

Shore D hardness of propylene-ethylene is in the region 60-70 comparable to that of UHMW-PE. Their method to deduce whether this matches the current sliding properties of UHMW-PE or post-treated UHMW-PE however, is significantly flawed in their patent. They employed a friction ramp testing method discussed in section 6.3, inclined at 15°. Sliding speeds were >1ms^{-1} on two snow test beds of -6° and -2°C snow temperatures, -4°C and 2°C air temperatures to replicate cold dry snow, and warm wet snow.

The UHMW-PE samples were simply abraded with abrasive paper (8µm grain average grain size) like the other two FX-base specimens tested. It would be logical to assume that a single wax coating and Plexiglas scrape would not remove the hairs arisen from abrasion. The FX-base is of a lower molecular weight to that of polyethylene therefore, protruding chains would not become an issue. There were no contact angle tests published on these three samples only a statement that an "extremely slidable film surface has been obtained, on which water drops spherically rolled off" in relation to the FX-smart base not contrasted with polyethylene.

The samples had a surface area of 80cm^{2} however; the weight of the slider and subsequent reaction force was not mentioned. Ski bases have the mass of the skier pushing them against the snow creating high local contact pressures. The sliding speed is extremely low <1ms^{-1} therefore it could be assumed that friction was predominantly in a dry friction regime without frictional heat generation from increased velocities or high pressure contacts. However, without sizeable pressure would the number of solid-solid interactions where the snow ploughs into the surface layer of the wax be significant enough to extrapolate the performance advantage? Even if a difference was evident, the generation of frictional heat and subsequent thickening of the water film may significantly change the conclusions drawn. It would have been beneficial to measure the relative humidity of the snow, at least in an attempt gauge the water content. Information on the snow classification (age and type and hardness) would also have been beneficial. It therefore can be assumed that the FX-Smartbase has yet to demonstrate its worth as a serious competitor to the current UHMW-PE ski base. Whilst it should not be discounted at this stage, further tests are necessary before it could be considered as a serious competitor material to UHMW-PE. As the aim of this thesis is innovation not invention therefore, polyethylene will remain the bulk material of choice for the ski base. A more suitable polymeric blend of polyethylene may be the way forward to reducing friction along combined with the subsequent refinement of its properties to tailoring it to optimise the progression of the water film.

Chemically modifying UHMW-PE to increase hydrophobicity and the use of nano technology should be of great interest to the snow sport industry. Methods for mixing highly hydrophobic nanoparticles and clays into polymer blends have recently been reported by Sentmanat et al (2009). However, much of this research and development remains unpublished or commercially sensitive. Nevertheless, commercially available products have been recently developed by manufacturers which consist of waxes with nano-composite additives to aid sliding (Holmenkol, 2012). Similar nano-composites are being investigated as additives into UHMW-PE and other polymer blends to enhance hydrophobicity and further lower the surface energy of the base. Adding enhancing components to create polymer blends is not new technology; fluorocarbons and graphite have been added to ski bases in the past. However, if a sliding surface could be created as hydrophobic as a traditionally waxed surface (contact angle >120°) then there would be little need for hydrophobic post-treatments. If a combination of improved base hydrophobicity and optimised base structuring could be achieved, would there be a need to treat skis with any additional chemical waxes in the future?

Hydrophobic fumed silicas such as *Aerosil*$^{(R)}$ have been used in a variety of applications to increase the hydrophobicity of surfaces. *Aerosil*$^{(R)}$ has been used as an additive in plastics, coatings and even for skin care (*Aerosil*, 2009). The fumed silica is originally hydrophilic but can be reacted with various silanol reagents to render the silica hydrophobic. There have been many patents filed on a variety of applications for such hydrophobic fumed silicas, although none of these, to date, have been for applications involving snowsports.

For the purposes of making a hydrophobic surface; *Aerosil*$^{(R)}$ 972 and 8200 are of interest. *Aerosil*$^{(R)}$ 972 is after-treated with DDS (Dimethyldichlorosilane) while the *Aerosil*$^{(R)}$ 8200 is after-treated with hexamethyldisilazane. An effect known as the “lotus effect” which minimises dirt adhesion due to the structure and high hydrophobicity can also be created artificially with *Aerosil*$^{(R)}$ LE1, 2 and 3, although this type of *Aerosil*$^{(R)}$ is not recommended for use with binders. *Aerosil*$^{(R)}$ has established itself as a very versatile additive; it has improved hydrophobicity in other products and could, arguably, have potential to be incorporated into a wax treatment or even into a polymer base itself.

4.5.Section summary

This section has focussed on the tribological system involved when skis slide on snow. Investigating sliding friction, particularly under the diverse conditions which exist in a real alpine environment is challenging. The development of a water film at the interface between the ski base and the snow is of major importance to sliding friction. Attempts to measure this have been discussed but it still remains a challenge to quantify this experimentally during a ski run. The material properties of both the ski base and snow are significant in the development of this lubricating water film as are the environmental conditions.

The scale of the profile of any base structure should be closely matched to the water film thickness in order to reduce wet friction. This should also be closely matched to the snow and ice gain size to reduce dry friction. There is some disagreement as to how thick the water film becomes especially in a range of snow conditions. However, the film thickness can be confidently inferred to be in the low micro and nano-meter scales. Appropriately matching base scale profile to the snow conditions should also be aimed at these scales. Currently little consideration is given to the micro-scale and even less to the nano-scale levels of roughness in the ski industry. Stone grinding, abrasive nylon treatments and repeated waxing and scraping are the methods used to influence the surface structure. Some hydrophobic plants and animals accomplish high levels of water repellency by dual scale micro and nano structuring with a chemical coating. This observation may provide an insight to future directions and possible advancements in ski base sliding friction.

Currently ultra-high molecular weight polyethylene (UHMW-PE) is the material of choice for the ski industry due to its superior sliding properties. The effects of base treatments, both chemical and physical and sliding friction on UHMW-PE have been discussed. Some potentially new strategies have been suggested to improve the hydrophobicity of ski bases. These include: modifying an existing wax treatment; modifying the surface structure; modifying the bulk UHMW-PE base material by including other more hydrophobic polymers. Methods of investigation will include; contact angle testing to assess hydrophobicity; scanning electron microscopy will be used to observe the surface structure at up to 10000x levels of magnification; Friction ramp and glide testing to assess the influence of friction on specific treatments. Overall, this section has informed the selection of chemical and physical treatments and the method of investigation which are described in detail in the next section.

Chapter [5]   Methods

5.1. Traditional treatment methods

Traditional waxing methods employ rather complex procedures with some degree of variability or choice. Most skis invariably have a base structure imparted by stone grinding and wear present on the sliding surface. Depending on the initial condition of the skis, the first step is to remove any contaminants and “condition” the base. A chemical base cleaner (solvent) can also be applied to soften previous wax treatments so they can be more easily removed. A light or non-abrasive cloth is used to remove the majority of the chemically softened wax. *Fibretex* is the trade name for *Swix* abrasive pads in which small abrasive particles are bonded to nylon fibres. They are available in a variety of different grades for deburring and cleaning the ski and are very similar to the *Scotch-Brite* household cleaning pads produced by *3M.* Due to the abrasive nature of the pads, these should be applied before edging because they can dull the edges. *Swix* (2012) seem to offer the greatest grade range of pads compared to other manufacturers. The finer grades are used to remove or polish the surface layer of UHMW-PE. This also removes ‘hairs’ or ‘fur’ which can form under abrasive snow conditions. These ‘hairs’ are the ends of the PE chains exposed from the polymer matrix. The non-abrasive grades can be used for polishing after waxing and can also be used with a chemical base cleaner to aid the removal of wax without removing polyethylene mass from the skis base. The method used in the investigations using this “traditional” method for waxing skis is described below, although it is acknowledged that there may be some variation in application during the preparation of some of the skis for glide testing.

Traditional base preparation method.

The base was first wiped thoroughly with a clean absorbent towel or cloth. It was then scraped with a Plexiglas scraper and brushed with a clean nylon brush prior to re-scraping with Plexiglas. Wax remover was then applied to a non-abrasive *Fibretex* pad and the pad was rubbed over the base approximately 20-25 times with one repeat application of wax remover. The base was then wiped with a lint-free cloth.

Wax application method

Following the base preparation, the wax was then applied to the surface using a hot-waxing process. An iron was used to melt the wax onto the ski. The iron was set to a specific temperature, just above the melting point of the wax and the additives used. This information is usually given by the wax manufacturer, however, generally, if the iron smokes then it is too hot. The wax was placed against the iron, on the correct temperature setting, and the wax droplets were sparingly dripped onto the base of the ski. The iron was then placed against the base and moved back and forth, from tip to tail spreading out the droplets. The iron was kept moving to avoid overheating any specific area of the ski's base as this can cause the base to de-laminate or bubble, although this rarely happens with modern skis. The skis or, in some cases sample sections of ski were then left to cool overnight, allowing the wax to solidify and the whole ski to return to room temperature in a clean environment in order to avoid contamination of the wax with grease or dirt.

The cooled layer of wax was scraped with a sharp plastic scraper leaving behind a thin layer of wax which was then brushed to expose the underlying structure. All skis and samples tested were scraped until no further wax scraping were removed then brushed with a nylon brush. This involved a different number of strokes depending on the hardness of the wax. The wax or treatment layer achieved by this repeated scraping and further brushing of the surface could be characterised as a very thin, uniform layer with the base structure partially exposed.

5.2. Wax modification

A constrained cross section of commercially available waxes was selected for contact angle testing and modification. The base waxes investigated both hydrocarbon and fluorocarbon additives and co-polymers, as shown in Table 3. These waxes were contact angle tested using the methodology described in section 5.2.2 with the objective of establishing a base a base level of hydrophobicity for a cross section of hydrocarbon and fluorocarbon waxes.

Table 3: Numbered samples of waxes subsequently treated with hydrophobic nanoparticle fillers

1	Untreated base	Cleaned with wax remover and light nylon abrasive
2	Ch4	Pure alkane hydrocarbon wax with a recommended operating temperature -10 to -32°C.
3	Universal wax	'Bottom of the range' alkane wax, with no recommended operating temperature.
4	*Swix* Cera Fluoro	Hydrocarbon-based, 'top' race wax containing high fluorocarbon concentrations with an recommended operating temperature of 0 to 10°C
5	*Toko* HF Dibloc yellow	Hydrocarbon-based, 'top' race wax containing high fluorocarbon-block-hydrocarbon co-polymers with an recommended operating temperature of 0 to -4°C

The waxes were applied to samples which were small (100mm) sections of a *Head* Factory World Cup GS (2004) ski. The base was black UHMW-PE containing a medium stone ground structure. All the samples were cleaned to remove any dirt or old wax with *Swix* wax remover with a light nylon abrasive. Twelve ski base samples were machined level by milling the topsheet and core material away to provide a flat surface for contact angle testing. The base samples were conventionally prepared according to guidelines set down by many of the ski wax manufacturers (*Swix*, 2009; Toko 2009; Homemkol, 2009) and as described in section 5.1. This included melting a small amount of wax on with an iron and removing it with a plastic scraper and nylon brushing to obtain a thin surface layer. Subsequent modification with hydrophobic partial fillers was also conducted using the majority of these waxes as a 'base' as described in the next section 5.2.1.

5.2.1. Wax modification with particle fillers

Samples of *Aerosil* 972, and VPR 411 were generously donated by *Ticona Chemicals*. An initial trial was conducted using *Aerosil* 972 which was deposited on a UHMW-PE base sample using acetone as a solvent, which acted as a wetting agent with the result shown in section 6.1.2. Whilst these coatings however could easily be wiped away, the purpose of this initial method of approach was to assess the hydrophobicity of the particles. It was evident that a binder was required to adhere these deposited particles to a ski base, albeit, semi permanently, due to the abrasive conditions experienced when sliding. Logically, the initial binders chosen for further investigation were current waxes used by the ski industry. Waxes numbers 3, 4 and 5 shown in Table 3 were chosen to be modified and compared with their unmodified counterparts.

The nanoparticle modified wax samples were created by melting the chosen wax in a heavy metal based pan using a halogen heat plate then adding *Aerosil* 972 and stirring for 15 minutes. The waxes was then poured into a mould and allowed to set at room temperature overnight. The temperature of the heat plate was adjusted for each particular wax used with the aim of preventing the waxes from smoking and vaporising. The manufacturer’s recommended iron temperature was used as an initial guide but adjustment was made to within ± 20°C from the stated iron temperature in order to maintain to maintain liquidity. Due to the fine particulate nature of the Aerosil, a mask with a level 2 particulate filter was worn as a safety precaution, following recommendations on the MSDS sheet. After incorporation into the wax matrix atomisation of the *Aerosil* particles was no longer possible therefore hot-waxing could be conducted in a well-ventilated area without a level 2 mask. The sample numbers, waxes and corresponding percentage weights of *Aerosil* and manufacturer’s recommended iron temperatures are listed in Table 4. These waxing were applied to ski base samples and contact angle tested with the results detailed in section 6.1.2

Table 4: Sample numbers and corresponding added % weights of *Aerosil* 972 for contact angle testing

Sample Number	Wax	Iron Temp (°C)
1	Ch4	150
2	Ch4 + 1% *Aerosil*	150
3	Ch4 + 5% *Aerosil*	150
4	Ch4 + 10% *Aerosil*	150
5	Ch4 + 15% *Aerosil*	150
6	Cera Fluoro + 5% *Aerosil*	120
7	Cera Fluoro + 10% *Aerosil*	120
8	Universal wax	110
9	HF Dibloc yellow	120
10	Cera Fluoro	120

Glide tests with such a treatment were conducted using the methodology defined in section 0. Initially the waxes were evaluated by contact angle testing which is described in the proceeding section. Similar nanoparticles (*Aerosil* VPR 411) were used exclusively in the glide tests. These nanoparticles particles contain higher fluorine content silanol groups which initially prevent them from being incorporated into wax. An additional wetting agent (acetone) was used in order to incorporate these particles into *Swix* F4, a fluorocarbon containing wax. The acetone was boiled off in the liquid wax for 3 hours which allowed the particles to be wetted and disperse in the wax before solidification. After leaving to cool overnight the wax was applied using a traditional hot waxing method for the glide tests. The resultant blend for the incorporation of Aerosil 411 into *Swix* F4 is described in more detail in preparation for the glide tests in section 6.1.2. The glide test results of this blend are described in section 6.1.3.

5.2.2. Contact angle testing

These investigations were conducted on a *First ten Ångstroms® type FTA 200* instrument to measure the contact angle of a water droplet, at rest on the surface of the substrate as shown in Figure 15. To calibrate the software, a video image was captured of an object of known size to obtain a scaling factor. This scale factor was then inputted into the software and used throughout the subsequent sample sets. This was conducted every time a new sample set was examined. An automated micro scale pump was used to ensure the same volume (1µL) of droplet during each run time. Water was selected in this project as the liquid medium and all samples were at room temperature (18-22°C) and in a normal atmosphere. The brightness of the front light and rear light was adjusted to obtain a good quality, contrasted image of the droplet on the substrate. To measure the contact angle, the pump was automatically run to squeeze the specific volume of water on the surface of the sample. The image was then captured using a digital camera and displayed in the software. A base line was manually drawn and the contact angle automatically calculated using the software, this is detailed in Figure 16(a) below. Figure 16(b) shows the same drop with the droplet angle sketched over the top for clarity. Each sample was tested 10 times using this tensiometer and an average taken.

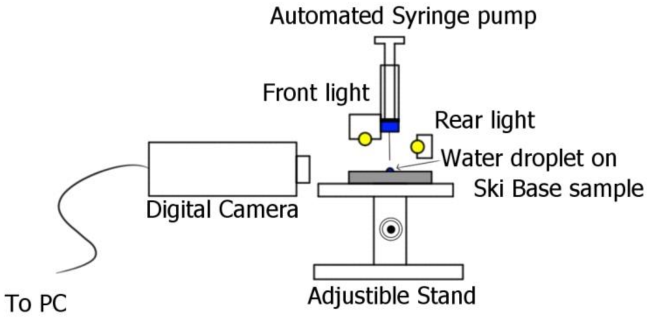


Figure 15: Diagram illustrating the method of contact angle measurement

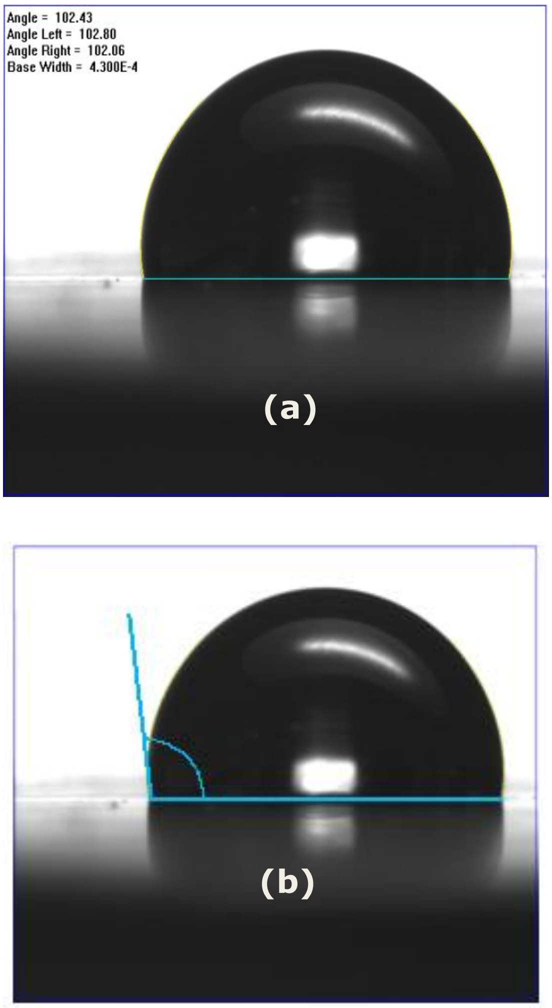


Figure 16: Water droplet on UHMW-PE substrate (a) and (b) showing subsequent measurement of the contact angle

5.2.3. Glide testing

Atomic is part of *Amer s*ports which is one of the major manufacturers of snow-sports equipment. Their business includes *Salomon* and *Atomic* ski brands which achieved FIS Alpine World cup brand /constructor rankings of 2nd and 3rd combined overall in 2012. Atomic conducts several glide tests sessions throughout the year collecting data over the course of each session using the same skiers for each session and whenever possible throughout the year. After manufacture, usually at the end of the summer or early autumn, each speed ski is glide tested to determine its relative performance within the whole factory stock. They use the same FIS level glide test team of six members throughout the season, a 500m glide test track in Solden, Austria, two skidoos and as many skis as they can carry; around 8 pairs per tester. They aim to rank these skis which exhibit tiny differences in velocity when travelling at around 100 Kmh^{-1} using the method described below. Once the skis are ranked they are given to the chosen team athletes for the upcoming Alpine World Cup Season. The fastest skis are usually given to the best athletes to provide the competitive edge needed when racing at such a high level.

The technique used is a glide test method in which a skier travels down a track in a straight line down to the bottom. A timing system is triggered at defined intervals down the track which gives overall and spilt velocities on different sections. There is a control skier who uses identical type of skis, of previously tested performance and which have undergone the same standard wax treatment. However, there are, as previously mentioned, so many variables associated with snow, equipment and the environmental conditions, how are these kept to a minimum as they are constantly changing? The glide test is conducted in the smallest amount of time physically possible to ensure minimal variations. An extremely quick turn-around of skiers, around three minutes per test ski, is achieved using the skidoos to tow them back to the top of the track. Automatic measurement of climate data is made throughout the course of the test including; Snow temperature (°C), Air temperature (°C), Air Humidity (%), Snow Humidity (%), Wind speed and direction aids are also used to detect track variations. Observations of snow type and clouds are also recorded on the final results sheet containing run times.

Figure 17: Tester in a tuck position descending the glide track at Solden, Austria.

The timing system adopted was an ABATEC AG LPM local positioning measurement system with 1000 samples per second. This type of real-time wireless timing system further sped up the process of data acquisition. The high frequency radio receivers were placed at the following intervals down the track: 30m, 90m, 389m and 509m. Each skier was fitted with a specific transmitter and simply lapped the track and the data was recorded automatically without adjustment. The track's gradient varied with a steep start section to build up speed, up to around 100Km/h, then a flatter glide section. This glide section was required to assess the skis ability to maintain its speed. The track was closed to the public and the stopping area at the finish was sufficient enough to allow the skiers to stop safety.

All of the test skis were Atomic DH 215cm length factory race stock and each skier had their own boots and cat suit which did not vary throughout the testing phase. The skiers prepared their given sets of 8 skis personally to minimise errors over the entire duration of the test. It is possible that each technician may have used slightly different pressures to remove wax and, in addition, they may have spent a varied amount of time melting and smoothing it over base. The standard hot-waxing method was used to apply *Homenkol Betamix Red* (-4 to -14°C) to the control skis. The waxing coating was further treated with a plastic scraper and a nylon and a horsehair brush Section 5.1 contains full details of the waxing method employed together with further explanation of traditional waxing techniques.

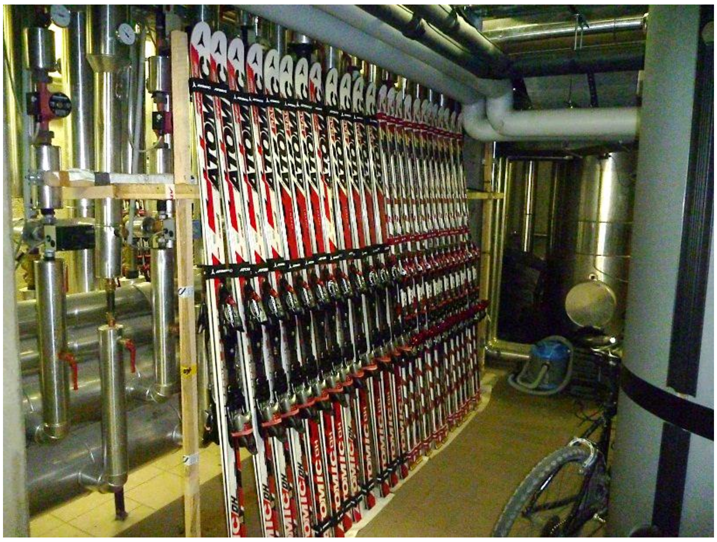


Figure 18: Atomic world cup downhill skis, serviced and ready to be glide tested.

The tests started early in the morning to ensure hard snow conditions with the skis having been prepared the previous day and brought up the mountain inside a van and then in a covered skidoo. During the course of the first test, the track was in the shade however, the sun did hit the track towards the end of the testing period. The 6 skiers were testing 8 separate pairs of skis, 3 runs per ski each in two batches: 1-4 (A) 5-8 (B). They were laid out in line beside the finish area in a position which identified the skier and placed face down on the snow. The skier then clicked into each pair in turn and was towed up the mountain behind a skidoo three at a time. At the designated start line the skier positioned themselves into a held stationary position, released their poles and immediately assumed a tuck position. Variations in tuck position can be minimised by ensuring that all the testers had a high level of skiing ability, however, some small variation would be inevitable. This method allowed track variations to be analysed by examining the times of the control skier but also to evaluate the effectiveness of the treatments. All comparisons of all treatments and skis were conducted against the same control skier. The high frequency radio receivers were placed at the following intervals down the track: 30m, 90m, 389m and 509m. The track's gradient varied with a steep start section to build up speed, up to around 100Kph between 30-90m, then a flatter glide section between 389m and 509m. This glide section was required to assess the ability of the ski to maintain its speed which was recorded. The track was closed to the public and the stopping area at the finish was sufficient enough to allow the skiers to stop safely. Three testers were used, all FIS level athletes or above. The control skier remained the same throughout but the other two testers were swapped between series.

Figure 19: Skidoo pulling the testers back up to the top of the glide track

Further investigations were subsequently conducted using the same methodology at the *Atomic* testing facilities as part of their glide testing schedule throughout the 2012 and 2013 seasons.

1. Fluorinated wax mixed with hydrophobic nanoparticles

The test skis were treated with unmodified *Swix* F4 universal glide wax containing fluorocarbons and additionally modified with 6% by weight *Aerosil* VPR 411 using the same method as described previously in section 5.2.1 with the results shown in section 6.1.3

2. Structural paste with skiving method

The structure paste was mixed PFPE (2024x) and 25% nanoparticles which thickened the fluid to form a paste. It was applied using a skiving method with a glass substrate in order to structure the base. This method was investigated in greater detail in the surface modification sections 5.3 and 6.2.

3. PFPE modified base material

Samples were prepared using a sintering process to produce a base material with 2% and 5% of PFPE additive content. These were then adhered to the same model of DH skis used in these tests. Further details on blending UHMW-PE and PFPE are to be found in the bulk modification sections 5.4.3 and 6.3.3.

5.3.Surface modification

In this investigation the base samples previously used were replaced with new factory ski base material which was manufactured using a press sintering process generously supplied by *CPS*. P-tex 4000 (white) and P-tex 4500 (black) both had a molecular weight of 9.2×10^6 g/mol. The unconfirmed raw material for these bases comprises of Tincona GUR 4150. The exact processing conditions and raw material is unknown due to commercial sensitivity. Two additional methodologies, scanning electron microscopy and the use of an incline plane friction ramp were employed to observe the microscopic physical structure and to measure static friction.

5.3.1. Samples and preparation

The samples were prepared by first initially securely clamping the UHMW-PE sheet material to a flat surface. The surface was first abraded with 800 grit sandpaper applied for twenty five strokes forwards and backwards, unidirectionally down the length of the sheet. A sample of a size appropriate for the intended experimental use was then cut from the sheet. The sheet was then treated subsequent treatments nylon and glass using 25 forward strokes in the same direction as the previous abrasion. The nylon pad was place onto a cork buffer to aid uniform pressure distribution. This nylon treatment method follows traditional guidelines for ski waxing and base preparation previous detailed in secion 5.1. The glass method used a sharp piece of newly cut glass and held with the thumbs distributing the pressure across its length. It was passed across the surface using light pressure. This method is similar to metal or Plexiglas scraping methods commonly used to remove waxes. The glass treatment was also combined with *Aerosil 972* which contains 16nm silica particles. A dust mask was used because of their likelihood to disperse when used without a wetting agent. As a glass scraper was passed across the surface the particles are also dragged along. The particles were additionally wetted with 2024x to form a lubricated ‘paste’. The wetting of the silica nanoparticles was beneficial as they did not atomise and the wetting agent lubricated the process encapsulating the removed debris. A small amount of the paste wax was applied with a microfiber cloth then scraped using the glass method.

5.3.2. Scanning electron microscopy

Using the scanning electron microscope shown in Figure 20, rather than an environmental SEM meant that only dry treatments could be investigated because the vacuum may vaporise any liquids or waxes present in the chamber. The surface structures of untreated, factory standard, UHMW-PE, both with (sample 1) and without black carbon additives (sample 2) were examined. After which, to simulate snow abrasion or stone grinding, the subsequent samples with all abraded with 800 grit glass paper (sample 3). The traditional method, described in section 5.1, for removing UHMW-PE polymer 'hairs' to render a smoother surface before wax application is a nylon abrasive and this method was used to provide sample 5. The effectiveness of using a ceramic rather than nylon was investigated in samples 4 and 5. The effect of using nanoparticles without PFPE lubricant combined with ceramic scrapping was investigated in sample 6. The samples, 10mm in diameter, were punched out of the appropriately treated UHMW-PE sheet, adhered to sample stubs using conductive silver paint then carbon coated. These were then placed into three sample slots into SEM chamber as shown in Figure 21. All the sample treatments are summarised in Table 5, shown below.

Table 5: SEM sample numbers and corresponding treatments

#	Samples	Combined with treatment
1	Untreated Black UHMW-PE	None
2	Untreated White UHMW-PE	None
3	Black UHMW-PE abraded with 800 grit glass paper	None
4	Glass scraped	3
5	Nylon abrasive	3
6	Glass scraped with nanoparticles	3

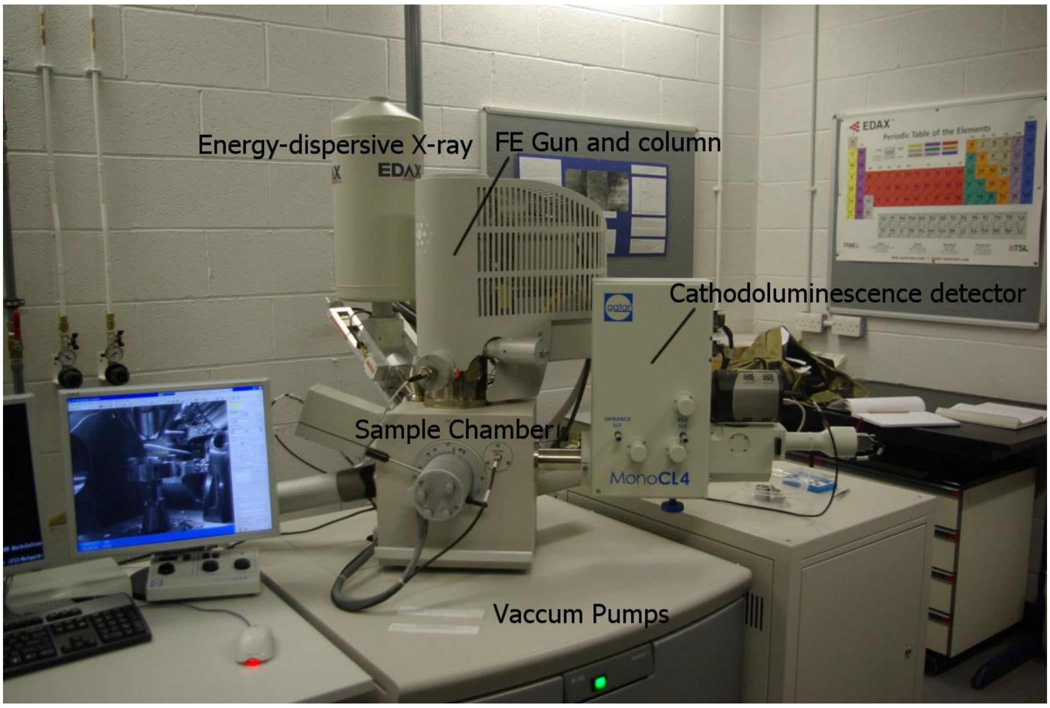


Figure 20: Scanning electron microscope (SEM)

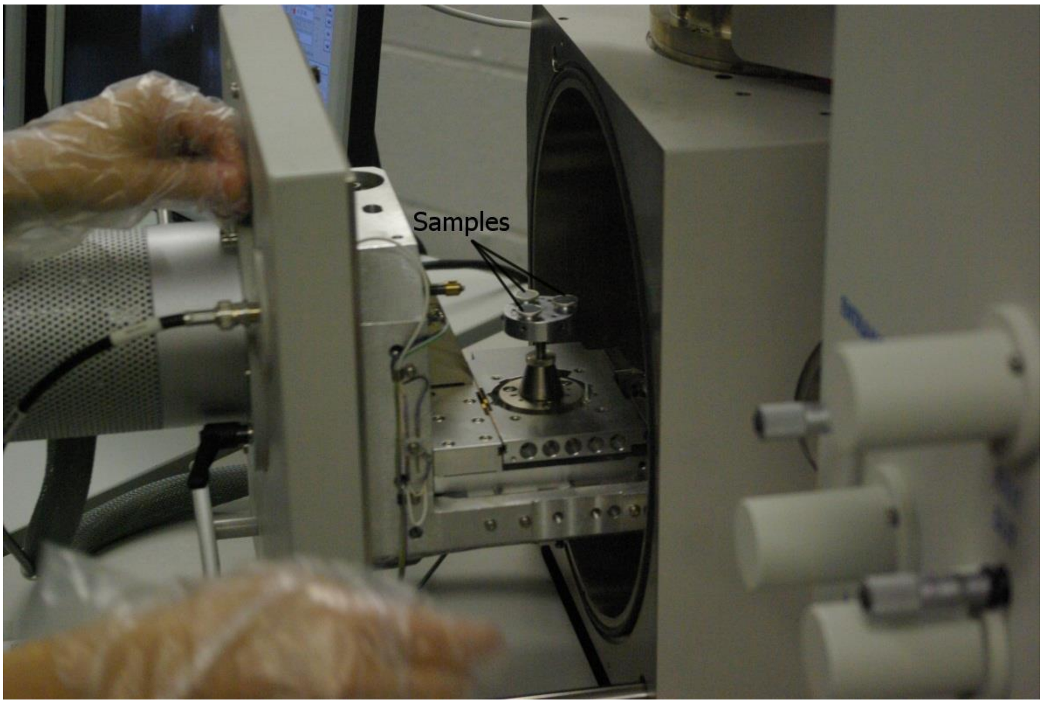


Figure 21: Shows the UHMW-PE samples being placed into the SEM chamber.

5.3.3. Inclined plane friction ramp

This experiment utilised samples of base material created by polymer blending (section 5.4.3). The UHMW-PE of the untreated base material P-tex 4000/4500 were roughened with 120 grit sandpaper on one side to aid adhesion to metal blocks. The sample blocks manufactured form steel of dimensions 90x50x20mm with an additional metal block screwed in with an M12 screw to bring the weight of the sample block system to be 850g with an accuracy of +/- 2g. The steel blocks had the same base area dimensions of the sample created using mould 2 (90x50mm). The samples were adhered using the same epoxy resin listed in Table 13 in the appendix at room temperature, 22-25°C, for 48 hours at a pressure of 1379 KPa. The plastic was the sanded at 45° on the front of the block to give a leading edge. The samples were then abraded with 120 grit sandpaper, scraped thirty times with a glass scraper and wiped with a lint free cloth with acetone to ensure a smooth and clean surface for testing.

A friction ramp with variable height adjustment was constructed by the technisions at Univeristy of Sheffield. The inclination of the plane could be increased gradually by slowly turning the screw on a laboratory scissor action jack.

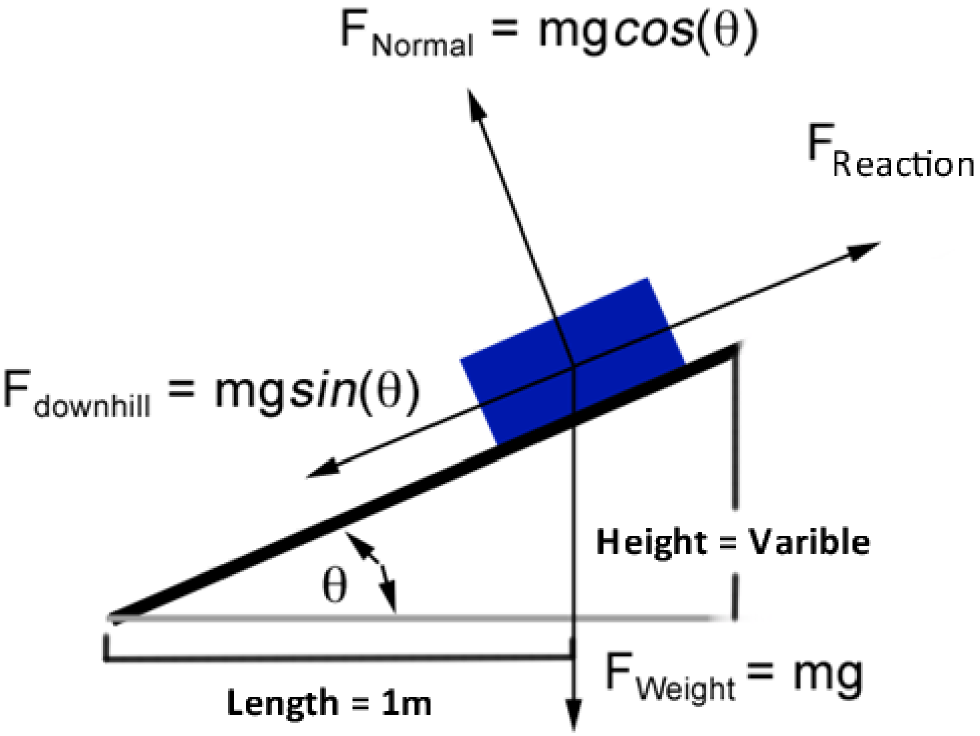


Figure 22: Diagram of the inclined plane friction ramp with the resolved forces included

Shown in Figure 22 is the body is in equilibrium at the onset of sliding. This state is denoted in Equation 10:1 below

$$\mathrm{mg}\sin\theta = \mathrm{mg}\mu\cos\theta$$

Equation 10:1

Therefore:

$$\mu = \frac{\sin\theta}{\cos\theta} = \tan\theta = \frac{\text{Height}}{\text{Length}}$$

Equation 10:2

As the length from the pivot is equal to one metre, the coefficient of static friction has the same numerical value as the height. The surface used for testing was an artificial ski slope material called *Proslope*™ fixed in place to the inclined plane using G-clamps as shown in Figure 23. The material was aligned so that that the pattern of the fibres was consistent in direction, facing down the plane.

The sample was placed so that the leading edge was in line with the 1m mark from the pivot. This was marked so that consistent placement was maintained between samples. The height of the plane was gradually increased until the onset of sliding. The height was then subsequently recorded with digital callipers accurate to three decimal places.

Figure 23: Image of the inclined plane, friction ramp with attached *Proslope™* surface and sliding block.

Snow preparation

The track was prepared the night before by packing snow into the tray levelling the surface using a smooth metal bar and left to sinter overnight. The surface was sprayed with 10ml of atomised water to aid surface hardening and the sintering process. The lowest temperature reached overnight was only -4°C. In the morning the track was levelled and a stop clamped to the ramp to prevent the sample from sliding too far. The sample was placed anywhere along the one meter mark carefully onto the snow, the ramp was raised slowly and the height was recorded. A temperature probe was also placed in the snow, and other environmental conditions recorded using digital and analogue devices. The setup is shown in Figure 24 and these results are shown in section 5.3

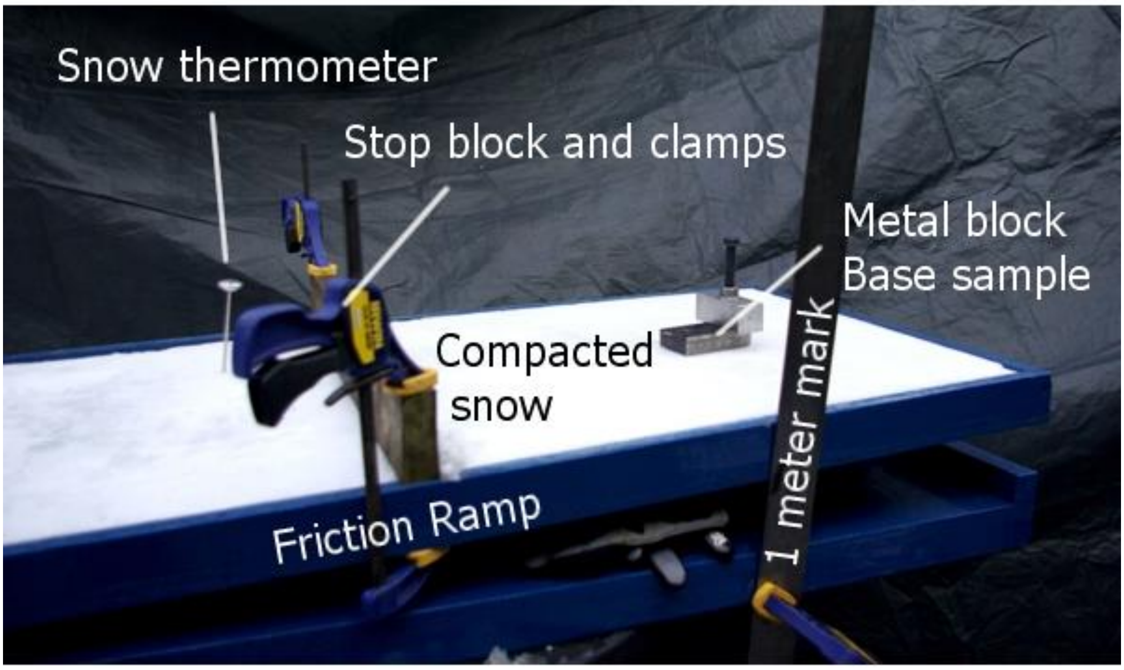


Figure 24: The friction ramp with a snow surface setup, metal base sample and stop block.

5.4.Bulk modification

Various chemcials were blended with UHMW-PE using serveral difference processing techniques. This was conducted with the view to producing a material which could be industrially processed and glide testing on skis. Labortory scale compression mould and small scale extrusion was conducted to assess the modified UHMW-PE as a suitable sliding material for further trials.

5.4.1. PDMS and UHMW-PE

The raw UHMW-PE used in these investigations was generously provided by *Ticona* (Oberhausen, Germany). Two forms of UHMW-PE were utilised: GUR 4150 is a linear polyolefin resin in powder form with a molecular weight of approximately 9.2 g/mol calculated using Margolie's equation and GUR 5113 is an injection moulding grade of UHMW-PE and is available in pellet form. The molecular weight of the latter is slightly lower (3.0 g/mol) than the GUR 4150 allowing for improved rheological properties which are required for manufacturing methods using injection moulding. However, the pellet form did not lend itself well to processing using the extruder or compression moulding processes. The powder form with the higher particular surface area proved far more effective at forming coherent samples. Due to the highlighted beneficial properties of PDMS, it was decided to investigate two new types of solid siloxane masterbatches containing a dispersion of PDMS in PE. Internal investigations by Dow Corning have shown the melt viscosity of other polymers have been reduced as a result of the blending of these masterbatches. An investigation to see if UHMW-PE and PDMS dispersed in PE can be co-extruded was undertaken and the resulting contact angle and morphology of the blends was examined. The masterbatches were generously supplied by *Dow Corning*. The polyethylene used was of various molecular weights including high (HDPE) and low (LDPE) and linear low (LLDPE) densities. The masterbatch was co-extruded at an average screw temperature of 180°C with GUR4150, then chipped and compression moulded into flat sheets at Bradford University, UK. The PDMS content of the resulting samples was 2%, 6% and 10% using four different masterbatches. Due to the variation in percentage content of PDMS in each masterbatch various amounts were added to obtain the required percentage weight of PDMS to PE. Dow Corning (2012) suggests that with the addition of PDMS the melt viscosity is lowered of other polymer blends. Assessment of the resulting samples will show if UHMW-PE combined with a masterbatch is compatible with an extrusion method. The results are detailed in section 6.3.1

5.4.2. Particle fillers and UHMW-PE

An initial prototype compression mould (1) was created, very simply, from a three pieces of type 316 stainless steel. It was designed to produce samples of 5mm± 1mm in thickness at 50mm diameter. The design was then milled by hand from a stainless steel bock and sheets by technicians at the University of Sheffield, Chemical and Biological Engineering Department. The stainless steel was subsequently polished with diamond lapping paste reducing in roughness, down to 0.5µm. It was filled to capacity (16g) with a powder form of UHMW-PE (Ticona GUR 4150), then closed and placed between the heated plateaus of a *George E Moore and Son (BHAM) Ltd. Type H008*, Amps: 7, Psi range: 0 – 1000 heated press. An attached cooling machine *Flowcool® System Ltd. Type: JDI-1* flushed the plates with water to cool the sample.

Various percentage weights of Aerosil 972 were dry mixed with the UHMW-PE at 1,3,5,10% levels. This investigation provided the basis for further investigation with PFPE with an improved mould design. The results, illustrating the samples are detailed in section 6.3.2

5.4.3. PFPE and UHMW-PE

A second mould (2) was also created to create to produce 90x50mm, rectangular samples, more beneficial for testing purposes. The difficulty of mould release was overcome by providing supporting regions of 10mm to the sides so it could be gripped firmly in a vice. The design consisted of a type 316 stainless steel main box with a top and a removable plate which fitted inside, machined to a tolerance of 0.2mm. The removable plate defined the thickness of the sample and could easily be replaced if a change of size was required or if fouled or damaged. To release the mould, two taped M10 holes were drilled into the bottom. The sample could then be released by two M10 screws imparting pressure on to the bottom of the inside plate, releasing the sample from the sides. The sides were highly polished with diamond lapping paste down to 0.5µm with a small hand held hobby drill for the inside of the mould and a sanding and polishing wheel for the flat plate sections. An addition of a small 1mm hole allowed a type K thermocouple to be inserted to measure temperature closer to the cavity.

The design for the mould was first sketched out, roughly on paper and then precisely drawn in 3D on *Autodesk AutoCAD* and *Inventor*. The design was then milled by hand from a stainless steel bock and sheets by technicians at the University of Sheffield, Chemical and Biological Engineering Department. An automated CNC process could have been utilised directly from the vector information outputted by *Inventor or AutoCAD* if required. Drawings of the design are shown in Figure 25, Figure 26 Figure 27 and Figure 28 below.

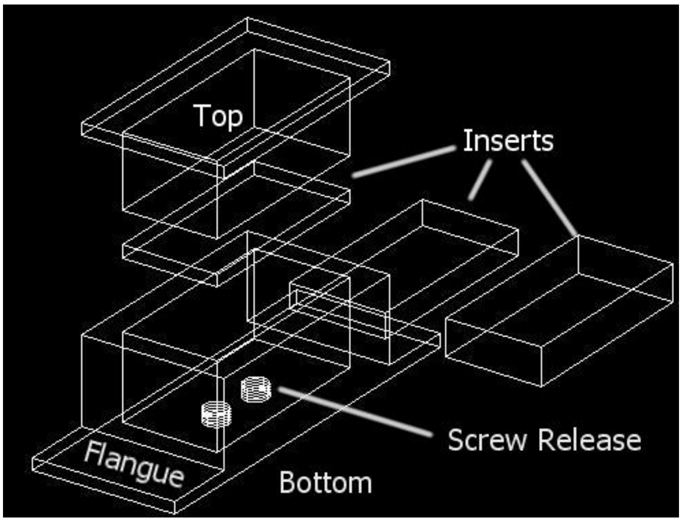


Figure 25: Three dimensional drawing of mould 2 *(AutoCad)*

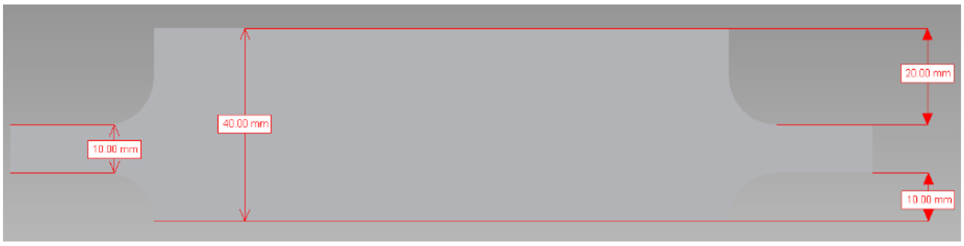


Figure 26: Side view model of the bottom of mould 2 with dimensions included (rendered on *Autodesk Inventor)*

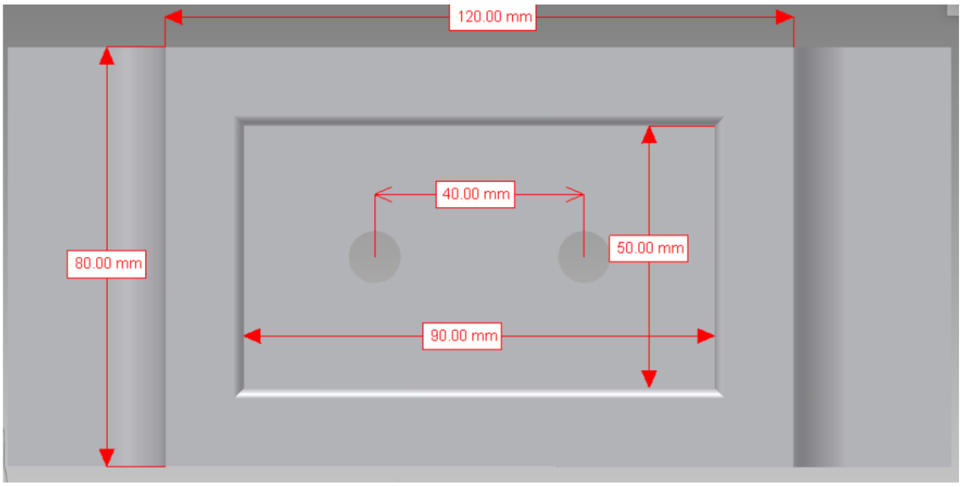


Figure 27: Top view of the bottom mould 2 with dimensions included (rendered on *Autodesk Inventor)*

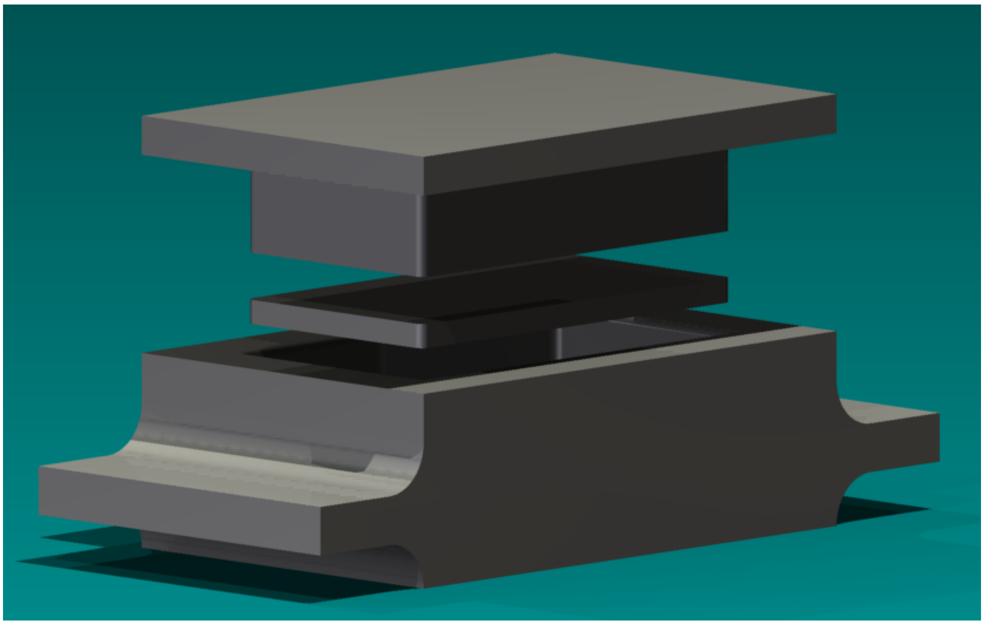


Figure 28: Three dimensional model of the complete assembly of mould 2 (rendered on *Autodesk inventor)*

5.4.4. Subsequent testing procedures

The testing methods used in the section included:

1. **Contact angle**
2. **SEM**
3. **Inclined plane**
    i. **Snowflex**
    ii. **Snow**
4. **Glide testing**

Base Samples were either:

A. **Used sections of Race Ski which had been investgated in the first section.**
B. **P-tex 4000 white (PEW) or 4500 black (PEB) UHMW-PE**
C. **Novel blends of UHMW-PE (GUR 4150) with various percentage weights of hydrophobic additives.**
D. **Standard black bases belonging to Atomic Race Dept DH Ski**

Wax modification utilised only two methods (1 and 4) and two samples sets (A and D). Following the course of the investigation, additional methods were used to explore the physical surface modification at a microscopic level. A variety of physical treatments described in section 5.3.1 were applied to new base sheet material (PEW and PEB) and investigated using a full range of methods (1-4). The concluding section on bulk modification involved the creation of novel blends, first in laboratory compression moulding trials then, a more industrial, sintering process. This section also makes use of the full range of methods. However, the glide testing method (4) requires the sintered test material to be incorporated into a pair of skis matching the dimensions of Sample D. This was conducted by *Atomic* Technicians, as were the second series of glide tests.

Using the investigative methods of contact angle and glide testing used with ski base sections and DH skis with modified and unmodificed waxes, the choice of methods was reviewed and expanded. This included SEM to compliment contact angle testing and the inclined plane method to complement glide testing. The aim of this was to provide further formation on hydrophobicity and friction. The measure of hydrophobicity using contact angle testing is reliant on the physical and chemical interaction with the water droplet on the surface. If the physical element of this interaction can be visualised, then this can add weight to the discussion of measured contact angles results. The variety treatment methods identified in section 5.3 and used on (PEW and PEB) will impart a unique texture to the UHMW-PE surface. These surface structures was examined using SEM and then contact angle tested with the aim of relating a physical surface to a measured set of contact angle results for each of the various treatment methods. Friction was measured using a glide testing and inclined plane method. These both these methods measure friction, however, one statically upon moment of release, the other dynamically at very high sliding speeds. Environmental data was recorded which included temperatures and humidities of both snow and air. Samples were tested using both SEM and contact angle in the surface modification and bulk modification sections. The proceeding results and discussion section evaluates the data and evidence collected using these methodologies in the context of the current understanding of sliding friction as discussed in Chapter [4] Tribology- the physics of sliding friction.

Chapter [6]   Results and discussion

The results in this chapter are grouped into three main areas of investigation namely: wax modification; surface modification and bulk modification of the polyethylene ski base.

- **Wax modification**

The contact angles of traditional hydrocarbon and fluorocarbon waxes were tested following application to a typical stone ground GS skis base. The aim of this was to establish the base level of hydrophobicity for each of the wax treatments.

Various waxes and novel treatments were then modified with silica nanoparticles and also contact angle tested and compared. The aim of this was to investigate whether the addition of these elements to the matrix of the waxes would influence hydrophobicity and glide test times.

- **Surface modification**

In nature, water resistant plants and animals have both a physical and chemical structure to improve hydrophobicity. This section investigates the difference between black and white, 9.2 million grams per mole, sintered and finished UHMW-PE using a variety of investigative methods. Contact angle testing methods are used to assess the effect of a range of treatments on the physical and chemical resistance to wetting. Scanning election microscopy provides a view of the physical sliding surface at micro-level magnifications. Small scale texturing has been suggested to significantly influence the development and maintenance of a water film.

Both traditional and experimental surface modifications were applied to a variety of base samples. Black and white UHMW-PE were first compared, and then abraded with a light abrasive in an attempt to replicate the stone grinding process or the abrasive wear mechanism experienced when sliding on snow/ice. Both these factors are known to cause UHMW-PE bases to become “hairy” and increase friction due to the larger increased contact area. The traditional method for hair removal is by using a metal scraper or light nylon abrasive pads. The nylon abrasive is claimed to remove these “hairs” as does the previously reported metal scraping method (Sturesson, 2008). A novel glass scraping method was trialled as a sharper cutting tool to plane or skive off these “hairs” or surface features. A nanoscale abrasive was then used, also combined with a highly hydrophobic polymer to form a chemically water resistance, polishing paste which has a physical element. These experimental methods are compared with the other, more traditional, treatments which also have an effect on the physical and chemical properties of the surface. This section concludes with results and discussion of the investigation of the above treatments on the coefficient of static fiction using an inclined plane method.

- **Bulk modification of UHMW-PE**

This section includes the modification of UHMW-PE using polymer blending techniques and a discussion of common industry processing methods for UHMW-PE including, extrusion, compression moulding and sintering. Polymer blending of a masterbatch of UHMW-PE-PDMS was first blended then extruded. The extrusion method, which is more common process for lower molecular weight polyethylene, was trialled with this polymer blend with the aim of producing a sample which could be practically tested. The silica nanoparticles, which were investigated in the wax modification section, are also used to bulk modify UHMW-PE using a compression moulding process. Using a combination of laboratory scale compression moulding and industrial sintering techniques, blends were also created with perfluoropolyether. These were subsequently tested using contact angle, SEM microscopy and friction ramp testing on both snow and artificial sliding surfaces. Additionally, these blends were mounted to downhill skis and glide tested in an alpine environment.

These testing methods seek to provide a measure of water repellence, an optical view of the sliding surface at high magnifications (100-10,000x) and a comparison of the influence of the various blends on friction. A visible view of the surface structure may aid the interpretation of contact angle as the physical element can be isolated and examined. This could also be beneficial in improving our understanding of different treatment applications and procedures to reduce ski base sliding friction.

6.1. Wax modification

6.1.1. Contact angle

Contact angle measurements were first conducted on standard, commercially available waxes with the aim of providing a base level of hydrophobicity before the addition of hydrophobic fumed silica. This method of testing is described in section 5.2.2. The waxes are specified in section 5.2 and include both hydrocarbon and fluorocarbon, cold and warm temperature waxes. The control was untreated black UHMW-PE, treated with wax remover. All the samples were base sections of a used *Head* Factory GS ski with a medium ground ski base structure which is commonly used on this type of race ski. Unfortunately, the opportunity did not arise in the earlier stages of the investigation to visualise the surface roughness by SEM microscopy which is later discussed in section 5.3. The hydrophobicity of the traditionally waxed ski base samples is shown in Figure 29 below detailing the mean contact angles acquired. Table 6 summarises the statistical analysis and Figure 30 shows a box and whisker plot of the results.

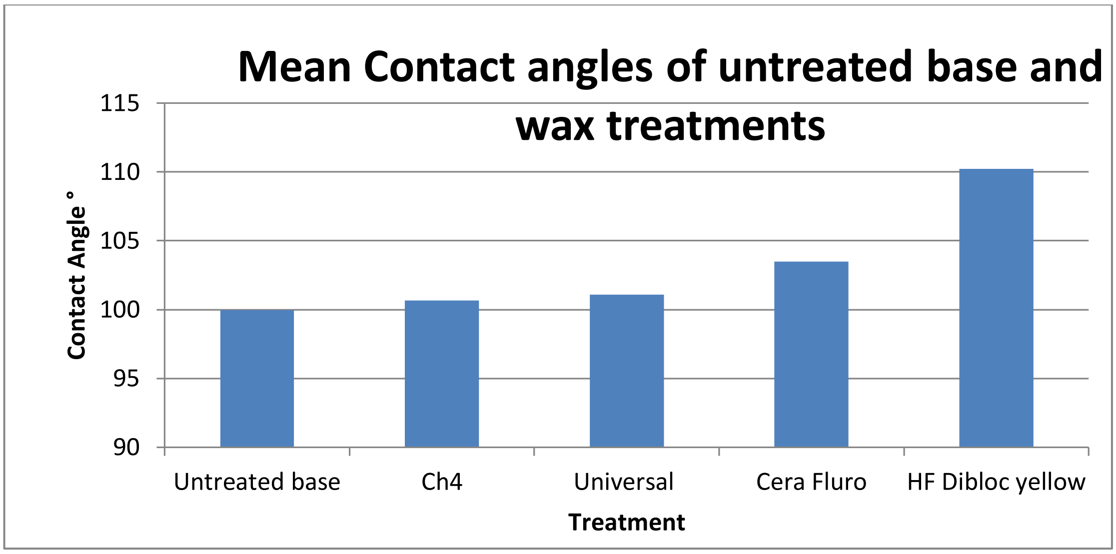


Figure 29: Mean contact angles of a UHMW-PE untreated ski base and a range of wax treatments.

Table 6: Statistical analysis of contact angles of a UHMW-PE untreated ski base and a range of wax treatments.

Sample:	Untreated base	CH4	Universal Wax	HF Dibloc yellow	Cera Fluoro
Mean	99.98	100.68	101.07	110.24	103.49
Min	95.49	94.36	96.16	106.93	101.46
Q1	98.49	100.32	100.87	109.69	102.50
Median	100.35	101.65	102.04	110.79	103.39
Q3	102.14	102.53	102.35	111.09	104.49
Max	102.32	104.16	102.78	112.83	106.19
Standard Deviation	2.34	3.33	2.16	1.81	1.50
Variance	5.49	11.11	4.66	3.28	2.24

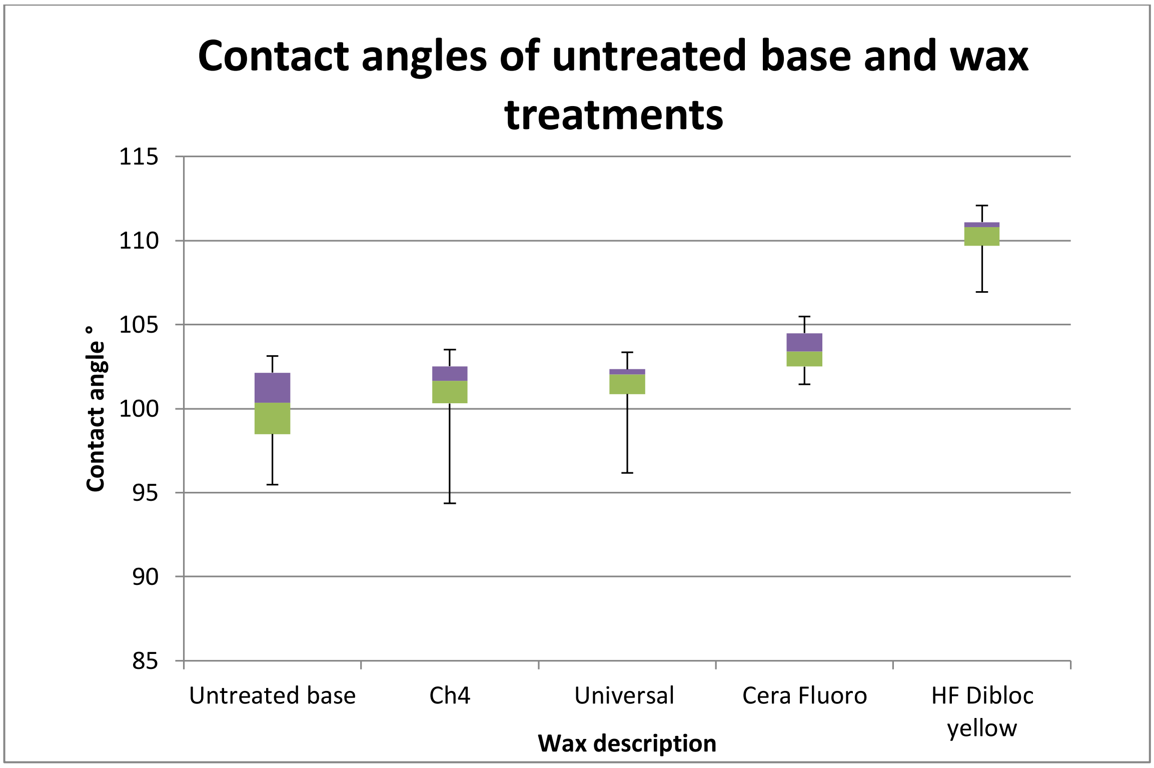


Figure 30: Box and whisker plot of the mean contact angles measured on a UHMW-PE ski base with a range of wax treatments.

An analysis of the mean values of contact angles, shown in Figure 30, indicates that waxes increase the hydrophobicity of the surface. The hydrocarbon based waxes (CH4 and Universal) increase the contact angle of the surface by only a few degrees, although, this may not be statistically significant due to the large spread of the results. As expected, the fluorocarbon waxes (Cera Fluoro and HF Dibloc) both increased the contact angle of the surface, however, it is interesting to note that the HF Dibloc outperformed in Cera Fluoro by approximately 6% in terms of average contact angle. Both fluorocarbon waxes contain fluorine additives, however, the co-polymer blend of the HF Dibloc seems to be more effective at increasing hydrophobicity. A small increase in hydrophobicity of the Cera-Fluoro was observed compared with the hydrocarbon waxes, although, this was not nearly as large as for the HF Dibloc.

As previously discussed in section 4.4, wettability and the resultant hydrophobicity is dependent on both the physical surface structure and the chemical interaction of the water with the substrate. Due to the nature of the UHMW-PE substrate used during testing and the imparted medium stone ground structure, there may be a significant variation of the large scale roughness evident on the surface. The wax, when applied to this surface and scraped and brushed using the current ski waxing method, described in section 5.1, creates a thin layer of wax. This thin layer of wax may help to fill in the features of this substrate, ultimately creating a smoother surface with reduced roughness. The larger features created by the stone ground process however, would still affect any measured contact angles and increase variability in the results. Different surface treatments, for example, surface abrasion, can cause the droplet to rest on the surface in a Cassie state, increasing the observed contact angle. In addition, any microscopic structures present in the ski base samples may also cause variability in the results obtained through this method. Further examination of UHMW-PE microstructures using scanning election microscopy combined with contact angle testing are reported in the surface modification section 5.3.

There is some variance in the contact angle results, possibly due to the varying roughness of the UHMW-PE sample, both microscopic and macroscopic. This variance is evident in the box and whisker plot in Figure 30. The base samples tested were known to have a large variation of feature depths due to the medium stone ground structure, as previously described in section 5.2. This structure was investigated because it was an authentic representation of the physical surface exhibited on nearly all modern skis. All of the base samples for the wax tests were taken from a used FIS World Cup Head GS ski; this was also representative of a stone ground ski subjected to some wear from sliding and repeated waxing treatments. The physical macroscopic stone structure as well as micro-scale roughness would also have an effect on the contact angle. Future investigation of untreated UHMW-PE and a selection of surface treatments are reported in Chapter [8]. This provides a more detailed investigation into the microscopic structure of the surface and how its changes with each treatment.

In conclusion, the rough surface of the ski base was not the most ideal testing surface for accurate comparison of the hydrophobicity of wax treatments using contact angle testing. However, it did provide some measure of hydrophobicity on a traditional ski base. There was a small difference between left and right angles, probably due to the surface structure however, all results were with two standard deviations of the mean. This method has demonstrated it can detect the well reported differences in hydrophobicity between hydrocarbon and fluorocarbon waxes and gave a base measure for these groups. In the next section the results using the same contact angle testing method are reported when a hydrophobic element is blended with the waxes.

6.1.2. Hydrophobic nano-particle fillers

Hydrophobic fumed silica (*Aerosil* 972) was found to be a remarkable material bestowing a very hydrophobic surface when deposited with acetone on the on the same surface substrate. An average contact angle of 144° was measured as shown in Figure 31 with angle in degrees (°) and base width in millimetres (mm). This result was expected as such nanoparticles are inherently very hydrophobic

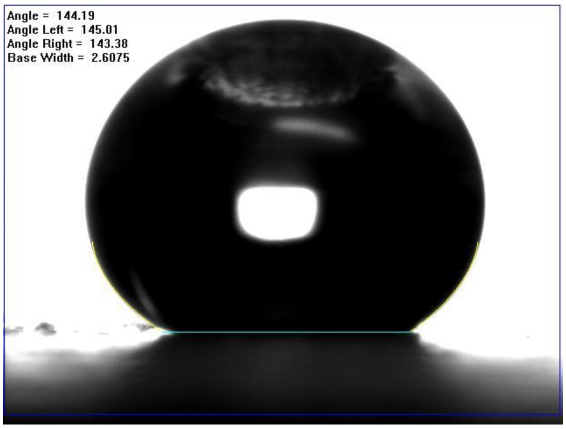


Figure 31: Contact angle of a water droplet on an *Aerosil* coated UHMW-PE ski base.

The wetting agent allowed the particles to be dispersed evenly over a ski base sample after the solvent had evaporated. This produced a temporary surface which demonstrated a significant increase in hydrophobicity. Unsurprisingly, this layer was very susceptible to wear and easily scratched off with a finger nail or wiped off. However, this initial trial did indicate the potential of these nanoparticles to improve hydrophobicity to near super hydrophobic (150°) levels. Whilst this method would not be viable as a ski base treatment, it raised an important question as to whether a binder could be incorporated to aid the adhesion between the nanoparticles and the UHMW-PE base.

One possible binder type was, of course, the traditional hydrocarbon and fluorocarbon ski waxes. The methodology for mixing the particles with the wax is described in section 5.2.1. The waxes previously investigated were mixed with various percentage weights of *Aerosil* 972 and their contact angles measured. The waxes were separated into two groups; hydrocarbon and fluorocarbon. Detailed in Table 7 the percentage weights added and mean contact angles observed for the treatments. This data was additionally plotted in two box and whisker graphs in Figure 34 and Figure 35 to display the spread of the data.

The glide tests, which are conducted in the next section 6.1.3, used *Aerosil* VPR 411, which contains higher fluorine content silanol groups. The Aerosil 972 would quickly dissipate in the wax matrix, however. When VPR 411 was added, it floated on top of the liquid wax and could not be wetted or subsequently incorporated. Because of the potentially advantageous properties of this type of *Aerosil*, another method was sought to overcome this problem. The methodology described in section 5.2.1 using a wetting agent (acetone) to lower the surface energy of the *Aerosil* to levels comparable to that of the wax *Swix* F4. The *Aerosil* VPR 411 wetted with acetone lowered the surface energy of the particles enough to be miscible with the wax matrix. The heat of the liquid wax was significant enough to evaporate the acetone leaving the VPR 411 incorporated into the wax. An additional heating period of 3 hours as opposed to 15 minutes for *Aerosil* 972 was required to boil off the acetone. This is evident in the clustering effect illustrated in Figure 32. At the beginning of the time period the *Aerosil* VPR411 clustered together, gradually dispersing once the acetone boiled away, leaving a fairly uniform dispersion towards the end of the 3 hours.

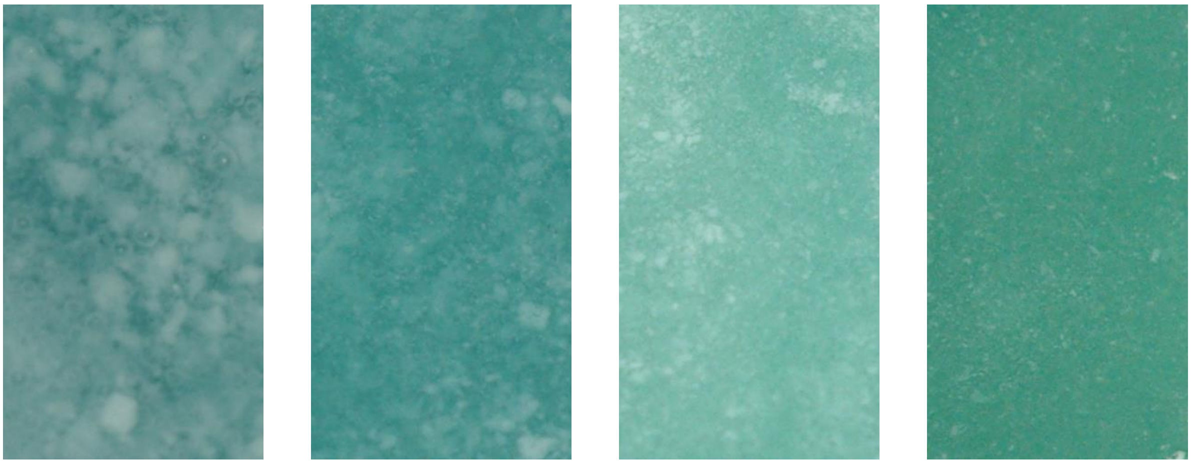


Figure 32: Photographic images showing clustering effect of *Swix* F4 mixed with VPR 411 nanoparticles over a successive time period (left to right)

The beneficial properties of the *Aerosil* VPR 411 with its fluorinated surface treatment, in comparison with other types of *Aerosil* containing methyl surface groups, may aid ski base sliding friction in wetter conditions. The glide test comparison with modified and unmodified versions of *Swix* F4 are detailed in the next section 6.1.3.

Table 7: Mean contact angles measurements with waxes containing nanoparticles.

Wax mixture	Mean contact angle°
Hydrocarbon waxes	
Ch4	100.68
Ch4 + 1% 972	100.63
Ch4 + 5% 972	98.04
Ch4 + 10% 972	97.33
Ch4 + 15% 972	99.00
Fluoro-Carbon Waxes	
Cera Fluoro	103.49
Cera Fluoro + 5% 927	101.45
Cera Fluoro + 10% 972	100.71
HF Dibloc yellow	110.24
HF Dibloc + 10% 972	111.29

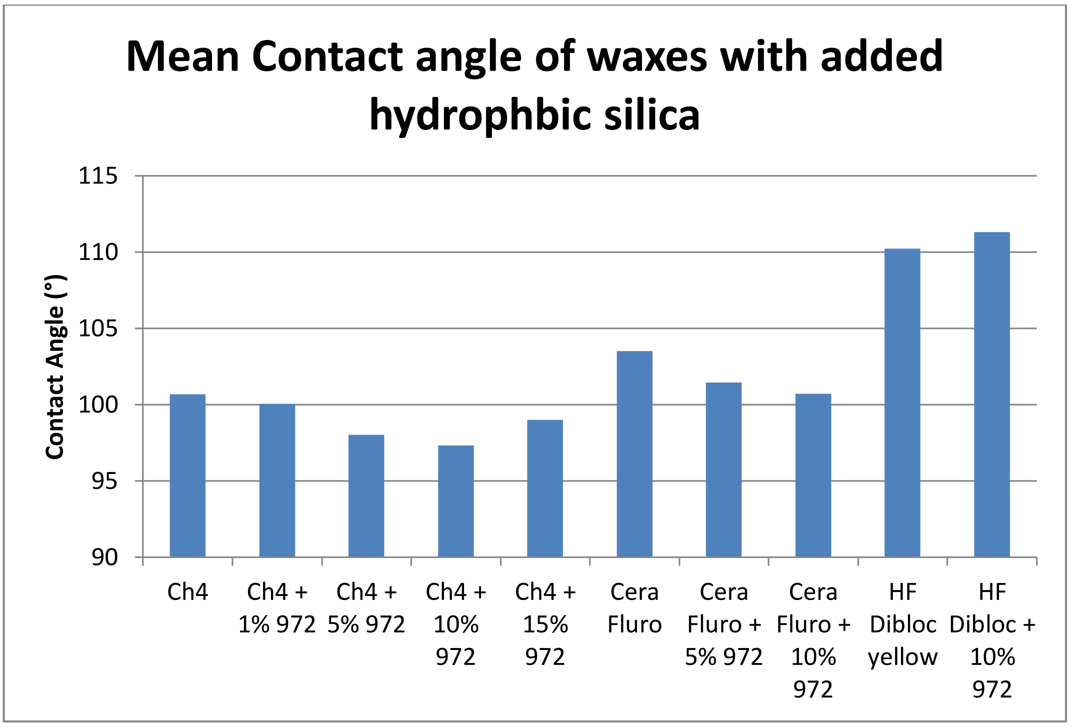


Figure 33: Mean contact angles of wax with added hydrophobic fumed silica.

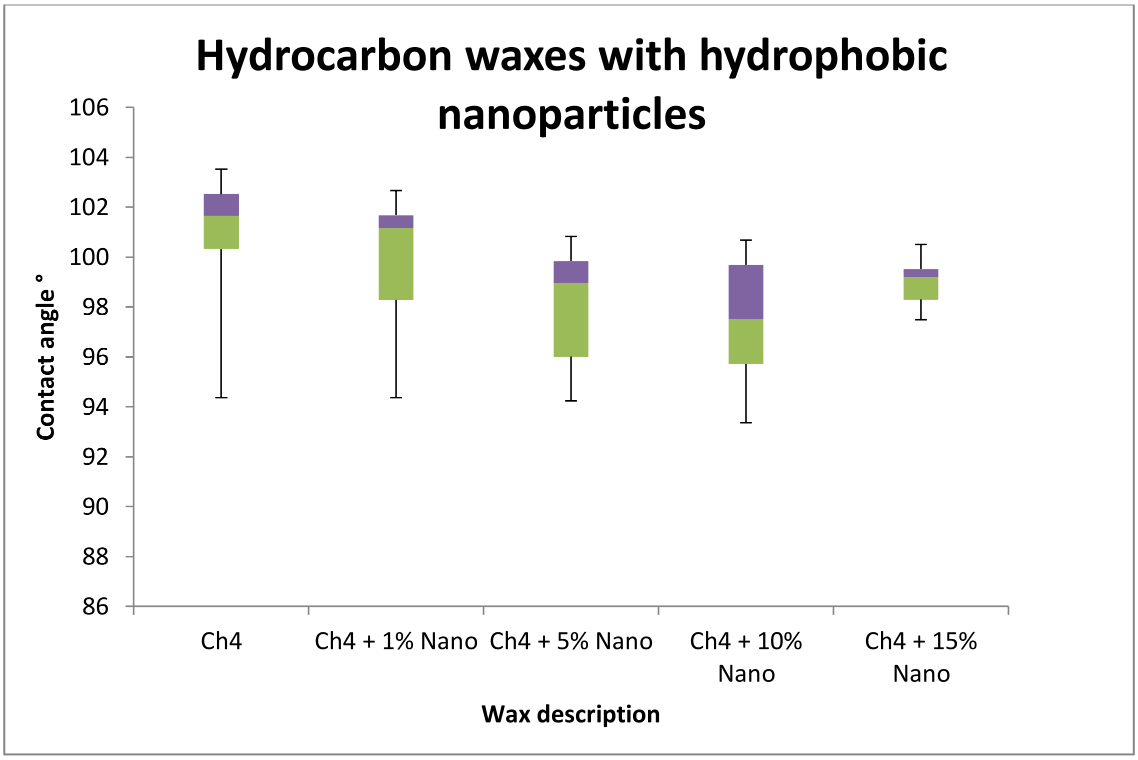


Figure 34: Box and whisker plot of the contact angles of the hydrocarbon waxes with added nanoparticles.

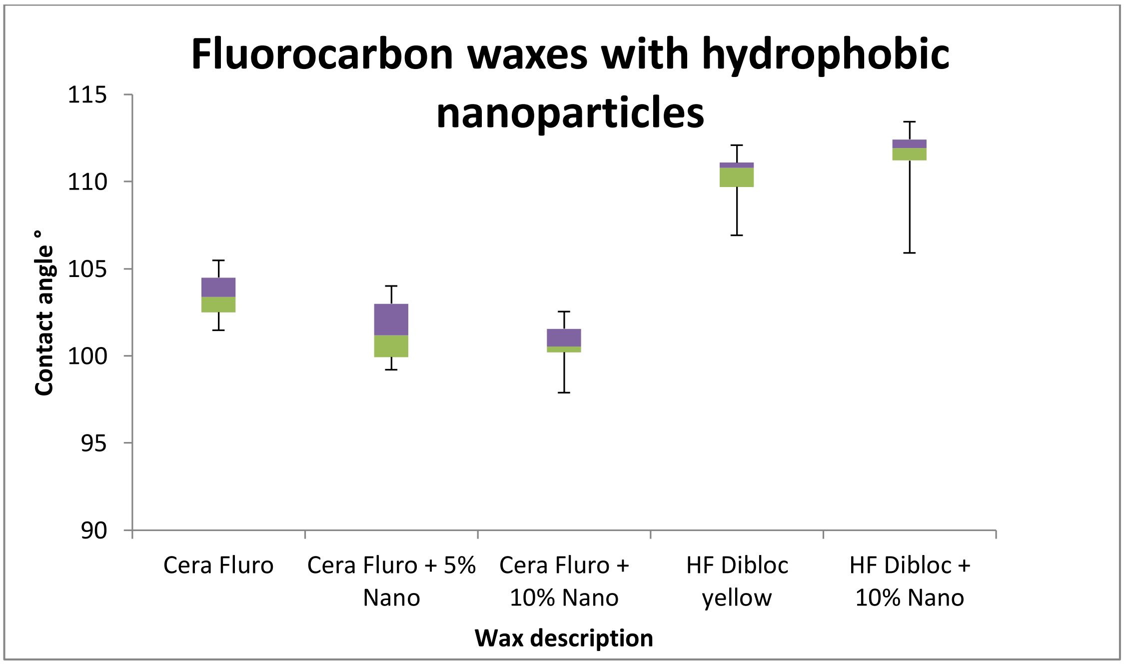


Figure 35: Box and whisker plot of the contact angles of the fluorocarbon waxes with added nanoparticles.

The hydrocarbon waxes with the added nanoparticles all demonstrate a reduction in mean contact angle compared to the standard untreated wax. There was a comparatively large variance within these treatments; this was explored by the use of an ANOVA test. Of the fluorocarbon waxes, Cera fluoro also demonstrates this same trend of reducing hydrophobicity with added nanoparticles and these results were also further examined. The HF dibloc was not tested at a 5% level so therefore no conclusions can be drawn from this data. However, at 10% levels of loading the mean angle decreased by 1° although there was a larger measured span with an interquartile range which was positively skewed. In comparison to standard HF wax no significant statistical difference can be presented that nanoparticles incorporated into waxes either increase or decrease the hydrophobicity of the wax.

Further exploration of both the CH4 and Cera Fluoro waxes with added nanoparticles using a two factor ANOVA was undertaken to ascertain whether there was a difference between each treatments and additionally to explore if there was a difference between the individual tests (ANOVA rows) conducted on each sample.

HYPOTHESIS 1

Null: There is no significant difference in contact angle with the addition of nanoparticles in hydrocarbon waxes

Hypothesis 1: There is a significant difference in contact angle with the addition of nanoparticles in hydrocarbon waxes

HYPOTHESIS 2

Null: There is no significant difference between contact angle tests conducted on each test sample of fluorocarbon waxes

Hypothesis 2: There is a significant difference between contact angle tests conducted on each test sample of fluorocarbon waxes

Table 8: Two factor ANOVA analysis of the hydrocarbon waxes containing nanoparticles.

Anova: Two-Factor Without Replication with hydrocarbon waxes containing nanoparticles

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
1	5	504	100.8	5.16095
2	5	499.98	99.996	2.53858
3	5	499.51	99.902	6.80412
4	5	495.76	99.152	10.55032
5	5	497.49	99.498	4.57017
6	5	491.39	98.278	9.49112
7	5	491.55	98.31	11.77085
8	5	504.72	100.944	4.61653
9	5	481.85	96.37	8.1902
10	5	484.73	96.946	2.53708
Ch4	10	1006.8	100.68	11.10744
Ch4 + 1% Nano	10	1000.43	100.043	7.734001

Ch4 + 5% Nano	10	980.35	98.035	5.933783
Ch4 + 10% Nano	10	973.37	97.337	7.235157
Ch4 + 15% Nano	10	990.03	99.003	0.766779

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	106.1261	9	11.79179	2.247621	0.04118	2.152607
Columns	76.05131	4	19.01283	3.624015	0.013961	2.633532
Error	188.8684	36	5.246344			
Total	371.0458	49				

BETWEEN TREATMENTS (COLUMNS)

F>F critical therefore reject the Null Hypothesis

P value does not exceed 0.05: the observation is consistent with the alternative hypothesis

There is a significant difference in contact angle with the addition of nanoparticles in hydrocarbon waxes with 95% confidence. However, this corresponds to a reduction in hydrophobicity, not an increase.

BETWEEN TESTS (ROWS)

F>F critical therefore reject the Null Hypothesis:

P value does not exceed 0.05: the observation is consistent with the alternative hypothesis

There is a significant difference between contact angle tests conducted on each test sample of hydrocarbon waxes although with a P=0.04, deviation from expected, the outcome is small enough to be consistent with a type II statistical error.

Table 9: Two factor ANOVA analysis of the fluorocarbon waxes containing nanoparticles.

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
1	3	302.52	100.84	2.0397
2	3	306.76	102.2533	1.087233
3	3	306.43	102.1433	2.324233
4	3	299.64	99.88	5.7757
5	3	305.56	101.8533	3.383033
6	3	309.27	103.09	4.2679
7	3	307.52	102.5067	10.55343
8	3	309.88	103.2933	2.188233
9	3	306.54	102.18	7.0707
10	3	302.32	100.7733	0.895633
Cera Fluoro + 5% Nano	10	1014.46	101.446	3.613649
Cera Fluoro + 10% Nano	10	1007.07	100.707	1.808823
Cera Fluoro	10	1034.91	103.491	2.239277

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	31.38015	9	3.486683	1.670241	0.169297	2.456281
Columns	41.59601	2	20.798	9.962958	0.001222	3.554557
Error	37.57559	18	2.087533			
Total	110.5517	29				

BETWEEN TREATMENTS (COLUMNS)

F>F critical therefore reject the Null Hypothesis

P value does not exceed 0.05: the observation is consistent with the alternative hypothesis

There is a significant difference in contact angle with the addition of nanoparticles in fluorocarbon waxes with 95% confidence. However, this corresponds to a reduction in hydrophobicity, not an increase.

BETWEEN TESTS (ROWS)

F<F critical therefore accept the Null Hypothesis:

P value does exceed 0.05: the observation is consistent with the Null hypothesis

There is no significant difference between contact angle tests conducted on each test sample of fluorocarbon waxes.

In conclusion, the waxes with the addition of nanoparticles do not increase the measured contact angle on a traditional ski base surface. It is suggested that the nano-scale particles which, on their own, are highly hydrophobic have become encapsulated by wax. The change in physical properties of adding particle fillers to ski waxes may be responsible for the slight reduction in hydrophobicity. The wax however, would be subject to wear, possibly exposing and releasing the silica. If the nanoparticles are exposed during sliding then their chemical properties may be beneficial in reducing friction. It was decided to practically test skis with silica modified wax using a glide testing method and the results are shown in the following section.

6.1.3. Glide testing

The influence of the hydrophobic nano-particle filler (*Aerosil* VPR 411) on dynamic friction was accessed by the glide testing method as described in section 5.2.3. The base wax used was *Swix* F4 which had a mean contact angle of 103.8° which is comparable to that of *Swix* Cera Fluoro, previously described in section 6.1.1. The hydrophobic fumed silica used was Aerosil VPR 411 a fluorinated-silane coated variety of the previously tested Aerosil 972 in 6.1.2. It was combined with the base wax by the method described in section 5.2.1. The downhill skis were treated with the hot waxing method and plastic scraped. Glide tests were conducted with *Atomic* however, the snow temperature of the tests was low (-7.5 to -8°C) for the proposed range for this wax. The temperature of this blend of wax was more appropriate to starting conditions II leading to III in Figure 9. The average time results for the glide test are shown below in Figure 36.

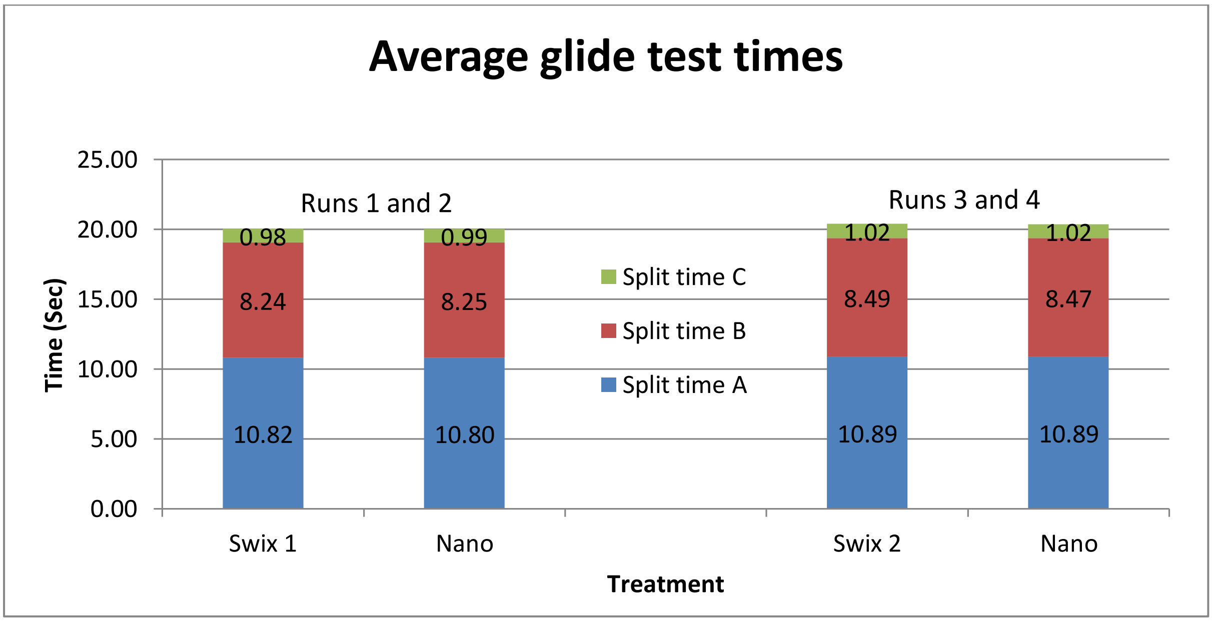


Figure 36: Glide test average times using *Swix* F4 and *Swix* F4 with added nanoparticles.

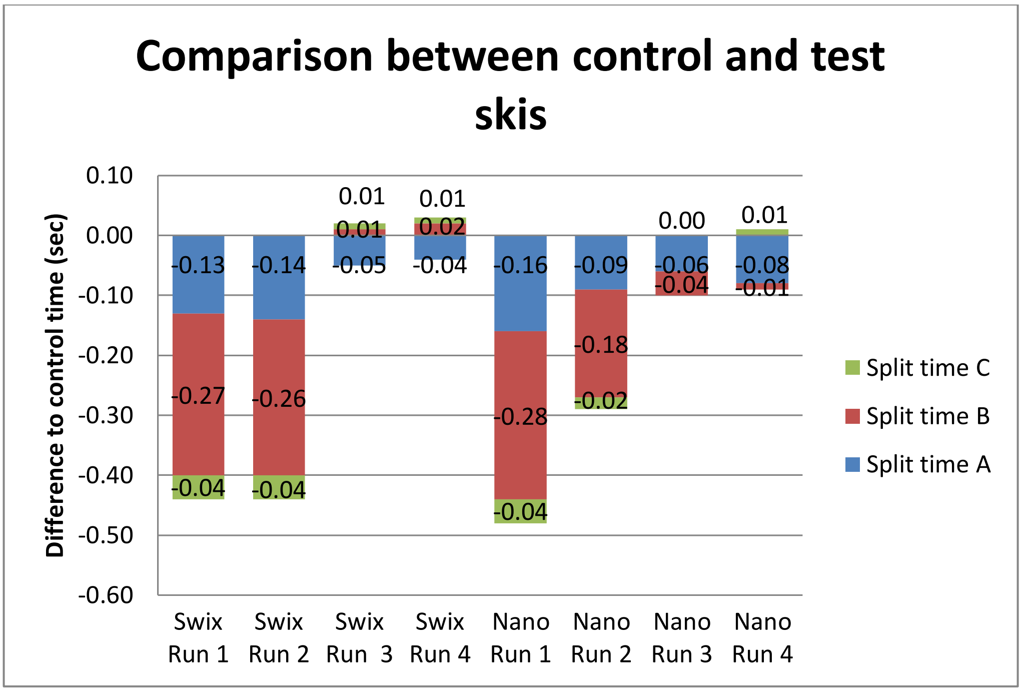


Figure 37: Comparison between the control skier and *Swix* F4 with and without nanoparticles.

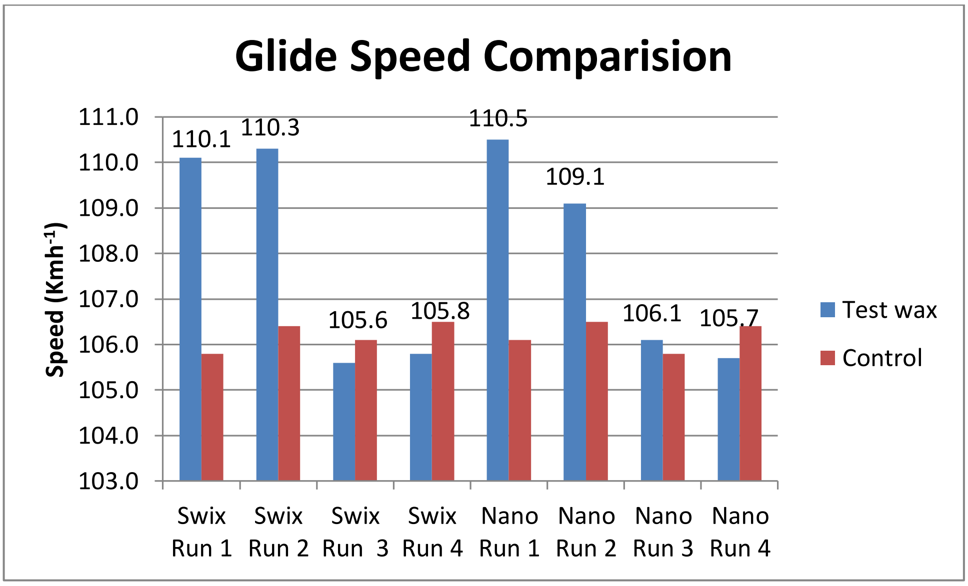


Figure 38: Comparison of glide speed between control and test waxes.

When comparing the control times and the test treatments of all four runs it would appear that *Swix* F4 containing fluorocarbons has a positive effect when compared to the control skier using a hydrocarbon *Holenkol* betamix wax in these particular test conditions. With the addition of nanoparticles to this particular wax, (*Swix* F4) when compared to the control skier, was, on average, 0.2s faster for both modified and unmodified treatments. *Swix* F4 with nanoparticles was 0.02s faster over the total time for all 4 runs. Comparison of the average times across all runs showed that the speeds of the skis with the nanoparticle wax were separated from the unmodified *Swix* F4 treatment by only 0.1Kmh^{-1}.

The presented results for *Swix* and nanoparticle modified *Swix* are very close, although only a relativity small number of glide tests were performed. This prevents a confident inference from being drawn from a comparison of the average times between each test run or from a comparison of the runs to the control runs. Further tests should be undertaken to evaluate the effect of adding hydrophobic fumed silica fillers to waxes. These tests should be performed in warmer wetter conditions as the surface coating of the silica is inherently hydrophobic. Although the contact angle results for hydrophobic silica containing waxes do not show an increase in hydrophobicity, each silica grain surface is likely to be encapsulated by a binder (the wax). It is suggested that the wear mechanism when sliding may expose the surface thereby allowing the superior chemical properties of the fluorine coated fumed silica to be exhibited. Once exposed, the silica filler may also support the break up the water film by creating a fine structure to the wax. The formation of capillary bridges may be reduced due to the physical structure of the grain of silica. However, glide testing in warmer and wetter conditions with a greater number of test runs would need to be undertaken to provide further evidence for this hypothesis; this is suggested in Chapter [8] Future Directions.

The contact angle method was used to measure the hydrophobicity of hydrocarbon and fluorocarbon waxes. It was conducted on a surface which represented a typical surface structure found on most high performance skis. Despite a macroscopic base structure present in the ski base samples, the waxes with fluorocarbon additives were easily distinguishable from the hydrocarbon wax or untreated base. The fluorocarbon waxes provided a more water repellent (hydrophobic) chemical coating evidenced by their higher measured contact angles.

The hydrophobicity of the particle filler (fumed silica) reported in in section 6.1.2 was very high (144°). When added to the hydrocarbon and fluorocarbon waxes, it did not improve hydrophobicity. The polymeric wax did ‘wet out’ the particles causing them to be incorporated into the polymeric matrix of the wax. Particles fillers which have been shown to have the potential to be more chemically hydrophobic required pre-wetting with a solvent before they would disperse into the wax. The fully wetted out particles, as may be expected, did not display the very high levels of hydrophobicity as they did previously.

Although these waxes did not improve surface hydrophobicity they still may have the potential to improved sliding friction. The glide testing method was used to compare *Swix* F4 wax which was additionally modified with nanoparticles, against a control ski waxed with *Holmenkol* betamix. The environmental conditions, specifically snow and air temperatures and humidities were not conducive to large water film generation. Additionally the number of runs conducted was insufficient to draw any firm conclusions on the effectiveness of nano-particle fillers in waxes. Although, comparison with the control skier showed that the wax with the filler was overall more effective than the unmodified base wax. Future investigations will endeavour to obtain a larger amount of data so firmer conclusions can be drawn from such a glide test, although access to world class glide testing facilities in Europe is limited.

Contact angle testing was used to evaluate the surface hydrophobicity of industry standard waxes. The un-waxed base, usually claimed to be the slowest, had the lowest level of hydrophobicity of all treatments tested. Hydrocarbon waxes slightly improved hydrophobicity with fluorocarbon additives improving contact angles even further. This is consistent with other studies such as Rogowski et al (2007) reporting increases in contact angle using a tilting plate method with fluorinated paraffin waxes. The silica particles did not improve hydrophobicity and due to the limited number of glide tests undertaken no confident inference could be made on their effect on sliding. The glide testing method does however provide a real-environment test to assess the performance of a treatment at high velocities (100Kmh^{-1} plus).

The professional glide the setup, provided by *Atomic,* was very useful for investigating the efficacy of experimental waxes and treatments in comparison other, established, wax treatments. Any treatment proposed would have to be tested in this manner in order to evaluate its effectiveness compared to other commonly used treatments on real alpine snow at comparable speeds. This type of glide testing methodology has been adopted by nearly all the manufacturers (Karlof et al*,* 2007) and has additionally been used in a relatively small number of scientific studies (Buhl et al, 2001; Nachbauer et al 1991; Spring 1988; Styring et al, 2012; Federolf et al 2007; Coupe 2008; Coupe and Spells 2009 , Kuzmin, 2006) as a definitive test for comparison between treatments. Few of these studies involved skiing at velocities above 30Kmh^{-1} and those conducted by Kuzmin were with cross country skis at low velocities. Although testing in alpine environment with human subjects introduces additional variables, the speed, loading and snow conditions cannot be replicated accurately in a laboratory-based environment. Giesbrecht et la (2010) adopted an interesting glide testing approach using small (25x 6cm) samples of base material with a range of treatments. These slid down a 35-40m Nordic ski track at around - 3°C. Speeds of descent were low (3.3 to 5.3 ms^{-1}) and relatively few test results were obtained for UHMWPE as a range of hydrophilic and hydrophobic materials were tested. A tribometer, adopted as the instrument of choice in many other scientific investigations, cannot replicate the speeds in skiing or accurately control the metamorphism of the snow between slider passes. The development of a water film on a slider can be investigated using a tribometer, however, a complete evaluation of the efficacy of treatments requires full scale glide testing at comparable speeds. However, some investigators (Coupe, 2008 and Federolf, 2006) have suggested further improvements to the glide test method to reduce the influence of unwanted variables. However, *Atomic's* method is considered to be of a high professional standard in line with current scientific methodology.

The properties of new untreated, factory manufactured UHMW-PE, rather than used, stone ground ski base material are investigated in the next section. Additionally, the use of friction ramp testing is explored. This method of measuring static friction can be used to provide additional evidence to dynamic friction information provided by glide tests. A fundamental question also arises as to whether the base material itself could be modified to exhibit more hydrophobic properties. Surface treatments are explored in the next section and these are also combined with bulk UHMW-PE modification in section 6.3.

6.2. Surface Modification of UHMW-PE

The physical surface structure, as well as the chemical composition of the base material has been shown to influence sliding friction. The assessment of dynamic friction using a glide testing method described in the previous section recorded differences of less than 0.02 seconds between the total times for each 500 metre run. This difference in time represents a variation in friction, which can be very small. However, the glide test method, with human participants and a natural snow environment with variable conditions can be susceptible to some error. Conventional ski waxing methodology, as described in section 5.1, could also be a significant variable because application and removal (scraping and brushing) of traditional waxes may not be totally consistent. Different scraping and brushing pressures may alter the surface or leave behind a varied thickness of wax. Experienced ski technicians are usually consistent in their approach to servicing skis; however, small changes in the underlying surface structure of the ski base may influence friction. The wax coating, which is applied on top of any ski surface, may have the effect of coating this surface, therefore minimising these small inconsistencies. However, the wear mechanism during sliding on snow would eventually expose the underlying surface.

This section investigates surface modifications to standard white and black UHMW-PE by measuring static friction using an inclined plane method as described in section 5.3.3. To visually inspect the effect of various surface treatments optical and scanning electron microscopy (SEM) was used as described in section 5.3.2. Contact angle measurement of water on the surface also gives an indication of both the physical and chemical hydrophobicity as described in section 6.1.

Conventional scraping treatments, plastic and metal, have previously been explored by Sturesson (2008). Treatments included in this investigation were abrasion with 800 grit paper, glass scraped and application of abrasive nano-sized particles. Each of these treatments was inspected visually with SEM, wherever possible, and the contact angle tested. The effect of treatments on the coefficient of friction was then explored in order for comparisons to be made between visual appearance, hydrophobicity and the coefficient of friction.

6.2.1. Physical (SEM) and Physiochemical (Contact-angle) analysis.

Materials and treatments examined in this section were:

- Untreated white, *P-tex 4000* ***(PEW)*** and untreated black, *P-tex 4500* ***(PEB)***
- Nylon abraded ***(Nylon)***
- Glass treated ***(Glass)***
- Glass treated with hydrophobic abrasive particles ***(AB)***
- Glass treated with ***(AB)*** and ***(PFPE)*** lubricant.

The associated application methods are described in section 5.3.1. This section incorporates the recommendations from the previous study, using new, untreated UHMW-PE both modified with carbon black and without. Surface abrasion with 800 grit (18µm) sandpaper was conducted on the remainder of the samples to replicate a wear mechanism with a similar particle size to that of some types of snow. The surface was expected to be “hairy”. The nylon treatment is a traditional treatment currently used as a physical structuring method for removing UHMW-PE hairs. Glass treatment is not commonly used, if ever, for removing UHMW-PE hairs, however, it provided an effective cutting blade similar to the industrial sintering approach of planing off a layer of the material from a block to produce the sheet. The physical structuring of the surface with a known nano-scale abrasive represents an interesting and novel inclusion investigating the possibility that these particles may texture the surface.

Black and white

As previously described in section 4.1 UHMW-PE is available in various molecular weights with or without the addition of carbon black. A number of investigation were conducted on both white and black base samples including contact angle and coefficient of friction determination together with an examination of the surface structure using scanning electron microscopy. The results of these investigations are reported in this section.

The measured mean contact angle of the P-tex 4000 (white) and P-tex 4500 (Black) sintered UHMW-PE, both with a molecular weight of 9.1 million grams/ mole, was 73° compared to 66° respectively. These samples were unmodified from the manufacturer’s sintering process; however, they were cleaned with acetone and dried before testing in order to remove any contaminants. Figure 39 below shows a box and whisker plot of both untreated samples.

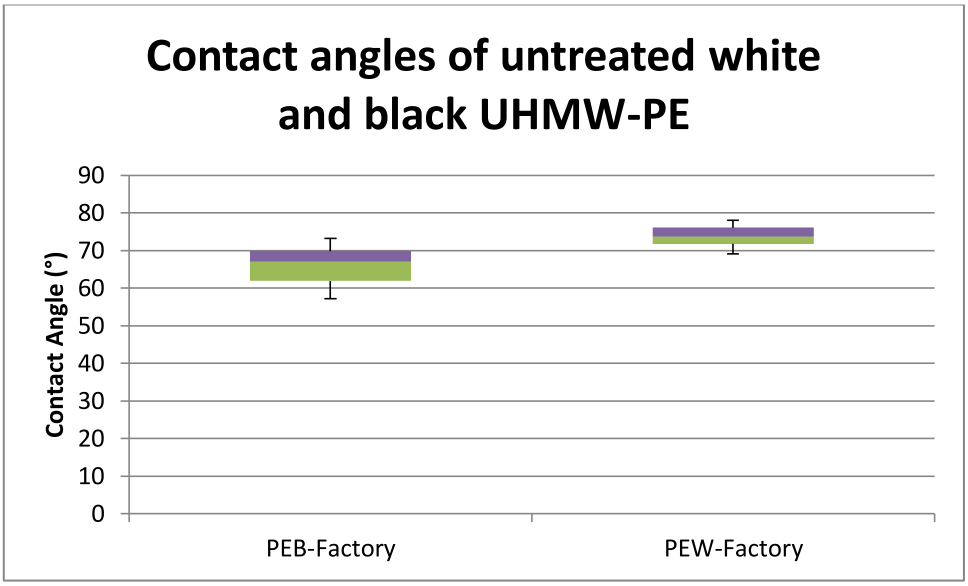


Figure 39: Contact angles of UHMW-PE black (PEB) and white (PEW)

P-tex 4500 black does have additional carbon black added which has been reported to give desirable, beneficial, properties as previously discussed, particularly pertaining to the absorption of solar energy and development of the water film. These results indicate that the contact angle is reduced when carbon black is added to the polymer blend. Hydrophobicity, as represented by the contact angle is influenced by both physical and chemical factors; could the cause of the observed difference lie in the physical surface structure? Further investigation of the physical surface structure of both P-tex 4000 and 4500 was conducted using a scanning electron microscope. The following micrographs; Figure 40 (black) and Figure 41 (white) show the detail of the surface at microscopic levels.

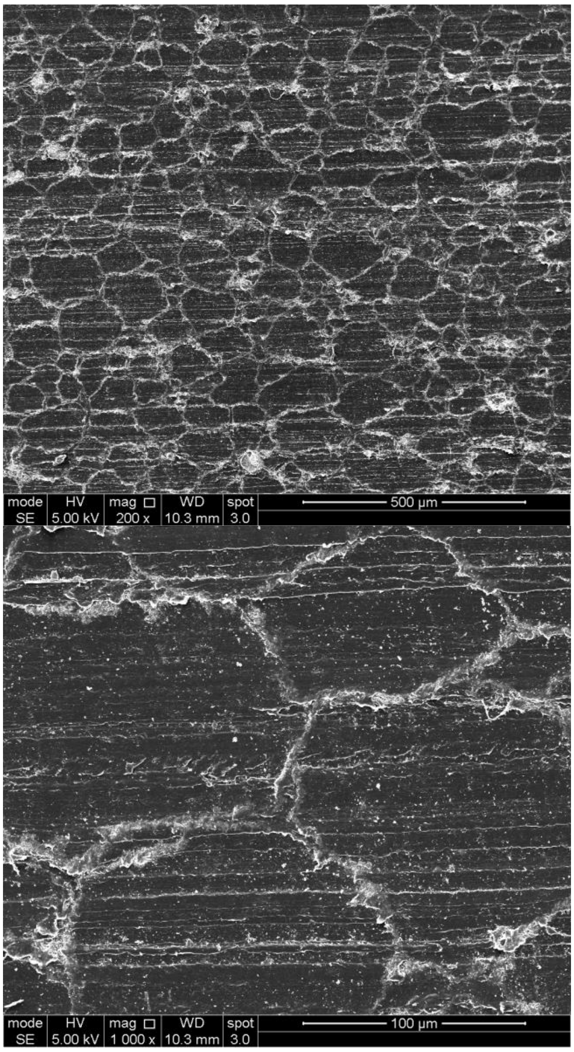


Figure 40: SEM images of an untreated black UHMW-PE base

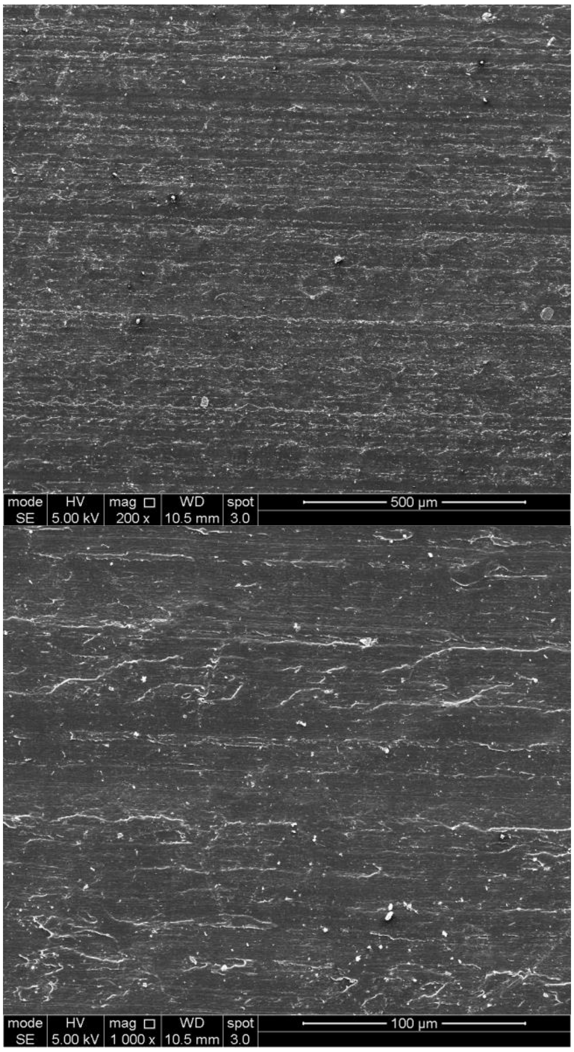


Figure 41: SEM images of a untreated white UHMW-PE base

A comparison of untreated, factory received, white and black bases at 200x and 1000x magnification indicates that the black UHMW-PE exhibits significant grain boundaries compared to the white UHMW-PE. Both bases were manufactured by a sintering process and as a result thin layers are produced during the planing or skiving process. Black bases are more commonly used on skis, especially on racing and high performance models. However, there is no published evidence as to whether these grain boundaries have a positive of negative effect on sliding friction. Karloff et al (2005) have suggested that amorphous regions may help to improve wax adhesion. Subsequent SEM samples all use black UHMW-PE but these grain boundaries are not as evident when the surface treatments are applied. All skis have to be ground and treated post-manufacture to ensure the ski base lies flush with the edges. Therefore, these pictures are of particular interest as the grain boundaries would not have been evident upon further treatment.

Abraded by nylon

The mean contact angles of the abraded and nylon treated samples were determined to be significantly higher than the untreated material. Black UHMW-PE (P-tex 4500) measured at 92° and White UHMW-PE (P-tex 400) measured at 90°. This was a 28% and 18% improvement of contact angle, respectively, compared to that of the untreated base material. Figure 42 illustrates a box and whisker plot of the measure contact angles of nylon abraded samples compared to that of untreated UHMW-PE.

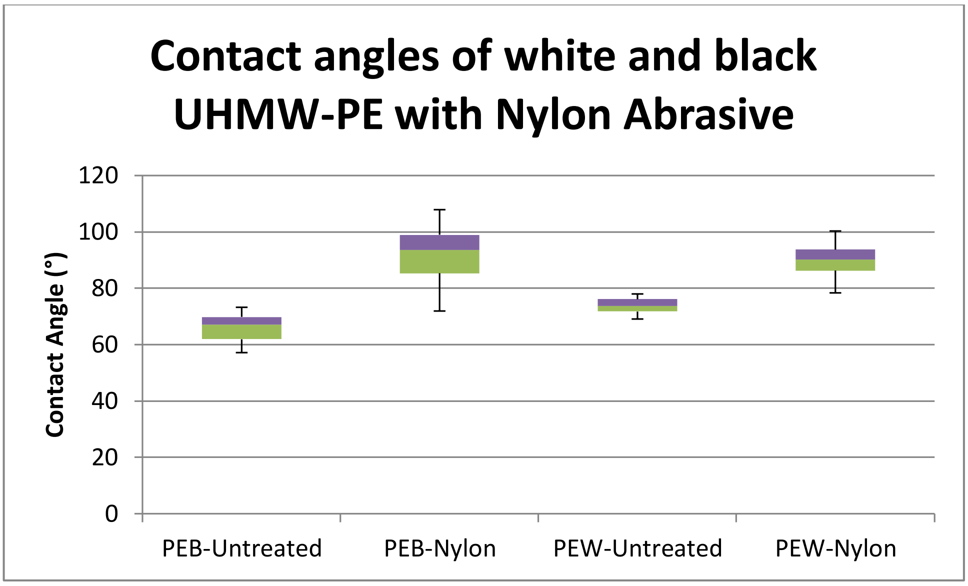


Figure 42: Contact angles of white (PEW) and black (PEB) UHMW-PE treated with a nylon abrasive compared to untreated UHMW-PE

This increase in contact angle can be associated with a change in the physical surface structure as no chemical change was caused by simply abrading the surface. The improvement in contact angle is could be due to the Cassie effect as discussed in section 4.4. An increased number of surface asperities were evident on the nylon abraded sample as shown in Figure 44. These asperities may allow micro pockets of air to be trapped between the water droplet and the base, thus increasing the measured contact angle. The influence on friction of the nylon abraded sample is discussed at the end of this section.

As previously discussed, abrasion is usually conducted using a stone or belt grinding process. The stone or belt grinding process usually provides a mechanism which is sufficient to remove a bulk of material from the UHMW-PE surface. Additionally snow and ice have been shown to act as an abrasive as discussed in section 4.2. During prolonged skiing without any surface treatments or on particularly abrasive snow and ice, the wear on the surface becomes noticeable with the naked eye. “Hairy” bases are a common phenomenon observed under these conditions. In an attempt to replicate this, the samples were treated with 800 grit sandpaper, unidirectionally, as described previously in section 5.3.1. The SEM images at increasing magnifications are shown in Figure 43 below.

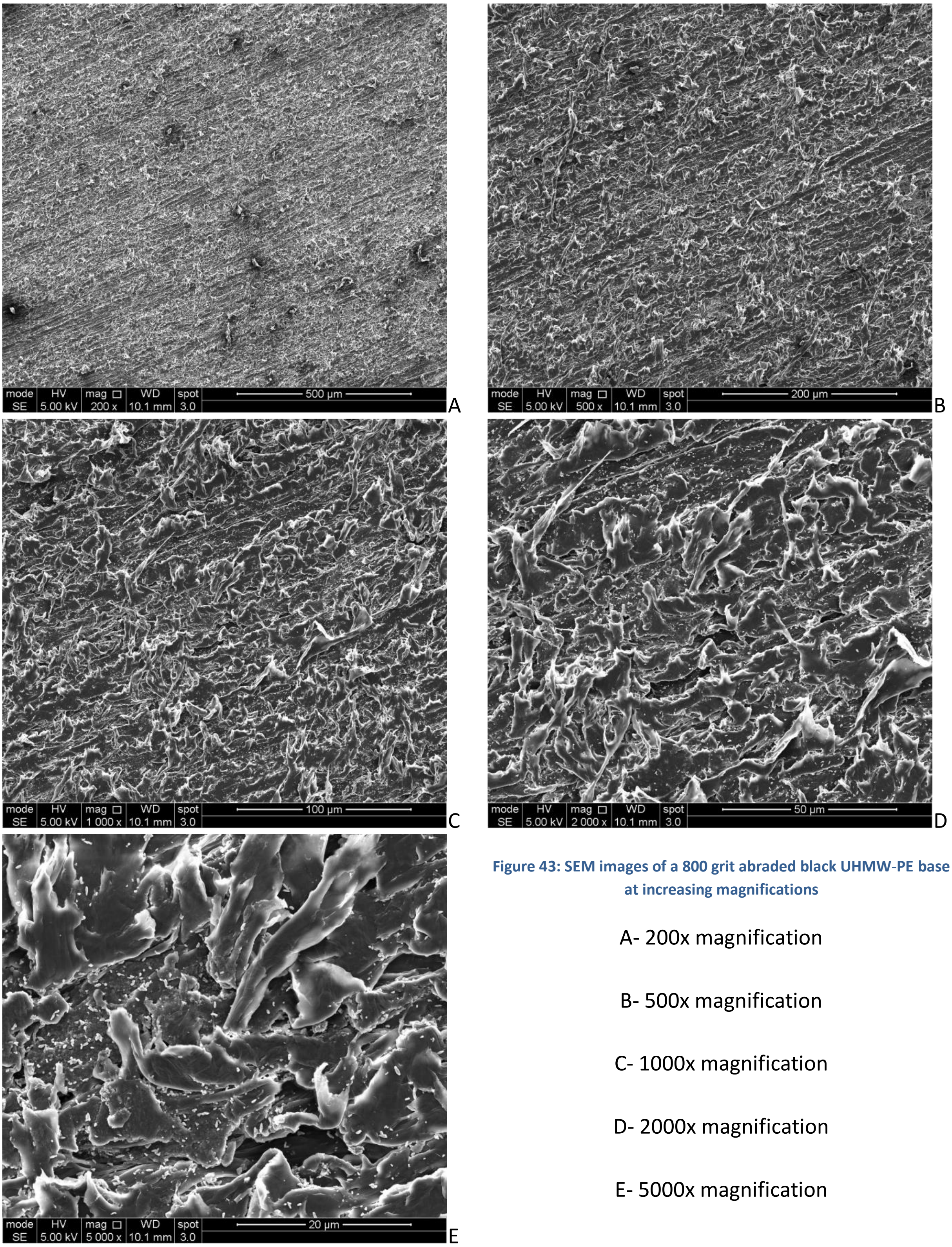


Figure 43: SEM images of a 800 grit abraded black UHMW-PE base at increasing magnifications

A- 200x magnification

B- 500x magnification

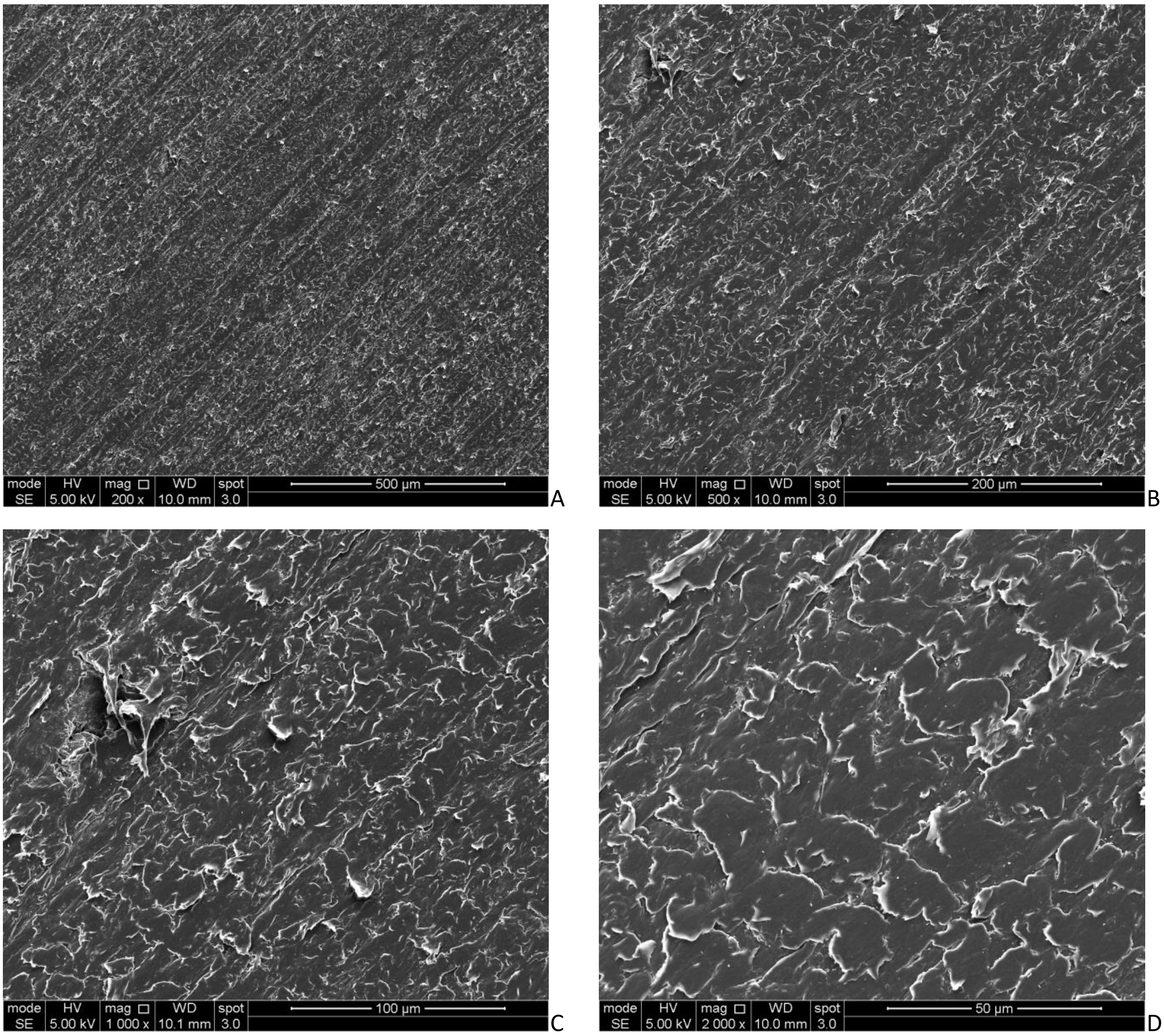
C- 1000x magnification

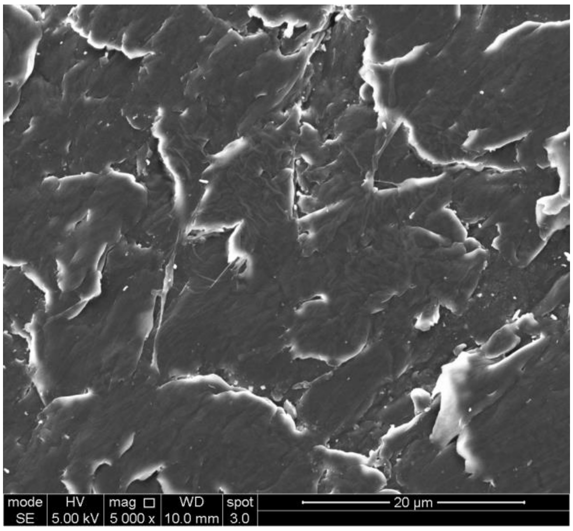
D- 2000x magnification

E- 5000x magnification

Figure 43 clearly shows the formation of surface features (hairs) at different levels of magnification. These hairs are probably the result of the ends of the long chain lengths of UHMW-PE protruding from the bulk material. The grain boundaries exhibited in the black UHMW-PE, shown in Figure 40, are no longer visible when the surface is abraded.

After stone or belt grinding, or abrasive snow conditions, a traditional method of removing hairs on a UHMW-PE base, described in section 5.1, is by the use of nylon abrasive pads. The purpose of these pads is to remove the surface features before hot waxing to create a suitably smoother gliding surface. The nylon pads, having finer abrasive particles compared with those of the stone/belt/snow, effectively polish the surface to a finer roughness. Any reduction of hairs or features could significantly influence the contact angle, dry friction and actual contact area. This treatment to remove the hairs was applied in the same direction as the sanding and the effects are shown in Figure 44.





E

Figure 44: SEM images of a nylon treated black UHMW-PE base at various magnifications

A- 200x magnification

B- 500x magnification

C- 1000x magnification

D- 2000x magnification

E- 5000x magnification

It is evident when comparing the 800 grit abraded surface shown in Figure 43 to the nylon abraded surface in Figure 44 (above) that a large majority of features are removed by use of a nylon abrasive pad. However, there are significantly large scale features (10-20µm) left on the surface which are evident at the 1000x to 2000x magnification level. Abrasive nylon pad treatment seems to be beneficial in the approach of large surface feature or “hair” removal, reducing the number of features and providing the base with an anisotropic pattern in the direction of abrasion.

Glass treated

Plastic and metal scraping methods, as previously described, are traditionally used for the removal of wax or to aid the removal of inconsistencies on the sliding surface, as well as base repair. However, metal scrapers tend to be only recommended for very hard, cold wax or base repair. There is no published evidence as to how metal scraped wax in cold conditions influences friction although Sturesson (2008) reports reduced friction for metal scraped un-waxed ski bases in a predominantly dry friction regime. The smoothest surface shown in the scanning electron micrographs so far is that of untreated white UHMW-PE. It has been shown by Giesbrecht et al (2010) and Moldestad (1999) that smooth surfaces do not always exhibit the lowest coefficients of friction as discussed in section 4.3. However, in certain circumstances, such as very cold, dry conditions, it has been claimed that such smoother textured surfaces reduce friction (Colbeck, 1996; Kuzmin, 2006). It should be noted however, that the definitions of what is smooth and rough when compared to the water film height described in section 4.3.5 are sometimes ambiguous. Certainly the nylon abrasive method reduces the number of larger surface asperities exhibited on the surface but can a planing or skiving process seek to further reduce the visible surface roughness or reduce the number of asperities by planing them off. The contact angle measured, as shown in Figure 57 below, was interestingly higher for the glass scraped surfaces compared to those samples which were nylon abraded.

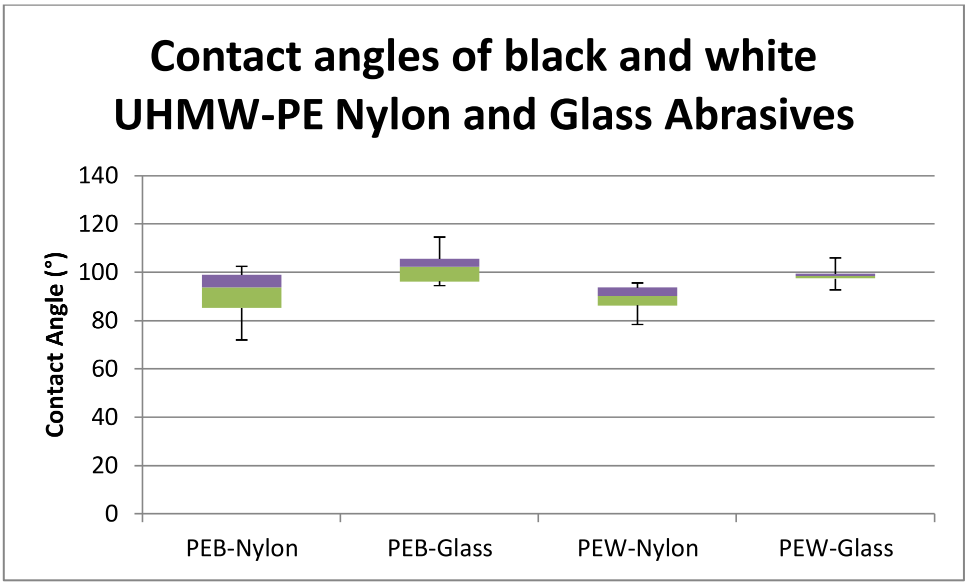


Figure 45: Measured contact angles of nylon and glass treated, black and white UHMW-PE

Comparison of the mean contact angles of the nylon and glass treated surface of black and white UHMW-PE shows a 10% and 8% improvement of the glass treatment compared to that of nylon. The visibly smoother surface of the glass treated samples, as shown in Figure 46, would not be conducive to the Cassie effect, as previously described in section 4.4, where the water droplet sits on top of the asperities. With a smoother surface the Wenzel effect is more likely where the asperities break the tension of the droplet. Smoother surfaces generally exhibit lower contact angles as the water droplet can spread out, wetting the surface and reducing the measured angle. The nylon treated surface, as shown in the SEM micrographs (Figure 44) removed a significant number of large asperities caused by the previous abrasive treatment with 800grit sandpaper (Figure 43). The contact angle form by a droplet on the surface can either be in a Cassie or Wenzel state, with the droplet either sitting on top or where the asperities have broken through the surface tension of the droplet. The significant increase (18-28%) in contact angle is likely due to the physical structure becoming rougher as a result of the abrasive treatments. The water droplet therefore rests onto or over these asperities resulting in larger measured contact angle. Contact angles are usually lower on smoother surfaces as the water droplet can spread out to wet the surface. However, a further 8-10% improvement in contact angle for the visibly smoother glass treated surface was recorded. The surface features still remaining may be of the right magnitude to allow the water droplet to sit on top of these features in a Cassie state rather than breaking through. It is possible that this may explain the increase in the measured contact angle recorded on the glass treated sample. The SEM micrographs of the glass treated surface are shown in Figure 46 below.

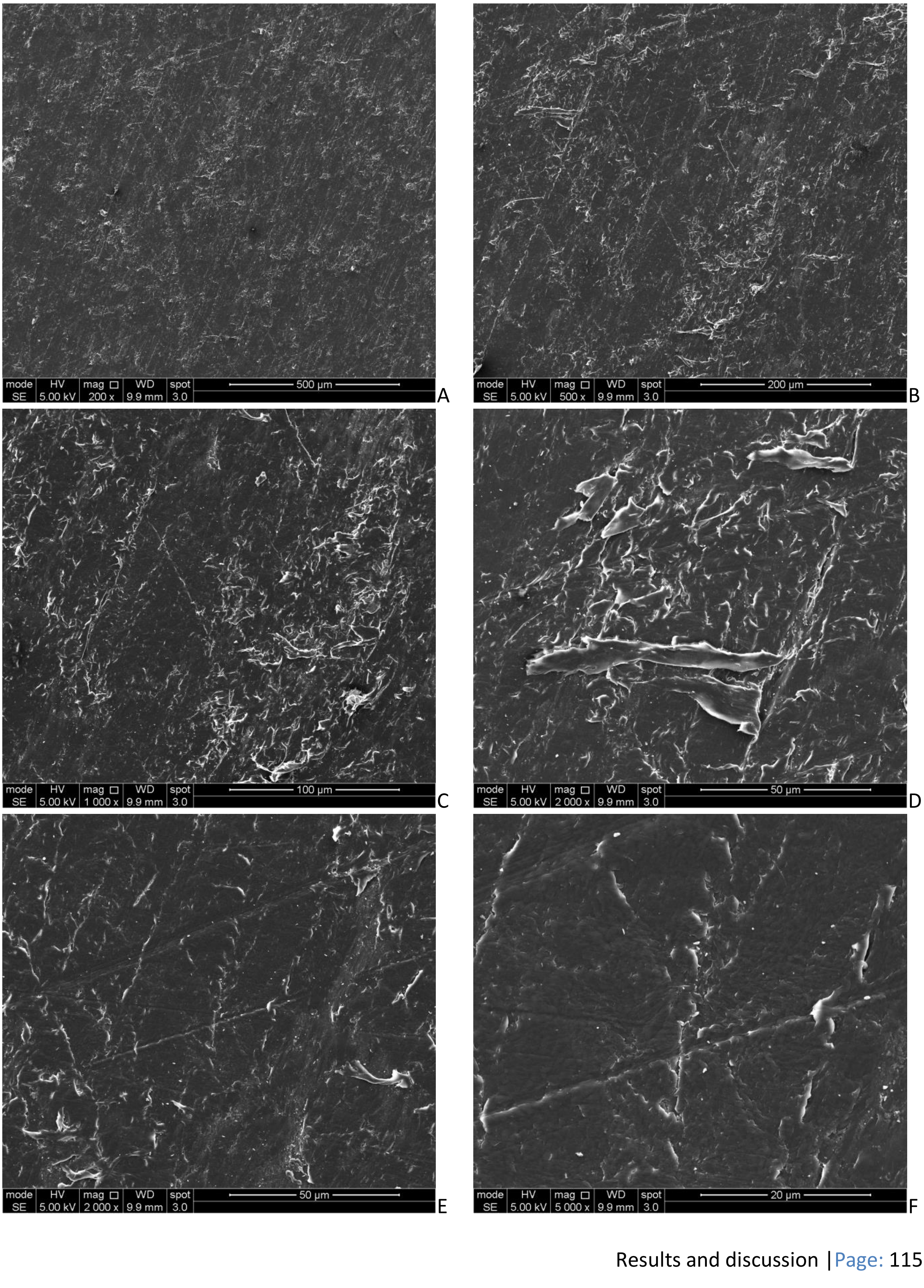
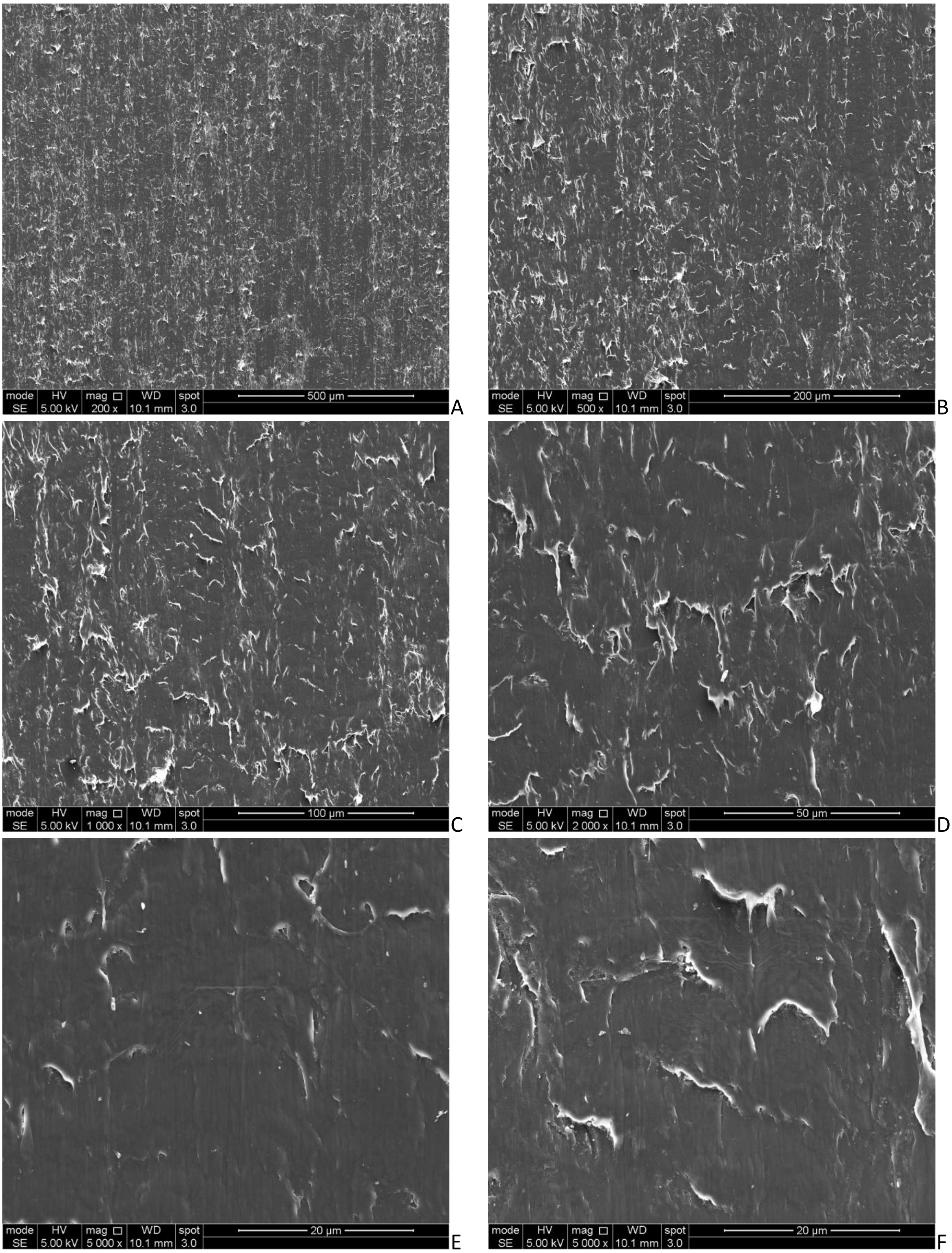


Figure 46: SEM image of a glass treated black UHMW-PE base at various magnifications. A- 200x magnification, B- 500x magnification, C- 1000x magnification, D- 2000x magnification, E- 2000x magnification. F- 5000x magnification.

Comparison between the abrasive nylon treated surface (Figure 44) and the glass scraped surface (Figure 46) at 500x magnification shows that on the glass scraped surface there are greater number regions with relatively fewer surface features. The glass scraping method creates a visually smoother surface than the nylon abrasive alone; there are, however, transverse lines caused by the glass which are visible in Figure 46. These lines, caused by the glass scraping method, could be more evident on the SEM samples than a normal ski base subjected to this treatment. The lines may be caused by increased pressure at a given point. Using longer strokes may provide a more even pressure distribution over the surface and may avoid the generation of these transverse lines. Due to the small surface area (10mm diameter) of the SEM sample equal pressure distribution is difficult to achieve. The material was cut out of a larger treated area however, even this did not allow of precision control of pressure due to the small working area compared to that of a ski length and width.

Glass treated with hydrophobic fumed silica

The nylon treatment is facilitated by the incorporation of bonded abrasive particles to the nylon filaments. Various types of particles are used for different applications but typically silicon carbide particles are used. The size of the particles used depends on the material and level of finished required. However, are silicon carbide nylon abrasives appropriate for abrading UHMW-PE with the view to reducing friction? A wide range of grit sizes are commercially available. Whilst only one size was trialled in this investigation, further investigation using a full range of sizes has been suggested in the future directions section. Smaller grit sizes have been demonstrated by Unal et al (2005) to reduce wear volume on UHMW-PE with 150/360/800/1200 grit sandpapers respectively using a pin-on-disk tribometer. The abrasive sandpaper used in this investigation was 800 grit, this had an equivalent average particle size of 22.8µm. In an attempt to impart a much finer surface finish to the UHMW-PE, hydrophobic fumed silica was used with an average particle size of 16nm. The silica particles were used as a dry abrasive and combined with the glass scraping method as described in section 5.3.1.


mode SE HV 5.00 kV mag 200 x WD 10.1 mm spot 3.0 500 µm
A
mode SE HV 5.00 kV mag 500 x WD 10.1 mm spot 3.0 200 µm
B
mode SE HV 5.00 kV mag 1 000 x WD 10.1 mm spot 3.0 100 µm
C
mode SE HV 5.00 kV mag 2 000 x WD 10.1 mm spot 3.0 50 µm
D
mode SE HV 5.00 kV mag 5 000 x WD 10.1 mm spot 3.0 20 µm
E
mode SE HV 5.00 kV mag 5 000 x WD 10.1 mm spot 3.0 20 µm
F

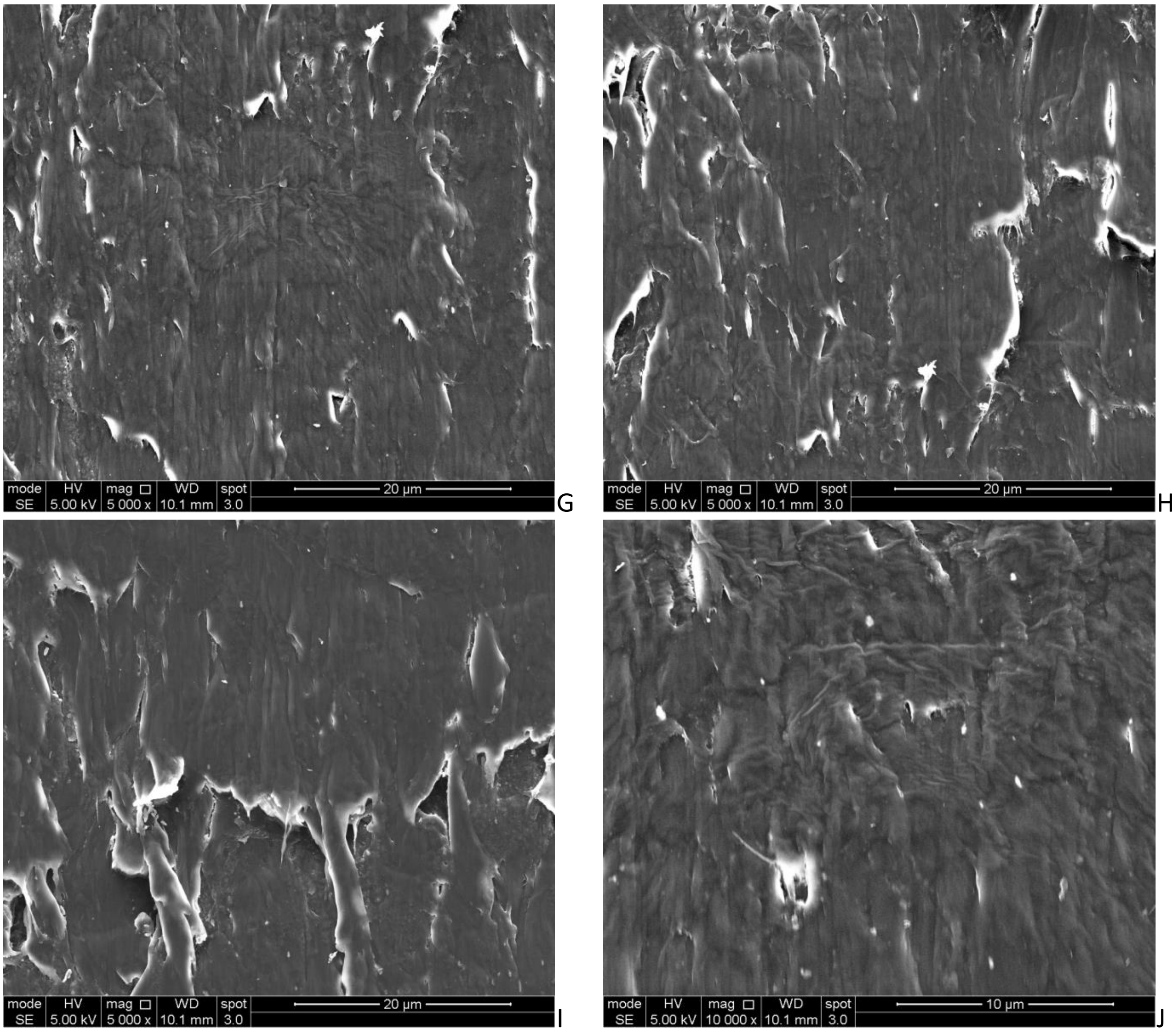
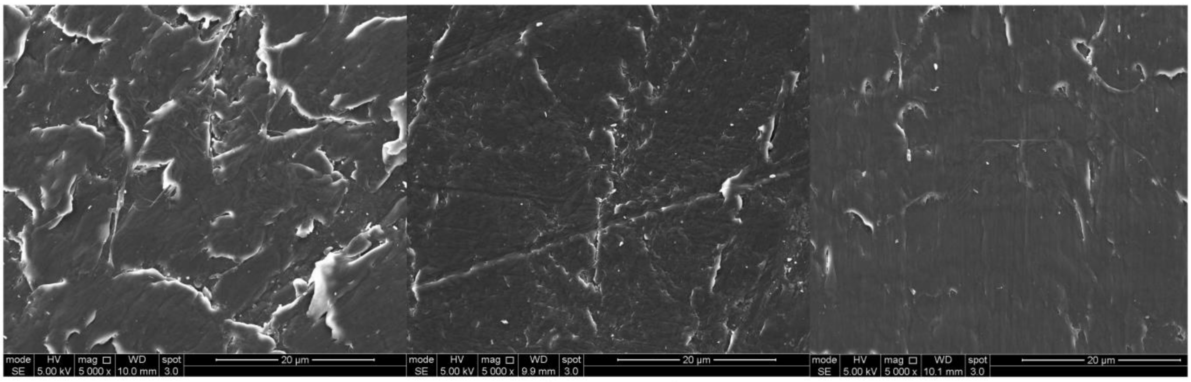


Figure 47: SEM image of a glass and silica treated black UHMW-PE base at various magnifications

A- 200x magnification, B- 500x magnification, C- 1000x magnification, D- 2000x magnification, E through to I- 5000x magnification, J- 10000x magnification.

If a comparison is made between the glass scraped surface (Figure 46) and the glass scraped surface further abraded with hydrophobic fumed silica (Figure 47) then it is evident that both samples have a defined anisotropic roughness in the direction of abrasion. There is a greater frequency of features visible on the silica treated sample (Figure 47) at lower magnifications (200x and 500x) however; the larger features that remain are of a reduced size compared to the glass scraped sample. Additionally, a larger proportion of these features appear to be flusher with the surface, aligned with the direction of abrasion.

Figure 48, shown below, compares the nylon, glass and silica treated samples side by side at 5000x magnification. At this higher zoom level, smaller scale peaks and valleys are visible at the 1µm scale. The glass scraped and nylon abraded samples also demonstrate this smaller scale patterning however, these are rather more isotropic in nature when compared to the silica abraded sample.



Nylon Abrasive Glass Scraped Glass and Silica Scraped

Figure 48: SEM comparison of nylon, glass and glass with a silica abrasive treatments at 5000x magnification.

The direction of abrasion of these samples 2 o'clock to 8 (Nylon), 1 o'clock to 7 (Glass) and 12 o'clock to 6 (Glass and Silica). Due to the rotary action of the SEM sample changer the direction of abrasion could not always be oriented vertically to align with the page.

In section 6.1.2 hydrophobic particles were tested without a binder or wetting agent present and produced very high contact angles (144°). Liquid PFPE (2024x) was used as a lubricating fluid which wetted out the hydrophobic particles for the glass and silica scraping method. High molecular weight perfluoropolyether (PFPE) was mixed with hydrophobic fumed silica using the method described in section 5.3.1 to form a paste. Encapsulating the hydrophobic silica particles in a liquid PFPE binder effectively formed a hydrophobic polishing compound with abrasive properties. The paste succeeded in providing a lubricant to the glass scraping process as PFPE is commonly used in lubricating 'high end' applications in industry. PFPE is also of interest for use in bulk modification (section 5.4.3). This process of encapsulating the nanoparticles also reduces the risk of the particles entering the respiratory system during application because the particles cannot be atomised. The hydrophobicity of the surface was assessed using contact angle testing on white and black UHMW-PE and compared with the previous samples. These results are displayed in Figure 49 for black UHMW-PE and Figure 50 for white.

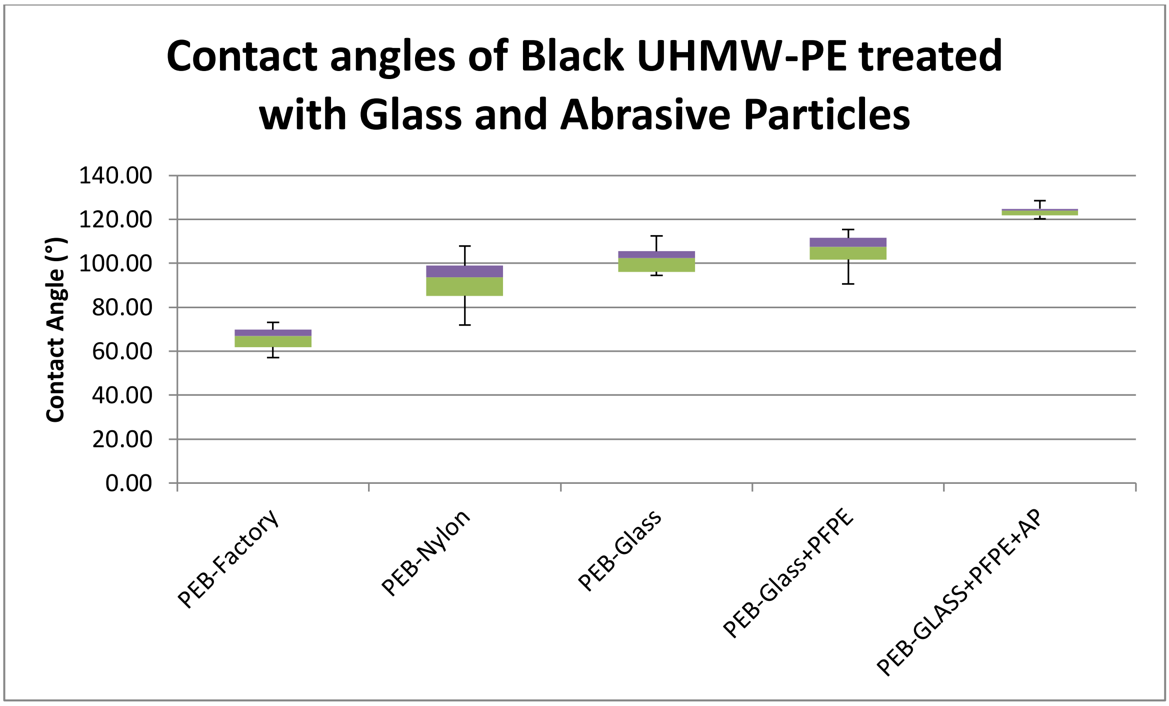


Figure 49: Contact angles of UHMW-PE black glass treated with the addition of abrasive particles and PFPE lubricant.

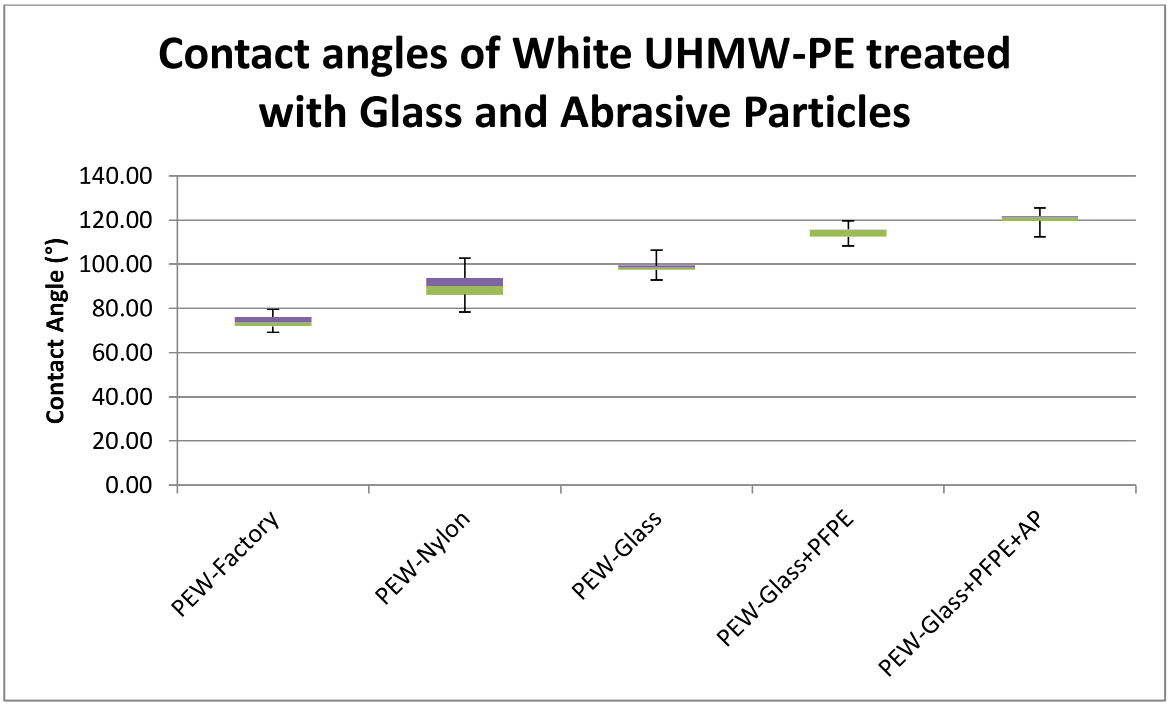


Figure 50 Contact angles of UHMW-PE white glass treated with the addition of abrasive particles and PFPE lubricant.

It is evident from both graphs (Figure 49 and Figure 50) that a significant rise in surface hydrophobicity can be achieved with the described treatments starting from a factory base. The highest contact angles observed are that of the glass with the paste treated base material. Both the physical and chemical elements of this treatment are most likely to be responsible for the high measured contact angle. The glass treatments also show small interquartile ranges indicating that the physical element of the treatment is perhaps providing a well-defined roughness. Unfortunately, the use of the paste wax could not be explored in the SEM study because of the potential vaporisation of the paste in the vacuum. Additionally, the initial coating of the sample with carbon or gold to obtain a conductive surface could have been problematic. However, there is evidence from the SEM images that dry nano-abrasive particles did produce a more finely textured surface

An environmental SEM could be used to gain further insight into the surface structure and visible roughness. Such an instrument was used by Sturesson (2008) together with the use of a three dimensional optical profilometer to further define the surface profile and roughness, although the SEM magnifications were lower (100-200x) than in this study. Optical profilometry was also adopted by Moldestad (1999) and Geisbrecht et al (2010). Geisbrecht et al identified the optimal roughness of a sole on a cross country ski to be 0.5-1µm. Similar methods of analysing the structures of ski bases have included fast Fourier transform (FFT) and scale-sensitive fractal analysis conducted by Jordan and Brown (2006).

The contact angle tests conducted in this section, when compared to the earlier investigations in the wax modification section, using stone ground section of GS ski, demonstrated a narrowing of the ranges measured in the results. The surface structure of the sintered UHMW-PE base material, used in this section, was not stone ground or previously used for sliding. Macroscopic roughness is provided by the stone ground structure; however, a much more microscopic roughness was evident on the traditional (nylon) and the alternative (glass and abrasive particles) preparation methods. Using the physical structuring methods, described in this section, the contact angle of black UHMW-PE could be varied significantly. The results seem to positively correlate the reduction of physical features and asperities demonstrated by the SEM pictures with higher measured contact angles. The measured contact angle range of an un-waxed base on a used stone ground ski in section 6.1 was 7° (95°-102°). The physical treatments (Untreated, Nylon, Glass) applied to black UHMW-PE in this section demonstrate an even larger range of 55° (57°- 112°) . This demonstrates that water repellency of a ski base can be significantly influenced by microscopic physical structuring methods alone. Wax treatment, with the addition of fluorinated additives (HF Dibloc yellow) and traditional scraping and brushing methods reported in section 6.1 increased to an average of 110° (range 106-113°). Chemical treatments combined with physical structuring (Glass, PFPE and Nanoparticle abrasive) methods recorded contact angles of 123° on average with a 120-128° range. However, it has been suggested, it is beneficial to have a highly hydrophobic surface when a water film has developed to reduce microscopic wetted contact area; will this be supported by investigations into static and dynamic friction?

6.2.3. Influence on friction

The treatments previously investigated with SEM and contact angle testing were further explored using an inclined plane method as described in section 5.3.3 to assess the static coefficient of friction (COF). The medium of snow was used as the sliding surface which is the natural skiing surface but whose characteristics vary with environmental conditions. Black and white control UHMW-PE samples which remained untreated throughout the course of the experiments were used to detect changes to the track. The black and white control samples UHMW-PE were abraded with 800 grit sandpaper and then treated with nylon before testing. The results which are subsequently shown compare any differences between the control and the described treatment. The environmental conditions recorded are detailed in Table 10, which show a warming throughout the test series 1-3. The difference in the COF of the black and white control samples across all three series are shown in Figure 51 and Table 11 below.

Table 10: Environmental conditions for the inclined plane testing method on natural snow.

Series	Snow temperature (°C)		Air temperature (°C)		Snow Humidity (%)	Air Humidity (%)
	Beginning	End	Beginning	End		
1	-2	-1.5	-1	0.5	82	62
2	-0.5	1.5	1.5	3	82	62
3	-2	-1.5	1.5	3	96	73

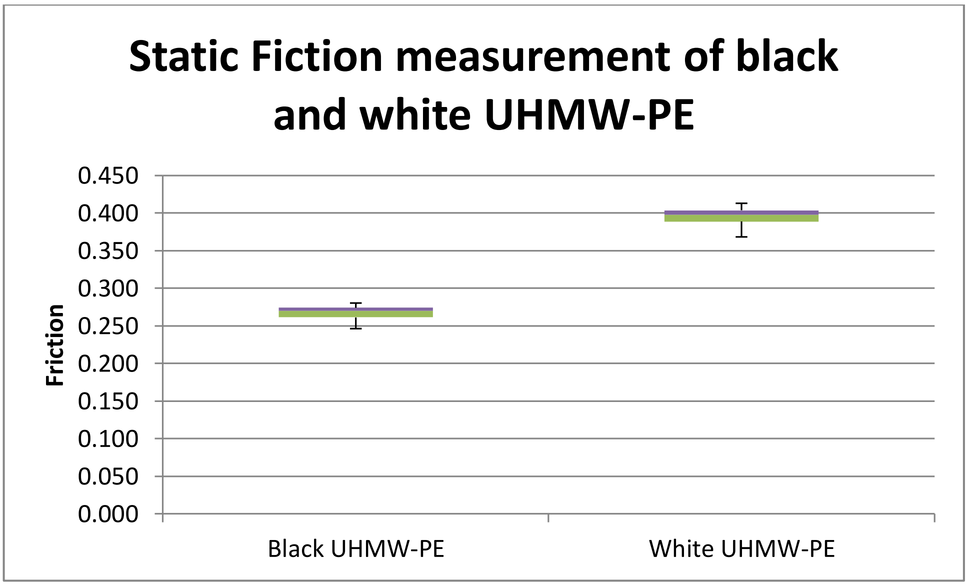


Figure 51: Static COF of black and white UHMW-PE control samples on snow.

	Black UHMW-PE	White UHMW-PE
Average	0.268	0.394
Min	0.246	0.368
Q1	0.2615	0.3885
Median	0.270	0.398
Q3	0.274	0.4035
Max	0.280	0.413
Standard Deviation	0.008651	0.012589
Variance	0.0000748	0.000158

Table 11: Summary of COF friction ramp data for black and white UHMW-PE controls.

The data shows a significant difference (0.13) between the white and black polyethylene control samples. It is suggested that differences in the absorption of solar radiation between the black and white base samples could explain the difference in COF. Colbeck and Perovich (2004) argued that solar radiation by a ski base can contribute significantly to the production of a meltwater film. They demonstrated that black ski bases ran at higher temperatures than white ski bases and that solar radiation was a very significant factor in this difference. The friction ramp experiments were conducted at relatively warm and humid conditions, very close to the triple point of water. This could have amplified any differences in the coefficient of friction between white and black polyethylene because of the differences in heat transfer due the absorption of solar radiation. The resulting water film may therefore have been a more ideal thickness for the black base than the white. This would be consistent with the findings shown in Figure 51 which show a significant reduction in static friction between black and white UHMW-PE.

The small spread of the data (black 0.034 and white 0.045, n=26) and small variance across the changeable environmental conditions (-2 to 1.5°C, 82% to 96% humidity and -1 to 3°C air temperature, 62 to 73% humidity), indicates that these control samples are comparable. When white and black are compared in series 3 in the same temperature range (n=10) the same difference was recorded between white and black UHMW-PE.

The subsequent treatments, as previously described for contact angle testing and physical examination, were then applied according to the method described in section 5.2.2. There were four abraded and nylon-treated sample blocks, two of which were controls (Black and White) the others were treated black (B) and treated white (W). The contact angles were measured for each of the various treatments, as shown in Figure 52 below.

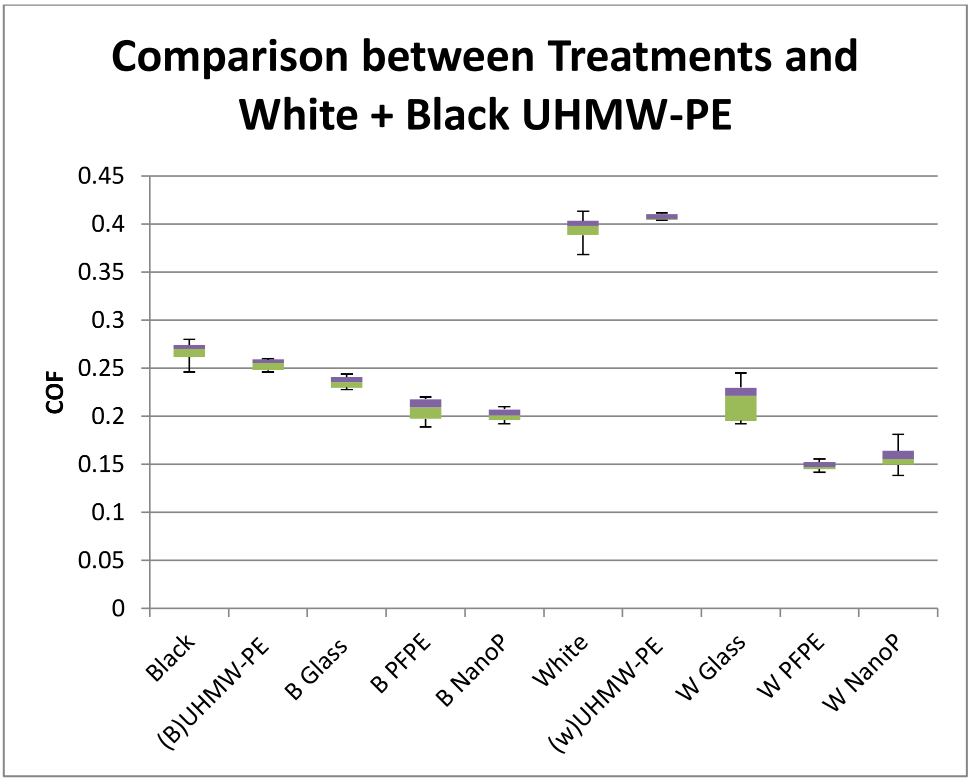


Figure 52: Comparison between treatments on white and black UHMW-PE

The box and whisker plot of the treated samples explores the measured range of treated samples as shown in Figure 52 above. This figure indicates a significant friction reduction advantage in treating white UHMW-PE with the various treatments compared to black UHMW-PE. Whilst most treatments on both black and white bases did reduce the COF compared to the controls, this was particularly noticeable on the white UHMW-PE. The control block and treated blocks (B) and (W) were initially compared to the corresponding control, and demonstrated that control block is comparable to the test block. Subsequent treatments show relatively small ranges and significant differences in COF. Interestingly, white polyethylene initially exhibited a higher COF of friction compared to black, as previously described. However, when treated, white UHMW-PE certainly equalled the black UHMW-PE and indeed gave the lowest measure of the coefficient of friction. The physical treatments, glass and glass with paste wax, imposed on the white samples may be more beneficial in terms of reducing friction. The results show a large initial difference in friction for abraded and nylon treated white and black UHMW-PE, this could be potentially explained by a combination of factors including of solar radiation or surface texture. Certainly in the warmer and wetter conditions that these tests were conducted in, a more hydrophobic disposition is useful on both black and white UHMW-PE.

The extent to which there is a correlation between the measured coefficient of friction and the contact angle (hydrophobicity) previously measured was explored in Figure 53.

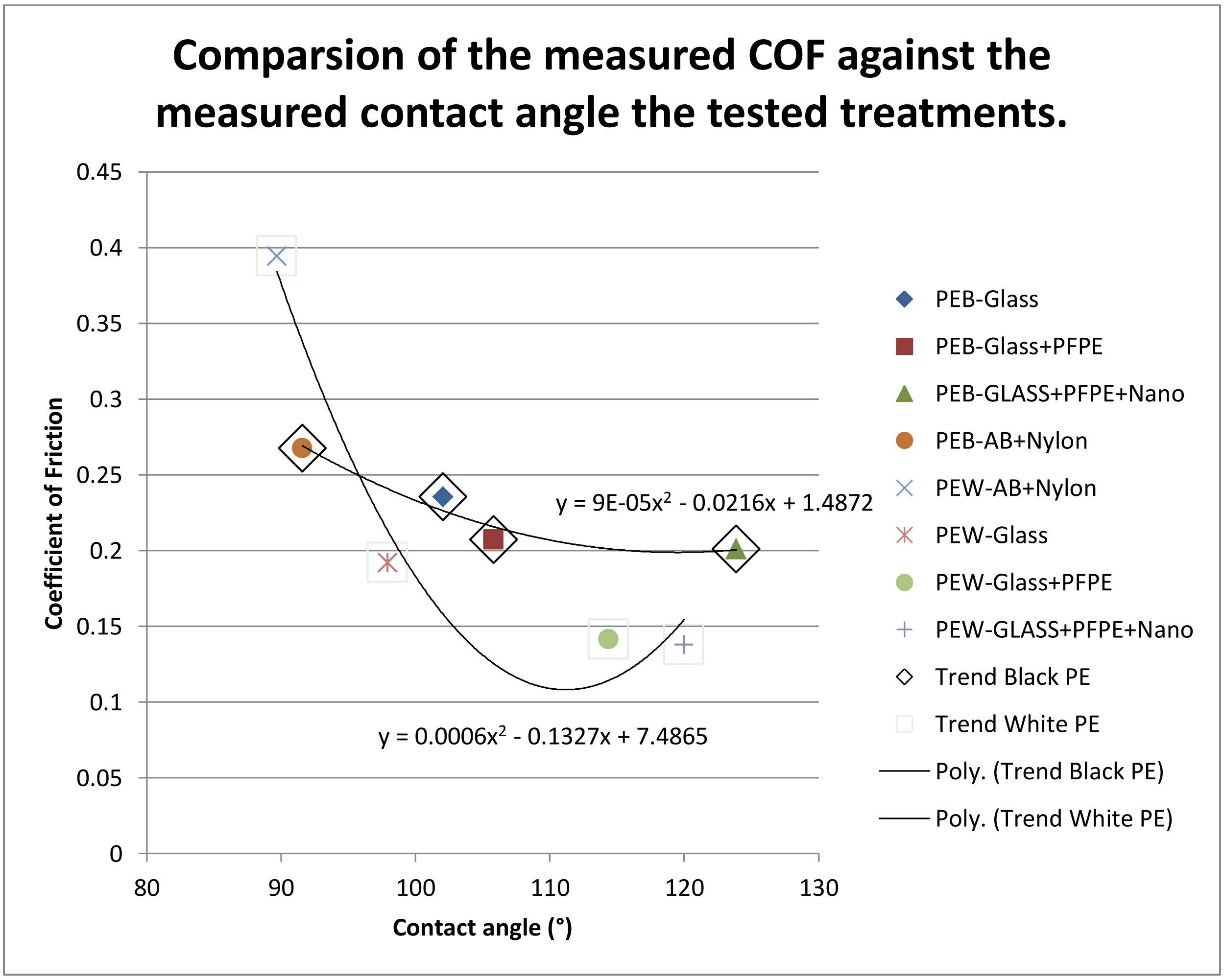


Figure 53: Comparison of the measured coefficient of friction and contact angle data.

The data tentatively supports a hypothesis that the higher the measured contact angles the lower the measured COF of static friction. This could be because a more water repellent surface (higher contact angle) may reduce the sum of the wetted contact areas. Less contact could reduce the force needed to overcome friction at every contact point in the interface. Although, this could only be postulated for the measured sliding conditions, which tended towards the warm and wet. In different snow condition such as those resulting from lower temperatures and low humidities, this hypothesis may not be valid. This is because a predominately dry friction regime would be more prevalent in colder conditions; therefore, the surface hydrophobicity would have a reduced effect, as there is likely to be a reduced amount of melt water at the interface. A greater range of environment conditions could be tested to particularly investigate the influence of contact angle on the static coefficient of friction in colder conditions. It must also be noted that at higher velocities, even at lower temperatures such as those experienced in alpine skiing, frictional heating may cause the film to thicken significantly enough for a hydrophobic surface to become beneficial. Certainly a physically smooth surface with small feature heights would be beneficial in reducing the dry frictional element.

In order to investigate the effect higher velocities would have on dynamic friction and how physical structuring and hydrophobic chemical methods would compare against traditional waxing products; a glide testing method was adopted. This investigated the most hydrophobic treatment from the previous experiments namely the PFPE+ nanoparticles or "paste". Testing was conducted on two identical models of ski with identical medium stone ground patterns. The paste wax was applied to the ski using the method described in section 5.3.1 and the other pair of skis, traditionally hot-waxed with *Holmenkol* betamix wax, Plexiglas scraped and brushed with nylon, then horsehair. The average split times for the paste wax method compared with a traditional waxing method using an alpine glide test is shown below in Figure 54. The comparison to the control skier, also using *Holmenkol* betamix, is shown in Figure 55. Note the differences in times between the same treatment and different skiers (0.4sec). The treatments were tested using the same glide test participant for that reason. The maximum speed (split time C) of the treatments was also compared in Figure 56.

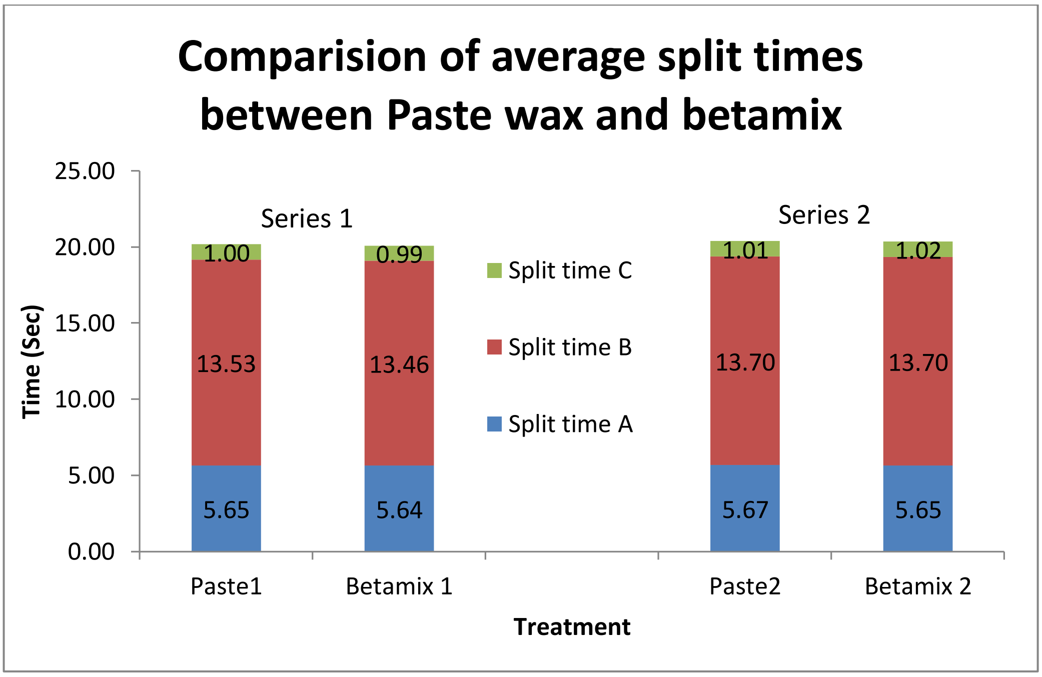


Figure 54: Mean times of glide test runs between the paste wax and *Holmenkol* betamix Red

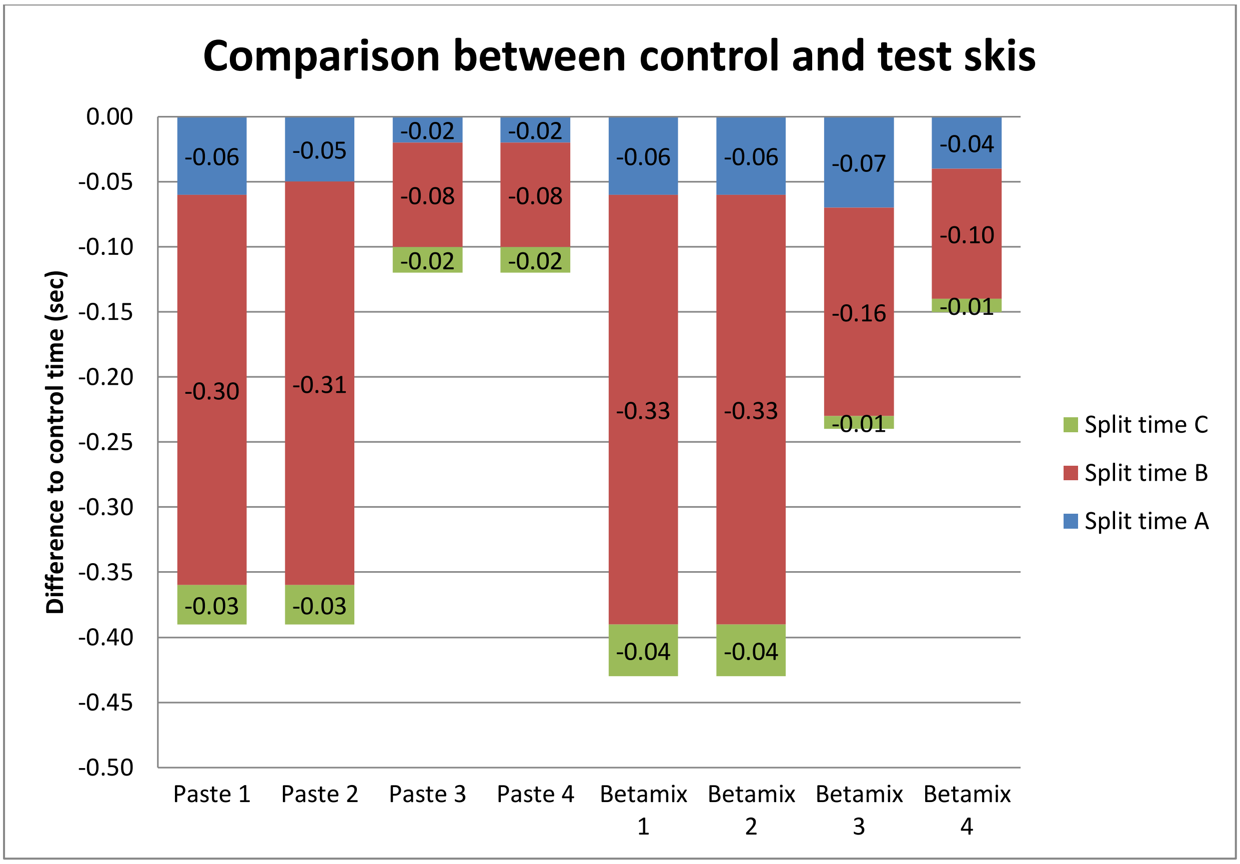


Figure 55: Graph showing differences in times between paste wax, *Holmenkol* Betamix Red and the control skier.

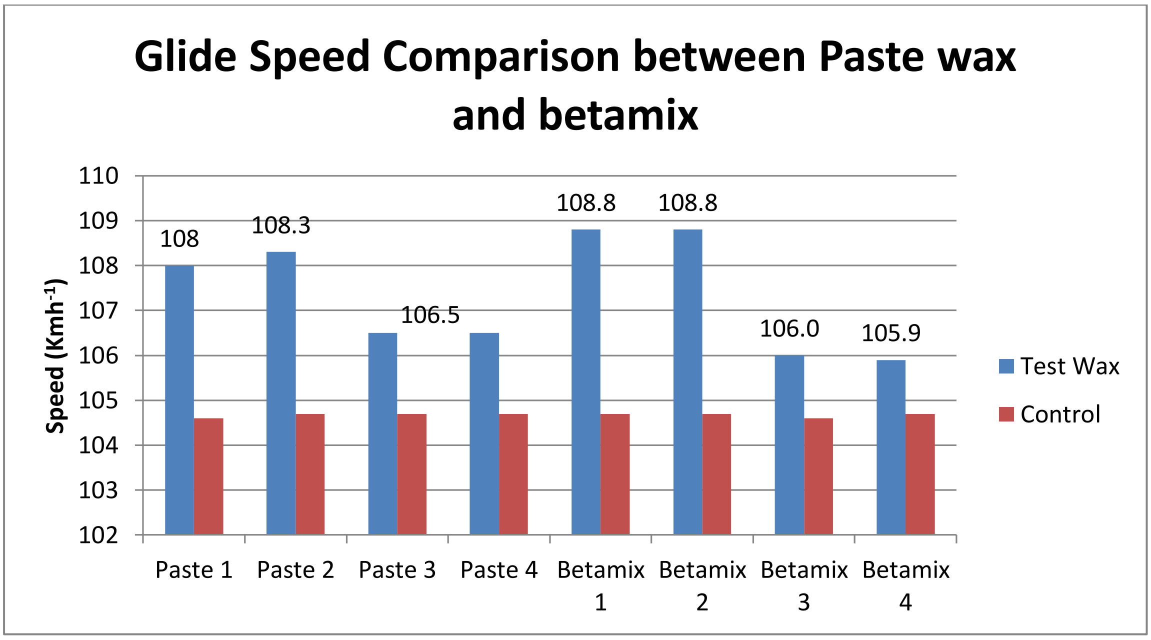


Figure 56: Calculated glide speeds of the paste wax and Betamix

When comparing the control times and the test treatments of all four runs it would appear that *Holenkol* betamix test skier experienced a positive effect when compared to the control skier also using *Holenkol* betamix in these particular test conditions. The paste wax also had a positive effect when compared with the control skier however, but this was probably not as large as with the *Holenkol* betamix treatment. The snow and air temperature was -11.5± 0.5°C, the air temperature was -1-0°C with a humidity of 20% which could have reduced the effectiveness of a highly hydrophobic treatment by reducing of wetted contact area. The starting condition for this glide test was perceived to be I leading to II therefore the water film would initially be too thin to be of ideal thickness. The smoothness of the base certainly had the potential to be beneficial in these conditions however; the wax may also have been advantageous in also reducing the surface roughness. The glide times recorded for the paste wax were certainly very close to that of the *Holenkol* betamix treatment compared to the control skier. During runs 1 and 2 the *Holenkol* betamix seemed to have a slight advantage over the paste wax compared to the control. However, if average times are compared then runs 3 and 4 are very close, additionally, if average glide speeds are compared over 4 runs (107.3 Kmh^{-1} for the paste wax and 107.4 Kmh^{-1} for the *Holenkol* betamix), then only 0.1 Kmh^{-1} separates the two treatments. The small number of glide tests performed prevents a confident inference from being drawn from a comparison of the average times between each test run or from a comparison of the test to the control runs. However, further glide testing investigations in a greater range of conditions with a more test runs would need to be undertaken to provide further evidence. Additionally, treating a ski with the paste wax method to structure the underlying surface then applying a traditionally hydrocarbon wax treatment would also be of interest; this method was previously investigated by Coupe and Spells (2008).

Evidently, it is of interest to raise the hydrophobicity of a ski base whether by physical structuring and chemical treatments or by the traditional hot waxing methods. There is evidence presented in section 4.3.3 to suggest that during alpine skiing there is significant frictional heat generated between ski base and snow which is sufficient enough to thicken an existing water film. This section has demonstrated that the affinity of a ski base to wetting by water can be changed by physical and chemical structuring methods. Selecting the appropriate resulting roughness for a range of environment conditions could not be practically achieved within the scope of the thesis. However, there is a clear link demonstrated in the static friction results that improved surface hydrophobicity reduces the coefficient of static friction. Dynamically, at high speeds, the chemical and physical paste method certainly comes close to matching traditional hot waxing methods. The size of the silica particles, contained in the paste wax, may be an important factor in determining the resulting surface roughness. Controlling the particle size would be beneficial in fine-tuning the microscopic surface roughness to the appropriate conditions and at an appropriate scale to that of the water film. The next section will explore whether the bulk material can be modified to increase hydrophobicity using a variety of different methods described in section 5.3.1. The same silica particles and PFPE used in this section are incorporated into the bulk ski base material to modify it rather than apply it as a surface treatment. UHMW-PE is also blended with PDMS which was identified in section 5.4.1 to have beneficial friction and water repellent properties.

6.3. Bulk modification of UHMW-PE

This is perhaps the ultimate goal; namely to obtain a sliding surface or base material which does not require post-treatments. Although, the achievement of such a goal may present a significant challenge because of varying sliding conditions and the profile of water film generation. The abrasive nature of snow and ice in general also requires a suitably hard wearing material to minimise this abrasion whilst sliding. As previously suggested, the current industry standard base material (UHMW-PE) combined with other polymers additive may prove beneficial in certain environmental conditions. Testing such blends in a full range of environmental conditions is a major challenge may be impractical, because of the very large number of real snow tests which would be required.

This section explores blending UHMW-PE with polydimethylsiloxane (PDMS), section 6.3.1; hydrophobic fumed silica, section 6.3.2 and perfluoropolyether (PFPE), section 6.3.3. The objective of which was to determine the feasibility of a polymer blending process using UHMW-PE as the bulk material to improve the sliding friction of ski bases. This investigation also includes the contact angle testing and the scanning electron microscopy methods used in the previous section, 6.2.1. Friction was measured using an inclined plane method and glide testing. Additionally, some of these materials were tested as additives to wax, (section 6.1) and surface treatments (section 6.2). They have demonstrated an increase in hydrophobicity and lower coefficients of friction. However, incorporating these polymers and fillers into UHMW-PE presents its own challenges due to the high melt viscosity of UHMW-PE. As previously described in section 4.1, UHMW-PE needs to be processed by either a compression moulding, ram extrusion or sintering process. Although some of the publicised advantages of polymer blending are that the melt viscosity can be lowered and that improved mould release can be achieved with PDMS masterbatch. An investigation of the feasibility of a screw extrusion method using UHMW-PE and PDMS masterbatch was undertaken.

6.3.1. Polydimethylsiloxane (PDMS).

A screw extrusion method was trialled using facilities at Bradford University with added polydimethylsiloxane (PDMS) and polyethylene masterbatch. The addition of the PDMS masterbatch combined with lower molecular weight polyethylene was intended to lower the melt viscosity of the UHMW-PE so it could be utilised in a screw extrusion process. The addition of PDMS to the polymer blend may also be beneficial in reducing the coefficient of friction and increasing the hydrophobicity of the resulting samples, as previously suggested in section 4.4.

The masterbatch combined with the UHMW-PE was extruded then compression moulded into flat sheets. However, sizeable grain boundaries were evident in the sheets clearly indicating that the masterbatch was not adequately dispersed in the UHMW-PE. Some sheets were chipped up into small pieces and then compression moulded a second time which reduced the size of the boundaries, although they were still evident. All of the resulting samples which were brittle with poor mechanical properties and therefore additional testing were not undertaken at this stage until a more suitable processing method could be devised. Heated blending, ram extrusion or a sintering process could be used to combine the masterbatch and polyethylene together more adequately. However, a larger scale process to that used in this thesis would have to be adopted. Both the moulds created (1 and 2), would not cope with the pellet form of the masterbatches, therefore, this line of investigation was abandoned. Combining PDMS with UHMW-PE may result in a polymer blend suitable for the application of a ski base but this would require another means of processing as suggested in the future directions, Chapter [8].

6.3.2. Particle Fillers (Hydrophobic Fumed Silica)

Results in this section are derived from methods described in section 5.2.1. Previous experiments involved mixing the hydrophobic fumed silica into a wax matrix as described in section 6.1. All of the samples produced with *Aerosil* exhibited a clustering effect of the *Aerosil* particles as evidenced in Figure 57. The particles were well dispersed before processing. However, following processing, the entire sample range exhibited *Aerosil* clusters surrounded by UHMW-PE. The inorganic nanoparticles exhibit very high surface energies because of their high surface area to volume ratios. During processing, when the mixture is a viscose liquid, the particles may cluster together to lower the interfacial energy in an attempt to decrease the overall energy of the system. This agglomeration is also evident in the dispersion of VPR411 in wax detailed in section 5.2.1. Without a suitable surface surfactant compatible with the processing conditions of UHMW-PE, the satisfactory dispersion of the silica in a UHMW-PE was not possible. Further investigations were therefore required in order to explore the possible addition of nanoparticles to a traditional ski base material.

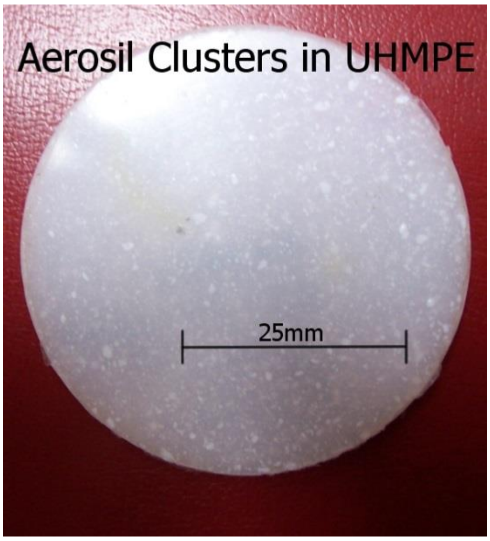


Figure 57: Image of a UHMW-PE sample with added nanoparticles which shows the subsequent clustering effect.

This mould (1) did, however, function effectively in creating samples of 5mm ±1mm in thickness and 50mm diameter although some resulting loss did occur as the mould was not adequately sealed. It was anticipated that this may be the case, however, the high melt viscosity of the UHMW-PE restricted flow to a minimum. Figure 58 shows a picture of the 16g UHMW-PE sample processed for 20 minutes at 200°C and 2758 KPa pressure with a 5°C/min cooling cycle. The unwanted melt flow is evident with a resulting loss of 0.8g on average.

Figure 58: Image of a UHMW-PE sample produced with mould 1

The initial bottom metal plate had a circle machined into it and after a few samples were trialled it was quickly evident that the mould would not release without a significant force which sometimes caused damage to the surface. The highly polished surface resisted the majority of adhesion to UHMW-PE. A mould release agent could also have been utilised although this may have introduced unwanted surface contamination of the resulting samples.

This design of mould was subsequently used to investigate the optimal processing conditions for producing samples which best compared to those achieved in a full scale sintering process. During the course of the life time of the mould, a range of UHMW-PE experimental samples at varying pressures, temperatures and cooling times were created as well as the polymer and nanoparticle trials. Over this period the mould became increasingly harder to release due to fouling and was therefore subsequently retired. This is illustrated in Figure 59 showing the fouling which subsequently carbonised to the metal under prolonged heating.

In summary, the design of mould 1 prevented the sample from being easily released and some loss of material was evident during processing at higher pressures. Another unknown inherent this design was the actual temperature inside the mould; rather than the temperatures recorded from the top and bottom heated plateau thermocouples from the press. It was concluded that a redesign was required for subsequent polymer blending as described in the following section 6.3.3.

Figure 59: Image of the stainless steel Mould 1 after extended use.

6.3.3. Perfluoropolyether (PFPE)

Perfluoropolyether (PFPE) was blended with UHMW-PE in the method described in section 5.4.3 using a laboratory compression moulding process. Mould 2 was utilised to create the samples described in this section. Mould 2 was a design improvement over mould 1, which allowed easier release with the tapped holes; utilised changeable plates for varying sample sizes; enabled higher pressures to be exerted without loss of material and facilitated temperature measurement via an inserted thermocouple. The ease of releasing the mould prevented damage to the highly polished surface which resulted in less fouling over the lifetime of the mould. The temperature disparity between the mould and heating press plateaus of the *George E Moore and Son (BHAM) Ltd. Type H008* was investigated, which would not have been possible with the previous mould. The temperature disparity between the inserted type K thermocouple and set temperature of the heat plates is shown in Figure 60.

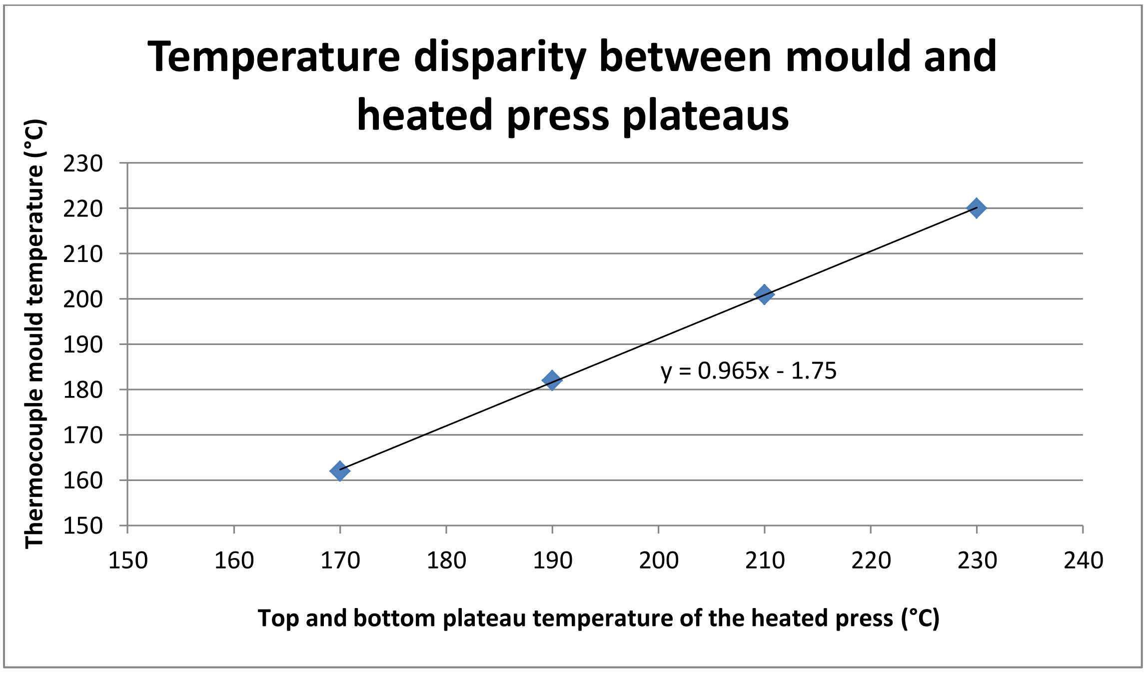


Figure 60: Graph showing the measured temperature disparity between mould 2 and the heated press plateaus.

Although only four data points were recorded over the processing temperature range of UHMW-PE the data points follow a line of linear regression. The resulting equation of the line can be used to predict the temperature disparity between the set temperatures of the plate to that of the actual temperature of the mould. The samples processed at a plate temperature of 210°C actually were only subjected to a temperature of 201°C, which is, nevertheless, still well within the processing temperature range of UHMW-PE (170-230°C).

The samples which were created with solid A10-P and liquid 2024X were very different in visual appearance. The A10-P, dissolved in an isopropyl alcohol/hexane solution did not exhibit a uniform dispersion after processing. The visible appearance of the sample, using A10-P as an additive, had white coloured solid regions contained within them. Although good dispersion of the A10-P pre-processing was achieved, the resultant clustering post-processing may lead to the loss of beneficial mechanical properties. The liquid 2024X, in contrast, produced samples of good visible appearance with no liquid regions present on the surface or within the polymer matrix.

The contact angle and coefficient of friction of both A10-P and 2024X were assessed using the method described in sections 5.2.2 and 5.3.3. The average contact angle of 2024x by percentage weight is shown in Figure 61 and A10-P in Figure 62.

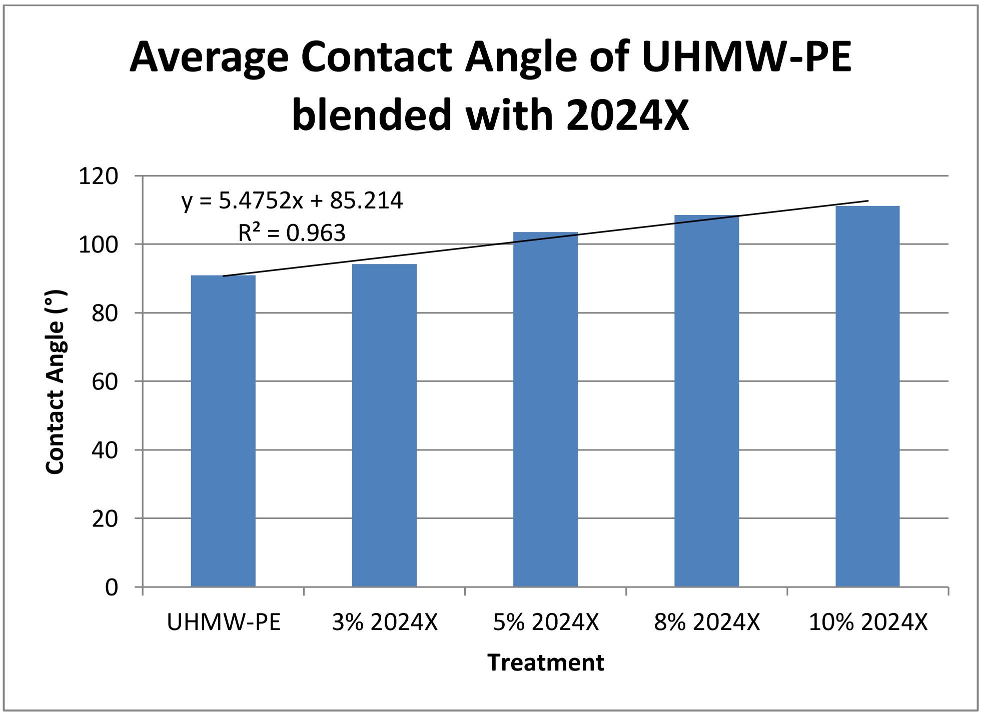


Figure 61: Graph showing the average contact angle measured on blends of UHMW-PE and 2024X

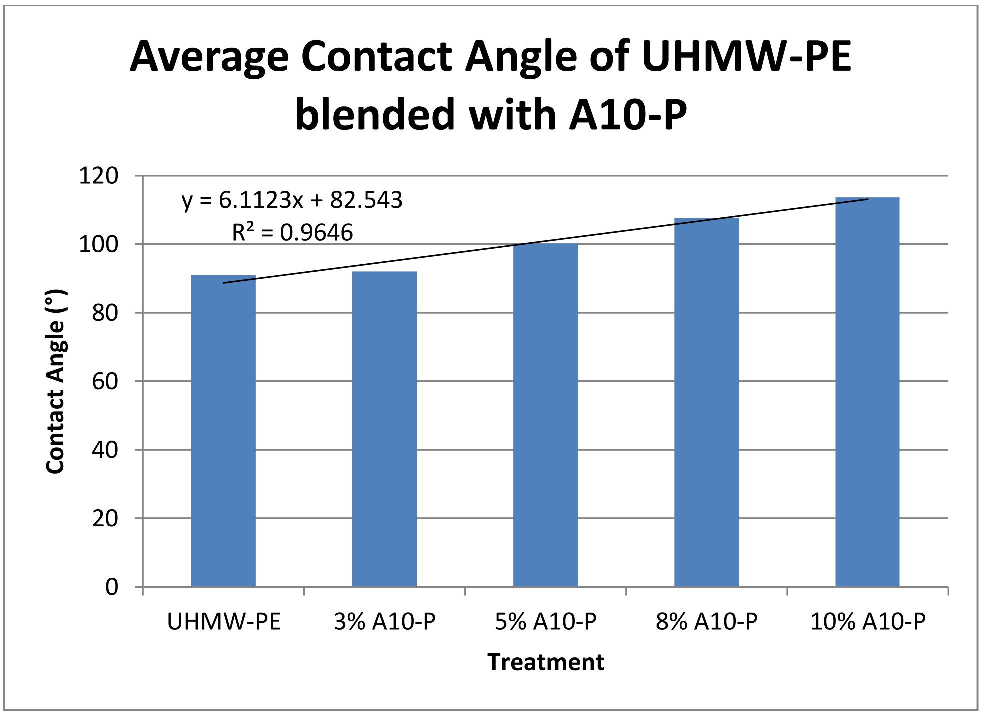


Figure 62: Graph showing the average contact angle measured on blends of UHMW-PE and A10-P

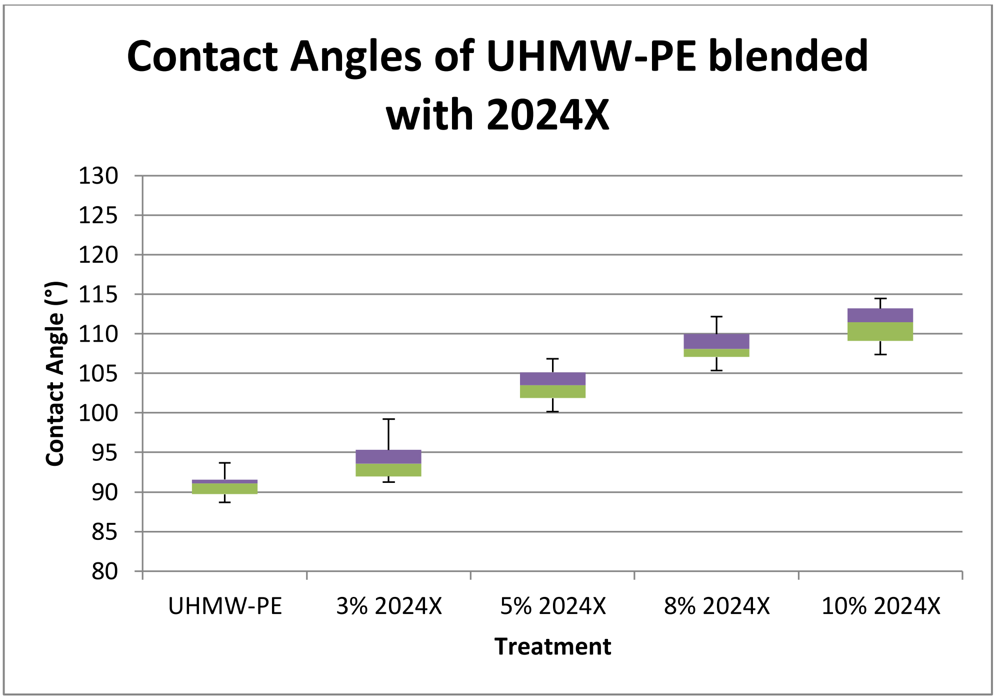


Figure 63: Box and whisker plot of contact angles measured on UHMW-PE blended with 2024X

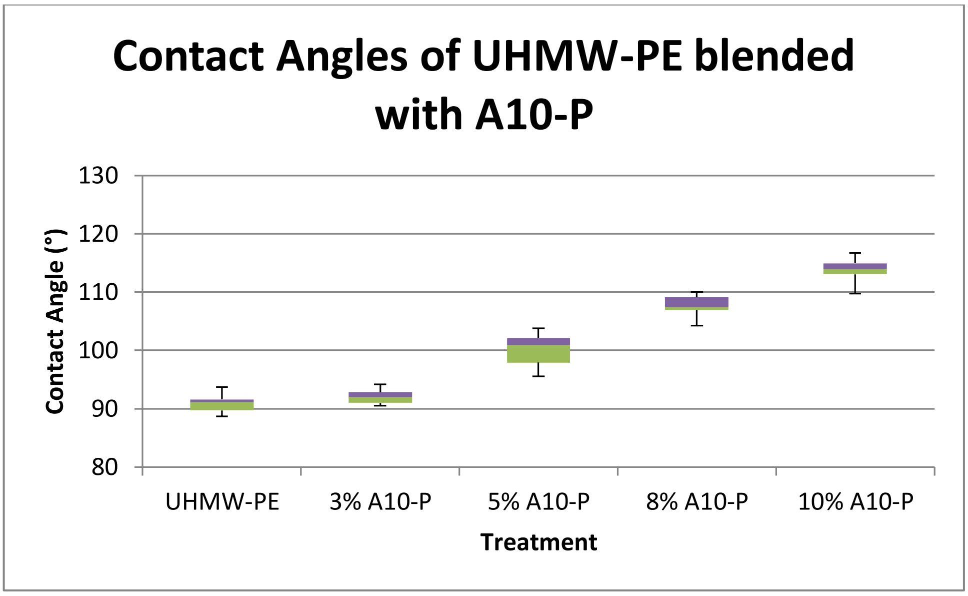


Figure 64: Box and whisker plot of contact angles measured on UHMW-PE blended with A10-P

The average contact angle results show a clear increase with greater proportions of 2024X and A10-P blended with UHMW-PE. Both additives at 10% levels showed significant improvement in contact angle which is representative of hydrophobicity; 18% for 2024x and 20% for A10-P. The 10% loading of 2024x has the largest interquartile range out of all of the treatments. However, the spread of this data shows that this is significant increase with only a small range of less than 6.7°. Also the 25th percentile of each of the 3%, 5% and 8% treatments is significantly greater than the interquartile range of the subsequent treatments for the majority of samples. Only the 3% A10-P did not demonstrate a significant difference in hydrophobicity compared with untreated UHMW-PE.

Further contact angle tests with a greater number of results may seek to provide a greater accuracy and reduce statistical error, although these initial results do indicate a positive effect on hydrophobicity with added percentage weight of 2024X and A-10P blended with UHMW-PE. Whilst contact angle results provide important information when deciding the ideal percentage of additive to be used, mechanical properties of the samples must also be considered.

The compression moulded samples were of a suitable quality to adhere to metal test blocks and the influence of the blended additive on the coefficient of friction was assessed using an inclined plane method as described in section 5.3.3. The sliding surfaces used were *Proslope ™*, an artificial ski slope material and snow. The results for the *Proslope ™* surface are shown in Figure 65 for the 2024x and Figure 66 for the A10-P additives.

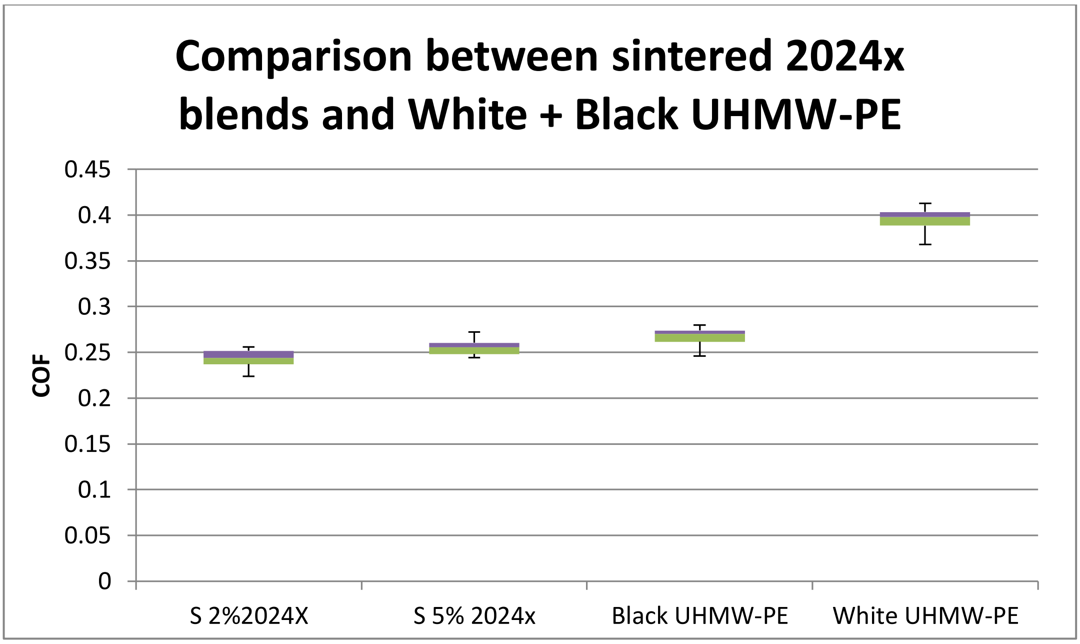


Figure 65: Coefficient of static friction of blends of UHMW-PE and 2024X on Proslope testing surface

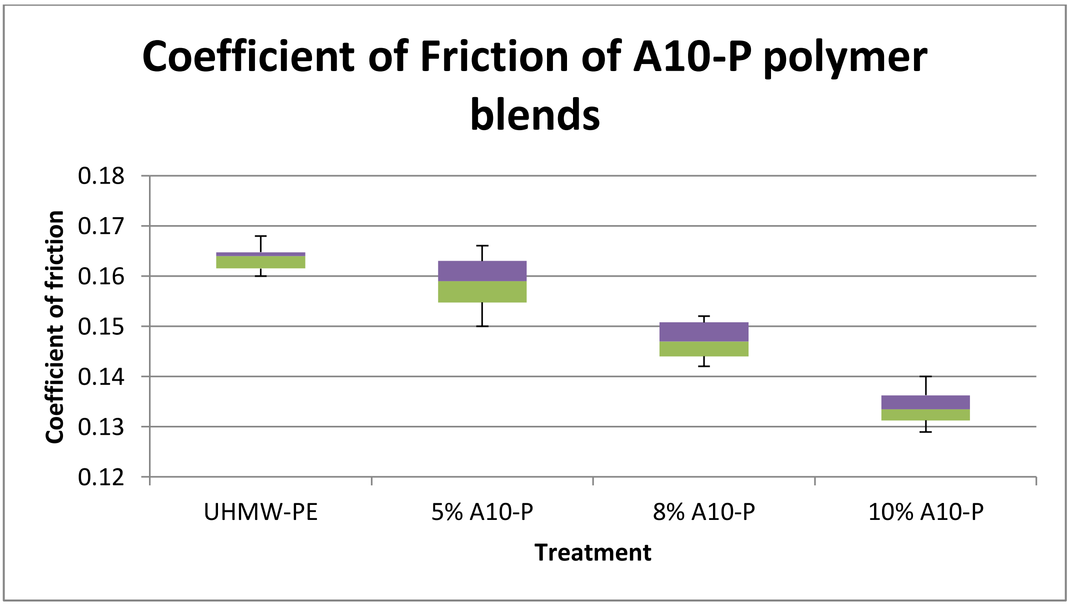


Figure 66: Coefficient of static friction of blends of UHMW-PE and A10-P on Proslope testing surface

Utilising an artificial ski slope material with fibres allowed for a basic measurement of the static coefficient of friction on an artificial skiing surface. The addition of 2024X to UHMW-PE showed a significant reduction of friction with added percentage weight. Whilst a slight disparity of the static friction measurement may have occurred on the non-uniform patterned surface this is, however, not apparent in the spread of the data. Further investigation on a uniform surface would reduce this error; however, subsequent testing on packed snow could be said to be the test surface of focus. The sample set was retested using a snow surface prepared using the method described in section 5.3.1. The samples were tested in the environmental conditions listed below which could be described as warm and wet. The air temperature changed by 4°C during the course of the experiment. The environmental conditions were not controllable in this experimental design and therefore out of this investigator's control. Each test base was, however, matched immediately with a control under the same conditions The results are also interesting as they do show the effect of changing temperature on the control sample which may be indicative of an increase in water film thickness with increasing temperature. A control of white UHMW-PE was used which was abraded and nylon brushed. Shown in Figure 67 below are the mean contact angle values of various percentages of additive, compared with the control sample. The spread of this data is shown in a box and whisker plot in Figure 68. Also detailed in Table 12 are the recorded environment conditions.

Table 12: Environmental conditions for inclined plane testing of PFPE additives on natural snow.

Snow Temperature (°C)		Air temperature (°C)		Air humidity (%)	Snow humidity (%)
-1	1.0	0.5	3	93	98

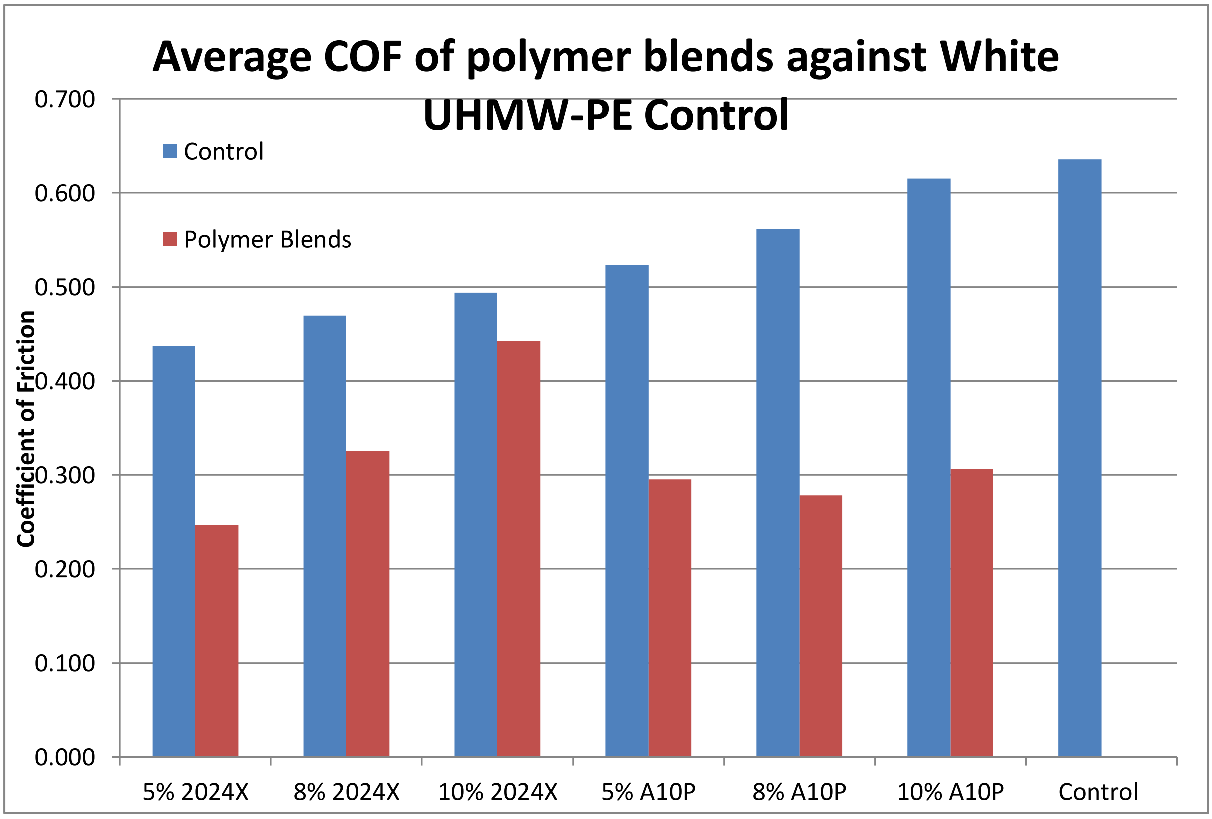


Figure 67: Average coefficient of static friction of polymer blends against white UHMW-PE control sample on a snow testing surface. (Note: Snow temperature changes from left to right from -1 to +1°C.)

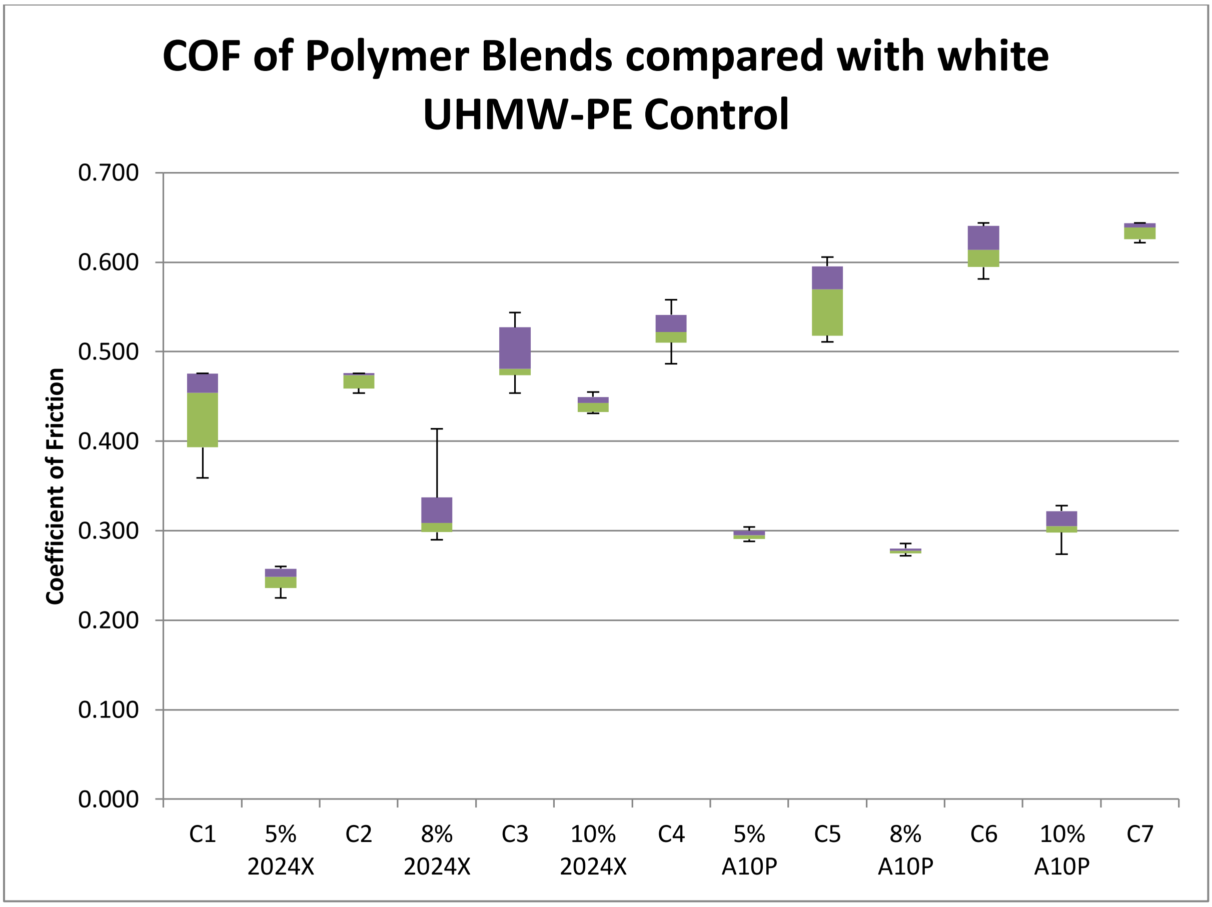


Figure 68: COF of polymer blends with white UHMW-PE control on a snow testing surface

The trend of the control clearly suggests the coefficient of friction between the sliding surface (snow) and the block increased throughout the course of the experiment. This was almost certainly due to the changing snow conditions caused by solar heating and an increase in air temperature during the course of this experiment, which caused melting of the sliding surface and created a thicker water film. The increasing melt water film height would cause an increase in friction as previously discussed in section 4.3.5 and illustrated on the Stribeck curve in Figure 4. All blends however, demonstrated a very promising reduction in friction compared to the control. The specific environmental test conditions may have suited a more hydrophobic surface. The additives are known to be more hydrophobic than standard UHMW-PE and may reduce the wetted contact area and therefore friction.

The greater the percentage weight of the 2024X additive the smaller the difference observed compared to the control block. Interesting, the A10-P demonstrated the opposite trend in which the greater percentage weight added; the more effective it became compared to the control. This sample set could be retested in stable environmental conditions which would be unlikely to demonstrate a trend in increasing friction during the course of the experiment. Previous results from static friction tests conducted on Proslope™ also demonstrated coefficients of static friction reducing with a liner trend and percentage weight added. Testing on both artificial slope materials and snow has the advantage of investigating friction properties on contrasting skiing surfaces. Snow testing is subject to an increased number of variables, as previously described in 4.2, especially at temperatures close to the triple point of water. However, conducting tests in these conditions could be particularly useful in exploring the effectiveness of the additives at reducing friction by increasing hydrophobicity.

Overall, the compression moulding process was effective in producing laboratory scale, bulk modified samples to conduct small scale testing. The static friction of these samples was successfully measured using the inclined plane method. Assessment of static friction across a wide range of environmental conditions is required to observe the effect of friction on snow. However, in the warm snow conditions tested (-1 to 1°C) the more hydrophobic treatments are known to be more effective at reducing friction. Currently wax technology involves the addition of high levels of fluorocarbon containing additives to improve water repellency in their hydrocarbon wax blends. The A10-P sample measured a higher average contact angle (113°) to that of the 2024X (107°) and also demonstrated lower coefficients of friction when compared to the white UHMW-PE control. The UHMW-PE blends could be said to be successful in matching the hydrophobicity of traditional fluorinated wax treatments. The measured contact angle of fluorocarbon containing waxes was conducted in section 6.1. The average measured contact angles of *Swix* Cera Fluoro and Toko HF Dibloc Yellow was 103° and 110°, respectively. The PFPE as a chemical surface treatment (Section 6.2) combined with a physical glass scraping method recorded contact angles of 114° on average. PFPE was also advantageous, in reducing static friction by 22% and 64% for black and white UHMW-PE respectively using glass and silica structuring methods. Glide testing PFPE as a surface treatment showed this treated surface was close to matching the speeds of decent of a traditionally waxed race ski. However, to dynamically test this blend using a glide testing method the material would have to be manufactured in long lengths in order to be adhered onto a 2.2m downhill ski base.

An industrial sintering process, most commonly used for higher molecular weight polyethylene was used and some of the properties of this material are reported in the following section. Assessment using dynamic glide testing would only be possible if the sintering process was compatible with the polymer additive. Fortunately, as a result of the UHMW-PE processing knowledge of *Atomic,* such a sintered sample was created with two different percentages of additives. The coefficient of friction of the resulting blends is assessed below.

6.3.4. Sintered Blends

The additive used was 2024X added 2% and 5% to GUR 4150 white UHMW-PE by percentage weight. These created the samples that were used for testing in this proceeding section. The 2024x additive was chosen due to its liquid viscosity at room temperatures and improved visual appearance post-processing in the compression moulded samples. It was also used in other areas of investigation, throughout this thesis.

To assess the effectiveness of the sintered blend, the sample was tested using a similar approach to the compression moulded blends and other polymer additives in sections 6.1, 6.2 and 6.3. The testing included quantifying the contact angle, coefficient of friction on a snow surface and additionally the observation of physical surface structure by scanning electron microscopy. The blends were also passed to *Atomic GmbH* for alpine glide testing as part of their on-going testing programme.

The physical surface of the UHMW-PE can be compared to the previous results for unmodified UHMW-PE listed in section 6.2.1. The treatments and method of application were identical to that of previous methods and detailed in section 6.2. These included abrasion with 800 grit sandpaper, nylon abrasion, glass scraping and glass scraping with abrasive particles.

All samples were coated with carbon in preparation for SEM analysis using the same method as previously described; however, some samples did not demonstrate an adequate surface coated layer. The samples which had the greatest affinity to carbon coating were those containing the higher percentage of the 2024x additive (5%). Additionally the 2% abraded and silica abraded treated samples were of poorer quality, even though they went through an additional coating cycle. Differences in the physical surface structures may affect the observed values for contact angle and coefficient of friction tests as previously described in section 4.4. However, previous compression moulded sample blends were not examined using SEM. The 2% 2024x sintered SEM images are displayed in Figure 69 for the un-treated blend; Figure 70 for 800-grit abraded; Figure 71 for nylon treated and Figure 72 for glass treated samples. They are compared with previously observed SEM results using identical methods for unmodified UHMW-PE in section 6.2.

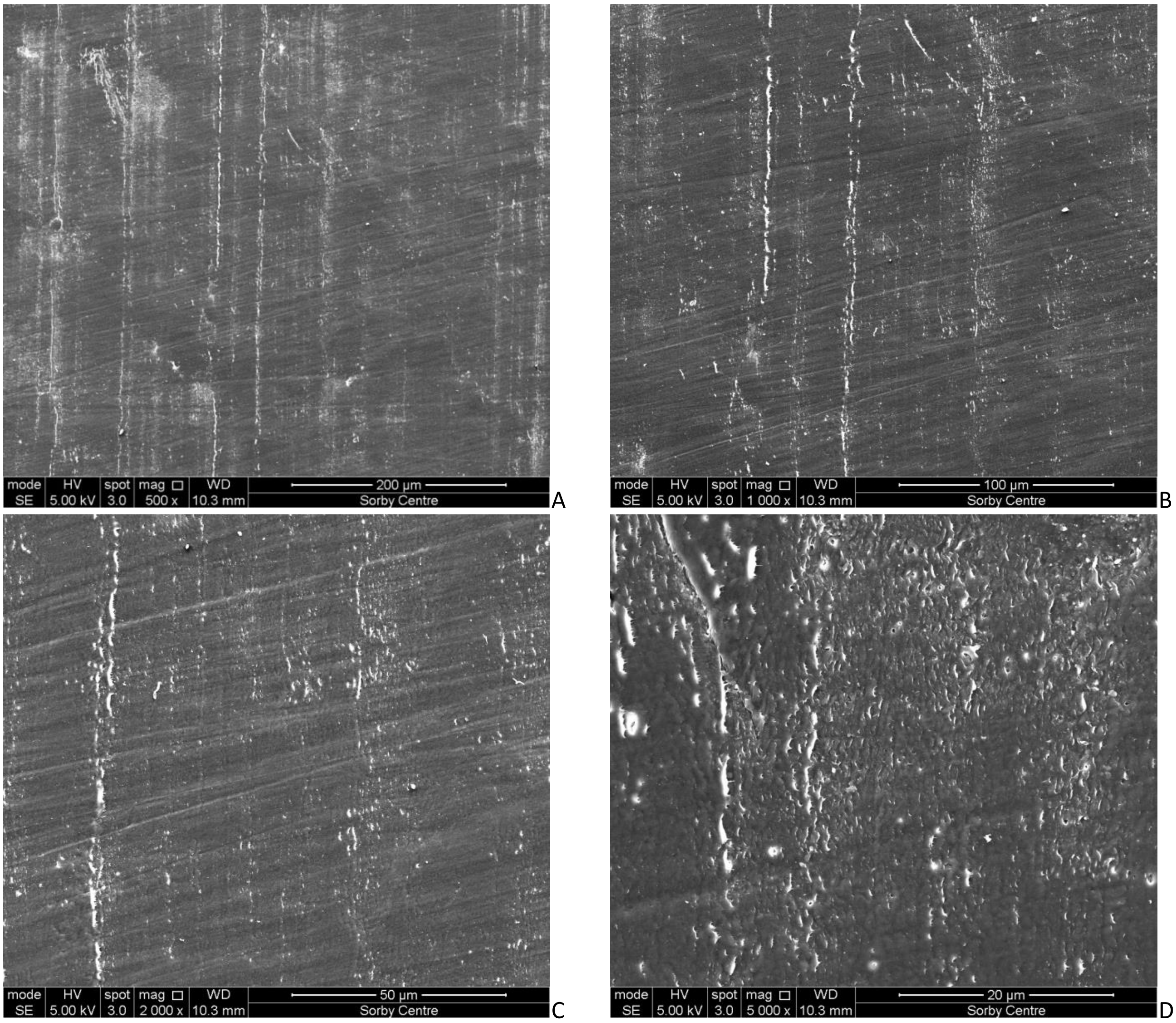


Figure 69: SEM images of an un-treated 2% PFPE, UHMW-PE base at various magnifications.

A- 200x magnification, B- 1000x magnification, C- 2000x magnification, D- 5000x magnification.

The un-treated base can be compared with unmodified black and white UHMW-PE in Figure 40 and Figure 41. The surface exhibits cutting marks probably due to the sintering skiving process used to plane a sheet off the block of material. The surface does not exhibit defined grain boundaries like the black untreated UHMW-PE. Additionally it is smoother in texture than the unmodified white. The next surface tested was abraded with 800 grit sandpaper as shown in Figure 70 below.

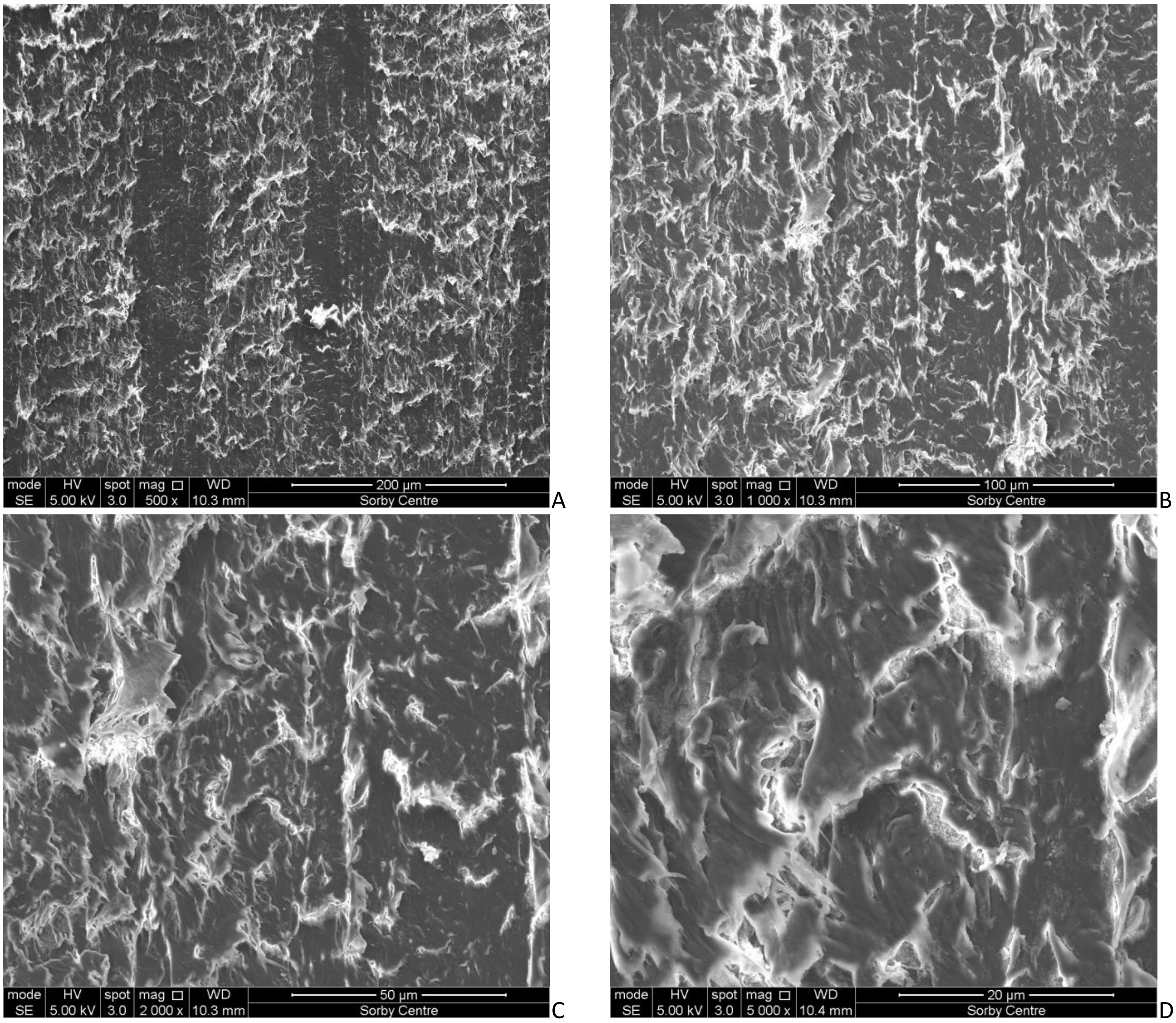


Figure 70: SEM imaged of an abraded 2% PFPE, UHMW-PE base at various magnifications

A- 500x magnification, B- 1000x magnification, C- 2000x magnification, D- 5000x magnification.

The abraded sample has a noticeable reduction of resolution due to the difficulties experienced in the carbon coating process. The features formed from abrasion, when compared with Figure 43 for unmodified black UHMW-PE, show a reduction in size and frequency. Some regions of modified UHMW-PE show no surface features. However, this could be due to slight irregularities in the surface level or alternatively unequal pressure during application. The surface was then treated with an abrasive nylon pad and the SEM images are shown in Figure 71 below.

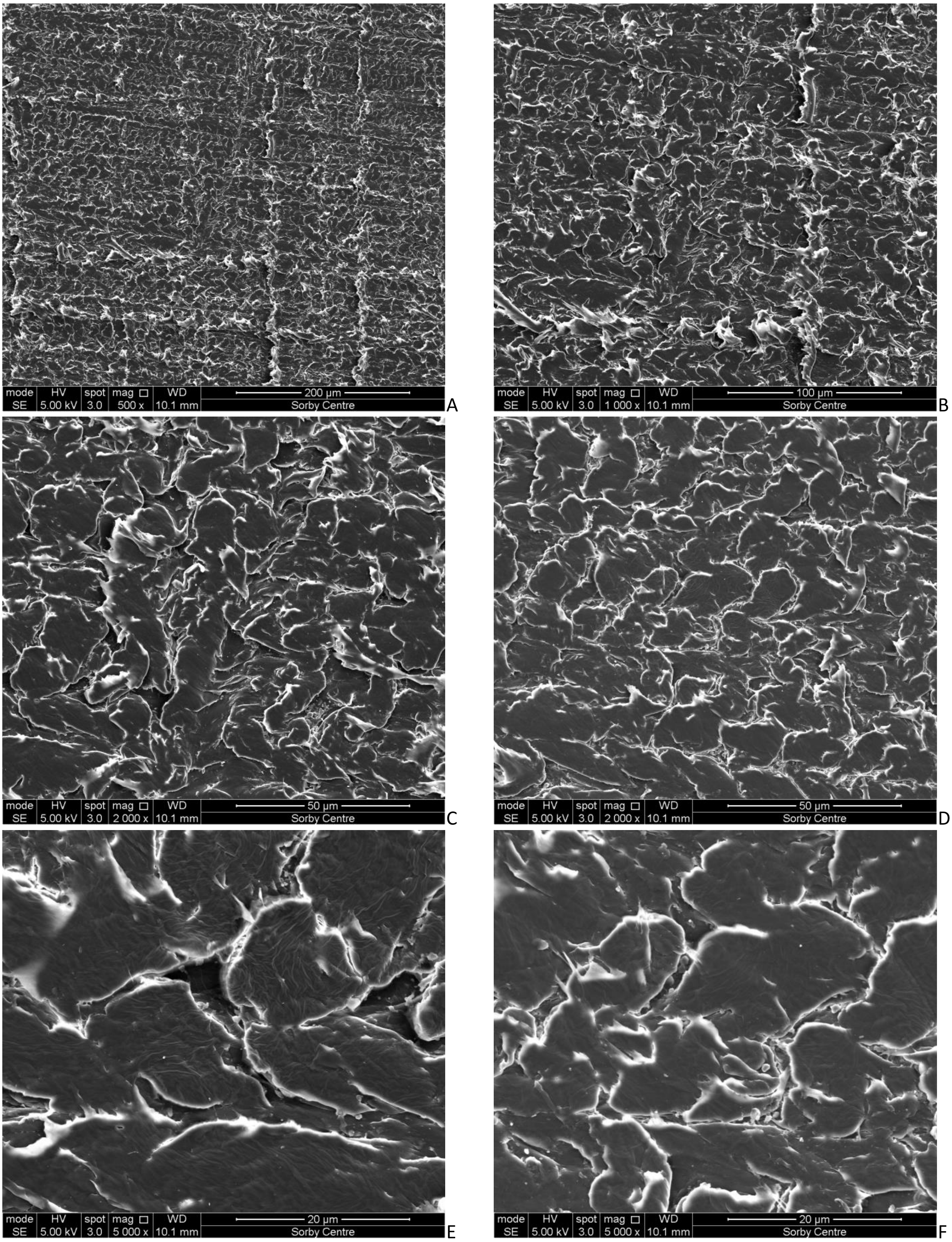
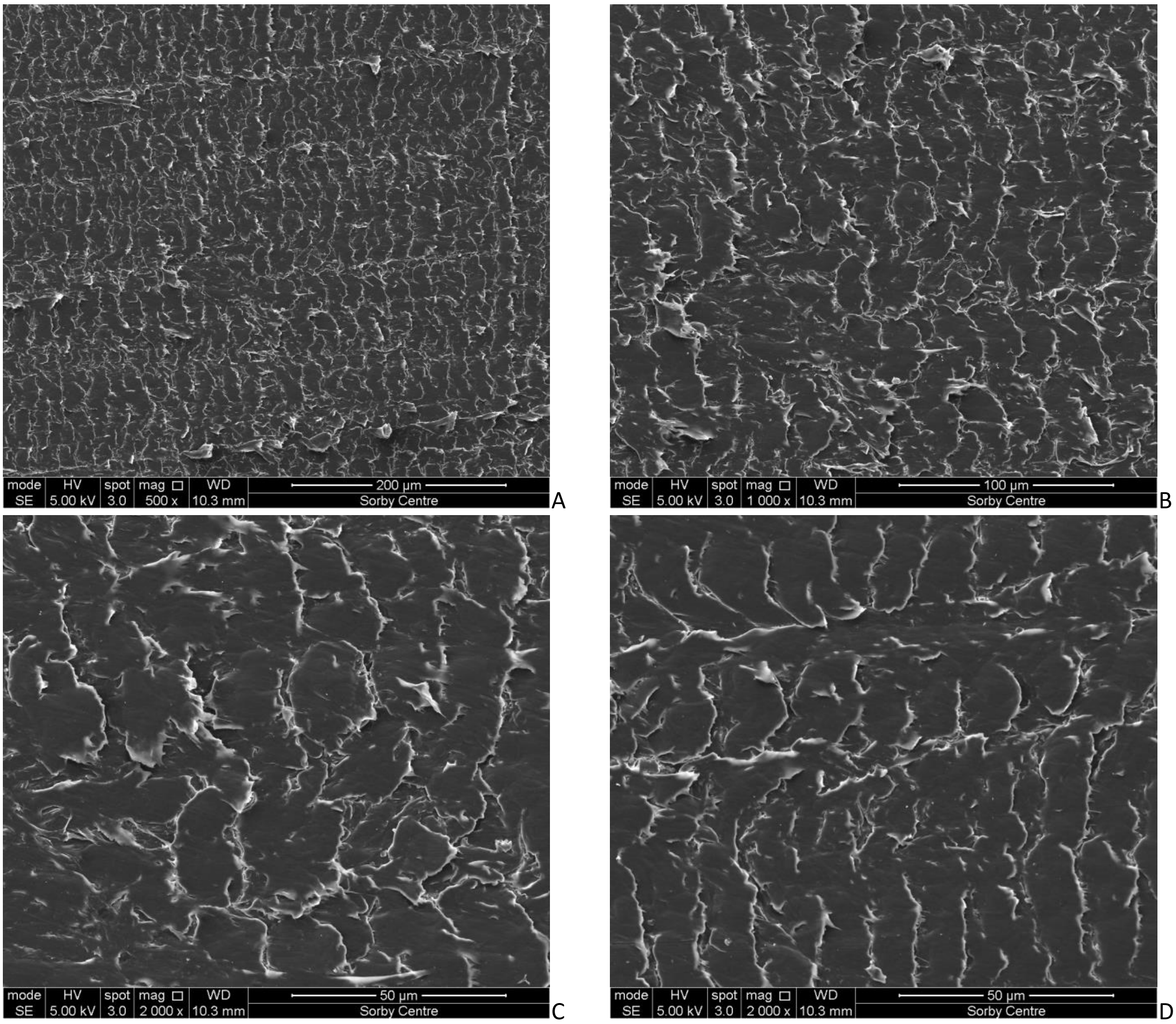


Figure 71: SEM images of a nylon abraded 2% PFPE, UHMW-PE base at various magnifications

A- 500x magnification, B- 1000x magnification, C- 2000x magnification, D- 2000x magnification, E-5000x magnification. F- 5000x magnification.

The 2% 2024X modified nylon treated sample, when compared to unmodified black UHMW-PE shown in Figure 44, demonstrates more grain boundaries which are flusher to the surface. There are some visible ridges evident on the sample from the manufacturing process especially at the lower magnifications. These ridges are reduced in the glass sample, shown in Figure 72 below; however, the glass scraped sample does demonstrate a reduction in size and frequency of surface features. The unmodified glass scraped surface is shown in Figure 46. When compared; an increased number of grain boundaries are evident in the bulk modified sample.



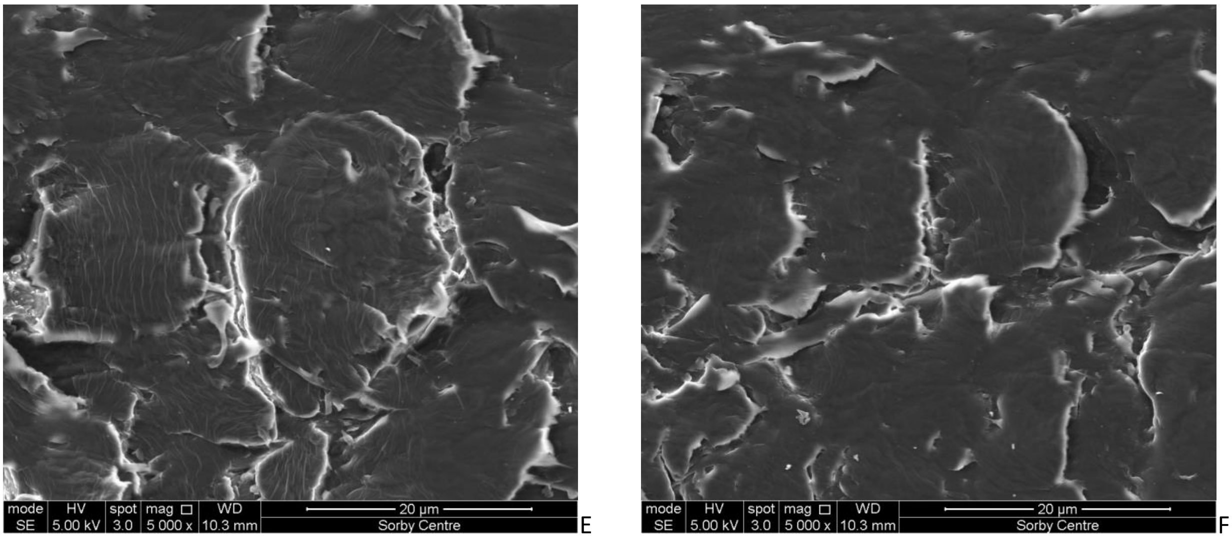


Figure 72: SEM images of a glass abraded 2% PFPE, UHMW-PE base at various magnifications

A- 500x magnification, B- 1000x magnification, C- 2000x magnification, D- 2000x magnification, E-5000x magnification. F- 5000x magnification.

This may be due to the poor coating of carbon on the surface. All the samples were carbon coated according the method described in 5.3.2 and used in 6.2.1. The carbon is bonded to the surface by burning a graphite filament in a vacuum. The atomised carbon is then electrostatically attracted to the surface of the sample in a thin layer (50nm). The decreased amount of carbon on the surface reduced the amount of back-scattered and secondary electrons being reflected and as a result, the picture quality is reduced. The samples with a larger percentage weight of 2024x additive (5%) did not coat sufficiently in the carbonisation process in order to achieve an SEM image. Only the abraded surface was effectively coated, probably due to the increased number of surface features. The additive 2024X is known to be hydrophobic but also exhibits dirt repellent properties due to its fluorinated groups. An attempt was made to carbon coat the 5% samples a second time, although the same effect was present. The repellence of electrostatic bonding of carbon to the surface is an interesting feature of the 5% additive samples. As previously discussed, dirt and other surface contaminates can lead to a significant increase in friction. Despite the problem of examining the surface of the 5% samples using SEM, if such a ski base does exhibit repellence to carbonisation, it may prove to be beneficial in reducing friction by resisting dirt adhesion.

The hydrophobicity of the samples were measured by the contact angle method as described previously in section 5.2.2 which was identical to that of the tests conducted for the surface modification and polymer blending sections. The contact angles of the 2% and 5% blends are shown in Figure 73 below and are compared with the white and black UHMW-PE previous tested in Figure 49 and Figure 50.

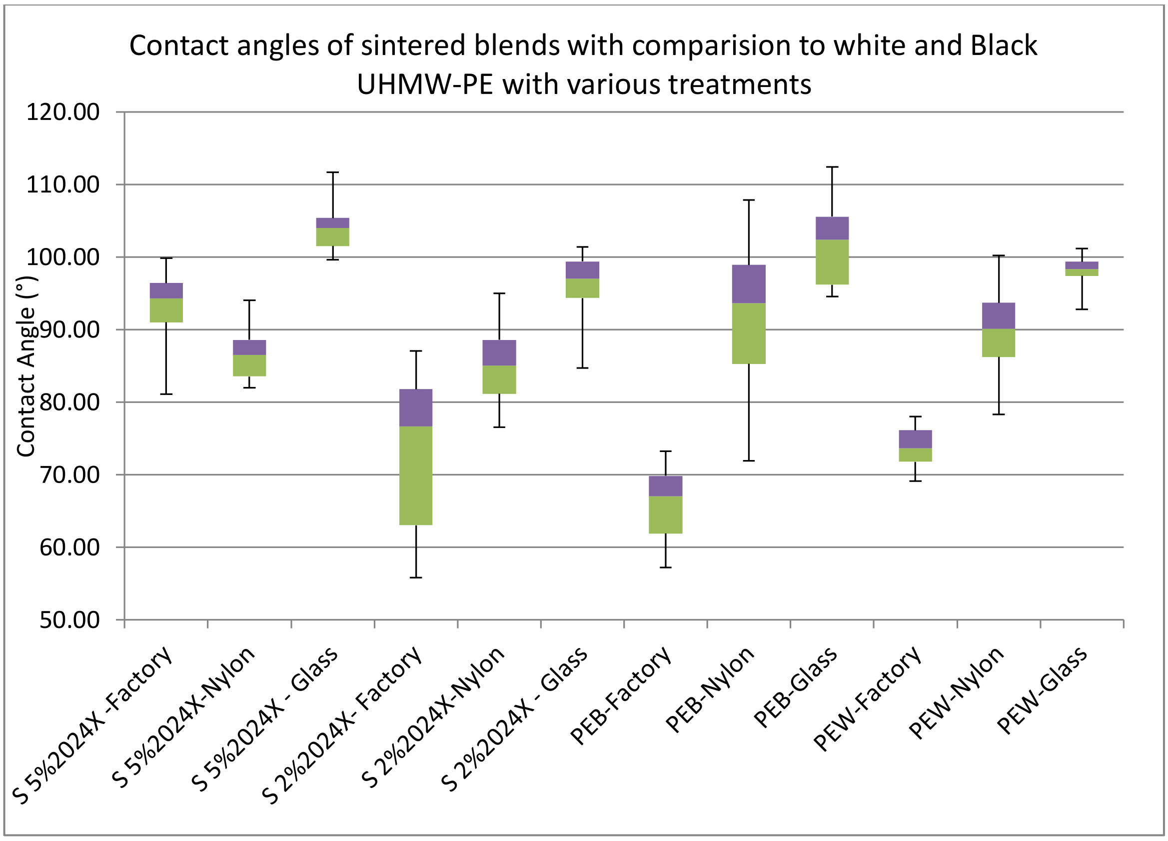


Figure 73: Contact angles of sintered 2024x blends with unmodified black and white UHMW-PE

On initial inspection, the majority of the results show an increase in contact angle when nylon abraded, then again, when glass scraped, with the exception of the 5% 2024X nylon treated surface. Comparison has been made to both black and white UHMW-PE in Figure 73. However, comparison to white UHMW-PE should be undertaken to investigate if there is a difference in hydrophobicity upon the addition of a percentage weight of 2024x additive, without the inclusion of a third additive. In the previous Figure 73 it is not easy to visualise whether there is a significant difference in contact angle between blends. The 25th, 50th and 75th percentiles with maximum and minimum calculated values for the difference in recorded contact angles of the 5% 2024x blend and PEW are compared in Figure 74 for improved clarity. Positive values denote an increase in hydrophobicity between treatments.

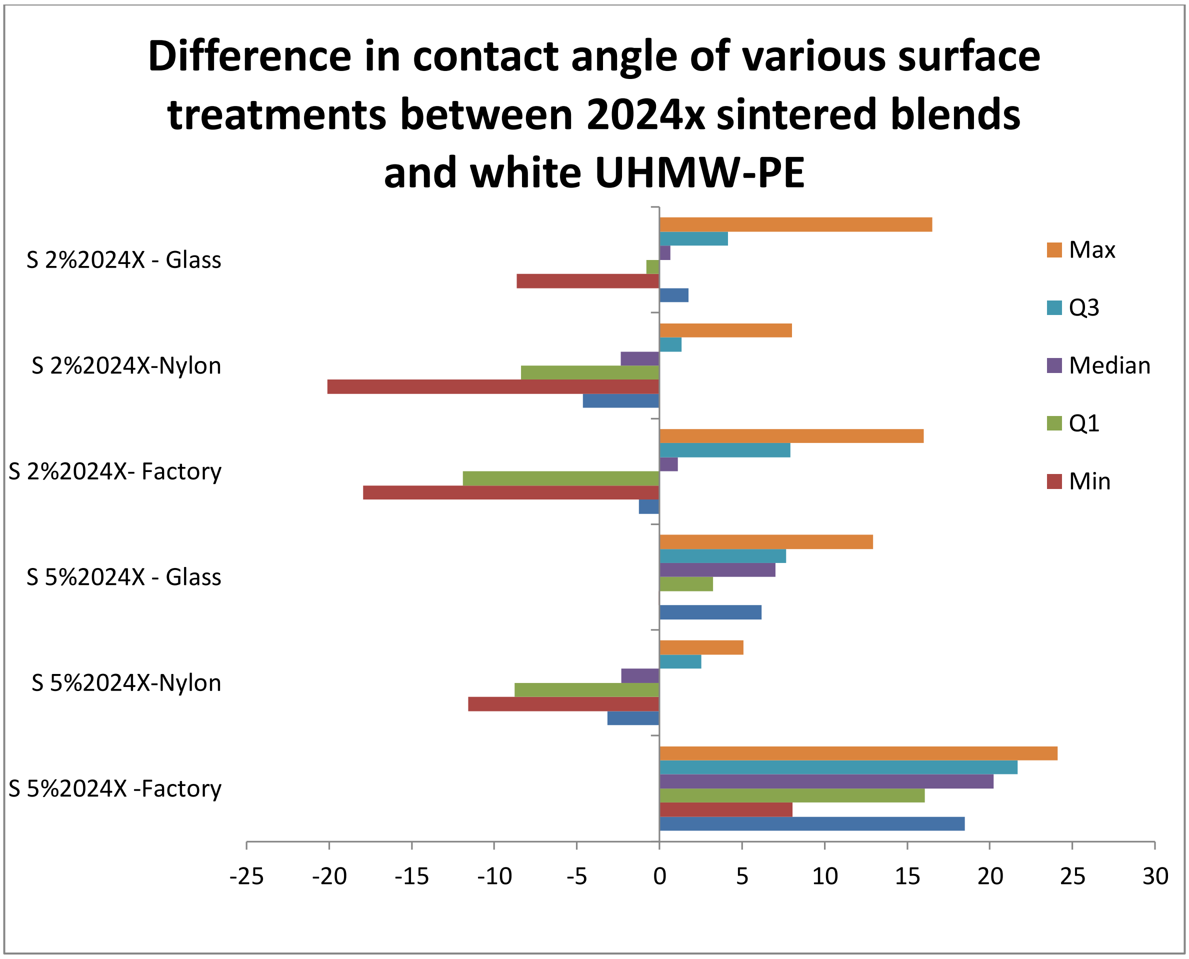


Figure 74: Differences in contact angle between untreated (factory), nylon and glass abraded surfaces

It would seem there is a higher contact angle with the addition of 2024X to white UHMW-PE. Each of the 25th percentiles of the two blends, are positive values. Although, due to the physical irregularities of the surface, as demonstrated in the SEM results, especially with the nylon treatment, some results of the data set show a slight reduction in contact angle and an sizable spread between the 25th and 75th percentiles between some of the samples, although all of these were positive. It could be concluded overall that the addition of 2024X additives does improve the hydrophobicity of the surface with all of the physical treatment methods. However, as previously demonstrated in section 6.2 the UHMW-PE with added carbon black demonstrated a reduced contact angle but lowered coefficient of static friction. Shown in Figure 75 below is the comparison of the coefficient of friction between 2% and 5% blends compared to white and black unblended UHMW-PE

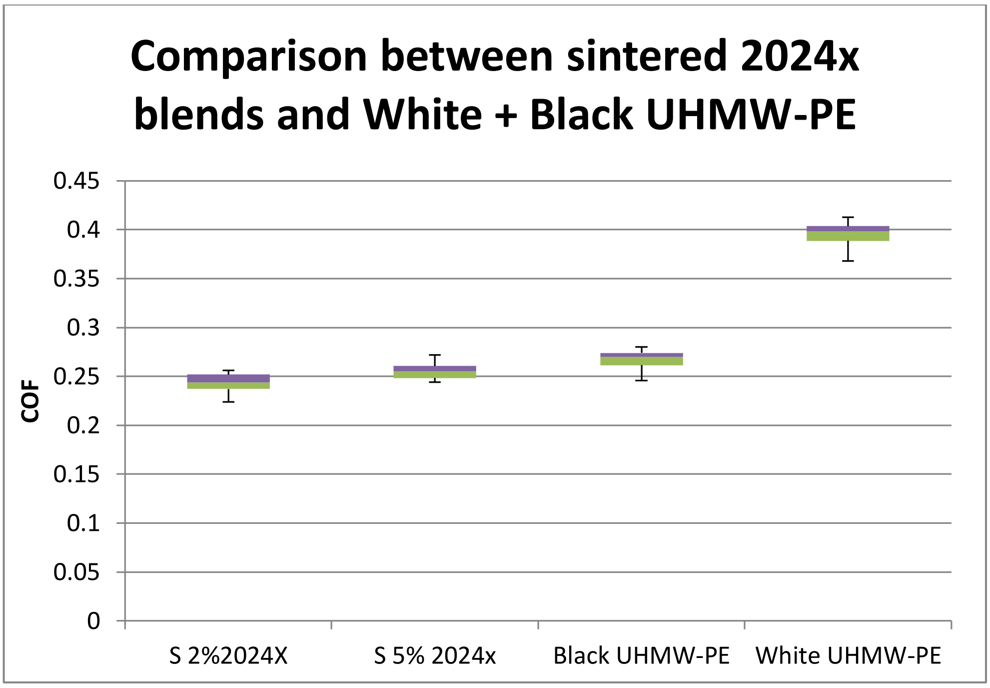


Figure 75: Comparison between sintered 2024x blends and white and black UHMW-PE

The white 2024x sintered blends show a significant reduction in the coefficient of friction compared to white UHMW-PE, shown in Figure 75 above. When compared to the black UHMW-PE this reduction is less significant. However, the sintered 2024x blends could also be modified with carbon black for a more equivalent comparison. Nevertheless, as previously suggested, the blends should be compared with the white UHMW-PE control as it is the blend's counterpart.

Overall, the significant reduction in the coefficient of friction of the white blends suggests that the hydrophobic nature of the 2024X additive is beneficial in reducing friction in warmer snow temperatures. The hydrophobicity was assessed using a contact angle methodology which showed an increase of more than 5° for all treatments (Glass, Nylon abrasive and untreated). The treatment methods were compared visually using an SEM and also contrasted with previous blends. Some differences are evident between the UHMW-PE and 2% PFPE modified samples however, no firm conclusions can be made. The 5% samples exhibited a resistance to multiple attempts to carbon coat the surface. The amount of 2024x additive added to the UHMW-PE would seem to be beneficial at lower (2%) levels. This blend had a lower COF when nylon abraded although it exhibited a smaller difference in contact angle than the 5% blend using all physical treatments. The resistance of the 5% physically treated blends to the carbon coating is very interesting and may suggest that the blend is more resistant to the attraction of dirt by electrostatic charging. This could be an additional benefit for such a ski base material in certain sliding conditions. The glass treated method produces contact angles of above 100° which is comparable to hydrocarbon waxes; this is evidenced in section 6.1.1.

Although the sintered blends were not friction tested using the full range of physical treatments, the nylon abraded samples show a promising reduction of static friction. This is, after all, the classic method of base preparation before hot waxing with the addition of a stone ground structure. An assessment of dynamic friction was undertaken to evaluate the effectiveness of the material blends in a hydrodynamic regime. This assessment included a wider range of temperatures than previously undertaken in sections 6.1 and 6.2

The Atomic 2013 Prototype base DH skis with 2% (PA-2) and 5% (PA-5) 2024x additive were tested against an identical control ski with a black modified base. Six series or sets of 4 runs were recorded and averaged. The same glide track was used as, described in previous glide testing experiments in this thesis, located in Sölden Austria. The glide times are ranked in Figure 77, below, which shows that the control skier was ranked first in 4 out of the 6 sets. However, PA-5 was more effective than the PA-2 and ranked first twice. The test was conducted in the following conditions over 6 series of runs and are shown in Figure 76 below. The majority of the test series (4/6) were conducted in -12°C to -7°C snow and -12°C to -1°C air temperatures.

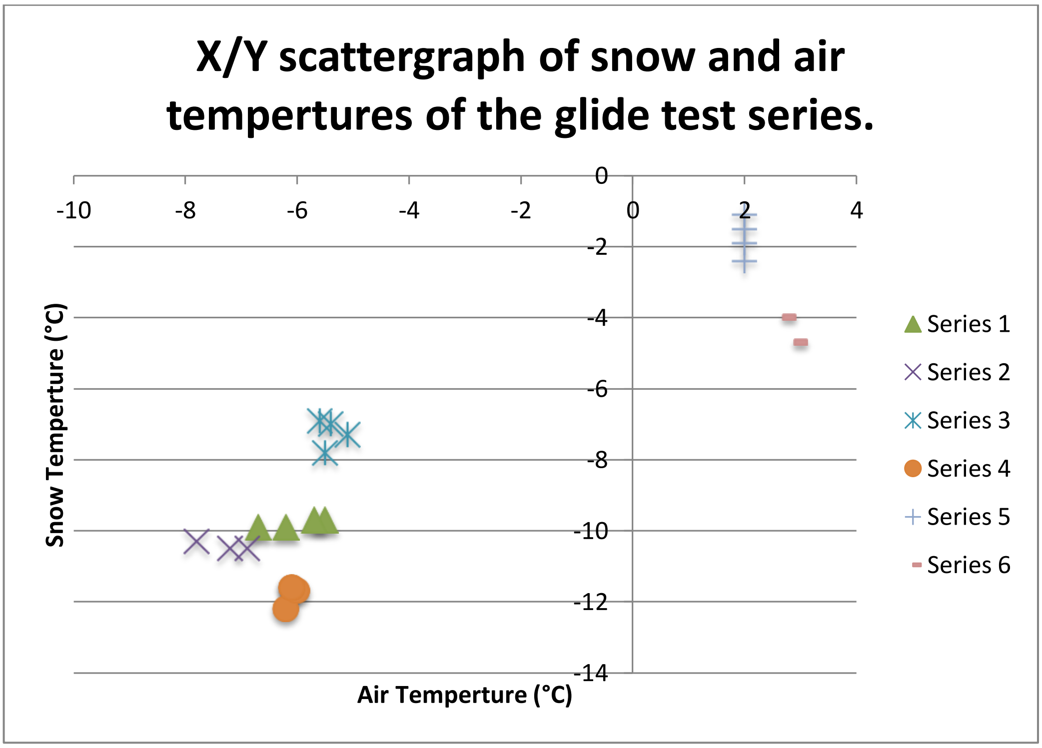


Figure 76: Scattergraph of the range of environmental conditions of the alpine glide tests of sintered 2024x.

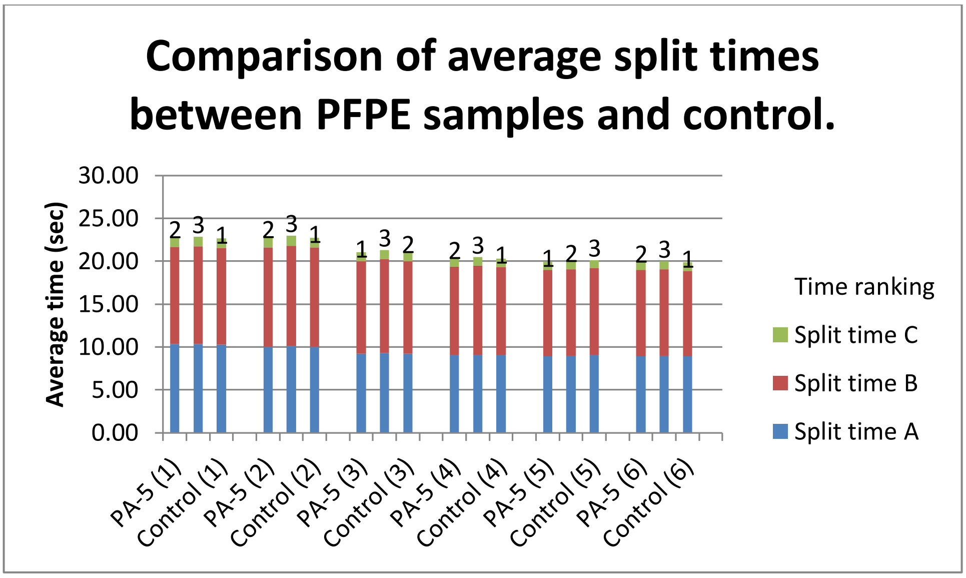


Figure 77: Ranked comparison of average split time between PFPE samples and control. (2% additive PA2, 5% additive PA5 series 1-6 indicated in brackets)

Comparison to the control ski, shown in Figure 78 below, further illustrates that the 5% blend was consistently faster and therefore more effective that the 2%. Particularly noticeable is the small difference in times between the 5% blend and the control with this blend being significantly faster than the 2% blend on every run. The glide speed times measured at split time C towards the end of the test run are shown in Figure 88 and are all above 90 Kmh^{-1}.

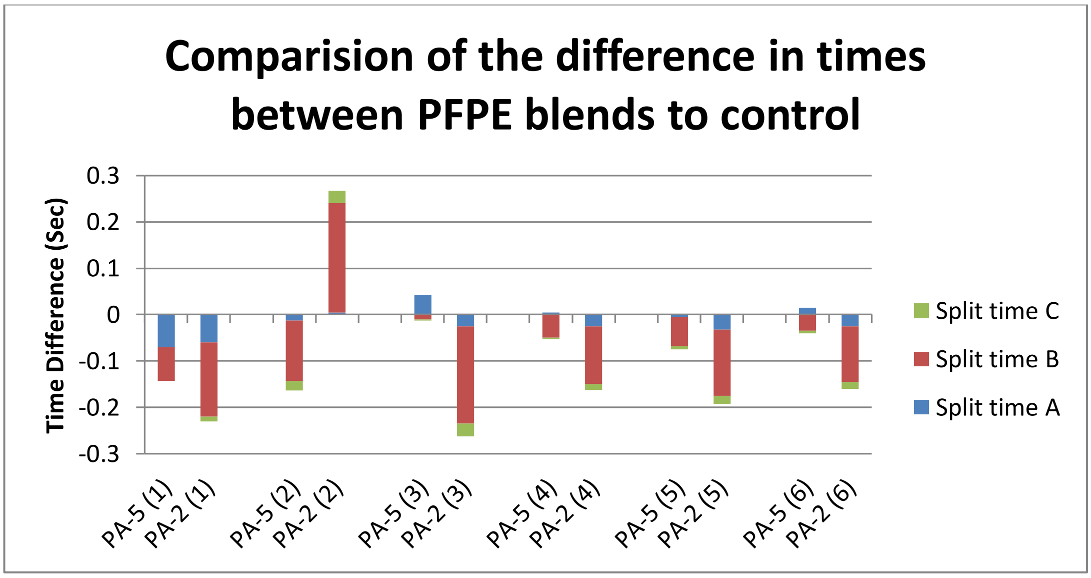


Figure 78: Comparision of the difference in times between test skis with white PFPE bases (2% additive PA2, 5% additive PA5) compared agained a control ski with unmodified black UHMW-PE base. (series 1-6 indicated in brackets)

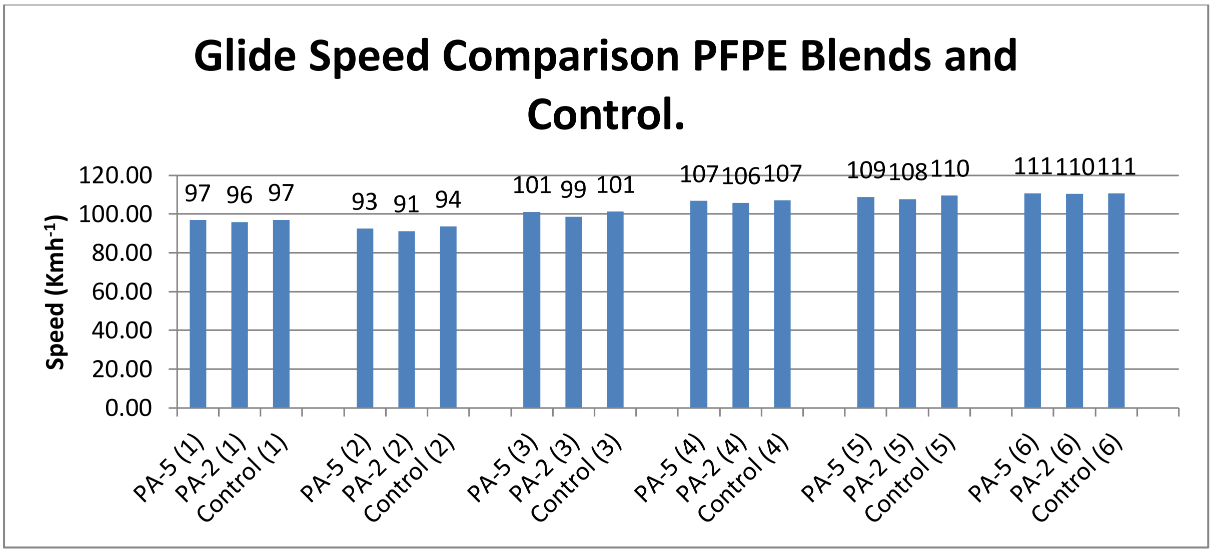


Figure 79: Glide speed comparision between PFPE blends and control.

As already discussed, glide tests are subject to some error, for example those resulting from changing environmental conditions. Acknowledging this, in the series of glide tests the 2024X blended white ski did not show any improvement over the black control ski. However, when comparing the two blends, there was evidence of a promising improvement in performance for the higher (5%) blend. Solar radiation has the potential to cause a significant difference in friction experienced between black and white bases on snow. This difference between bases was also shown in previous experiments, where untreated white bases demonstrated higher levels of static friction compared to black UHMW-PE. Base colour would usually be kept constant within a glide test series designed to compare skis or treatments in order to minimise differential absorption of solar radiation. The untreated control ski time of decent, can be compared to detect any track changes caused by solar radiation or repeat runs over the course of the test series. Additionally, the snow and air temperatures, humidities and solar radiation were recorded for each series of glide tests and can be compared against the results. Given that the test skis where white and the control skis were black, the addition of carbon black to the UHMW-PE may have caused a significant difference independent of any effect of the additive. Previous experiments have also shown significant differences in contact angle, physical structure as well as friction between black and white UHMW-PE bases. Colbeck and Perovich (2004) clearly demonstrated that black bases absorb significantly more solar radiation. White bases are usually not found on today's modern alpine race skis because they are generally considered by the manufacturers to be slower, although they are often used on Nordic skis as they may have advantages at high temperatures where too much melt water can be present and capillary drag increases ski friction. These prototype bases did not have carbon black as an additive in order to specifically identify the effect of the addition of 2024X. The white UHMW-PE base with 5% 2024x additive has shown potential even when compared with untreated black bases. It is recognised that it would have been beneficial to include a white unmodified control ski in the trial to compare the performance with a standard white, unmodified base. Additionally, it is suggested that the modification of the 5% 2024x blend with carbon black would show promise and trials of this blend are planned with *Atomic*. Other molecular weights and 2024x may also be beneficial at higher percentage levels, above 5%, of loading. From the previous compression moulding results in section 6.3.3, blends with A10-P also have a significant potential to be effective. A number of aspects have been suggested as future directions for continued research.

6.3.5. Summary

Experiments conducted in the first part of the results section (6.1) included investigations on cut sections of a ski with a UHMW-PE base which had been exposed to the wear mechanism of snow and also had a medium stone ground profile/texture on the running surface. Contact angle testing on rough surfaces (micro and macroscopic) may have been responsible for a greater interquartile range of measured contact angles. They nevertheless provided some 'base level' information related to the hydrophobicity of a used, race ski, bases. Treatment applications, which are commonly used by the ski industry and technicians, were also investigated. These included the application of hydrocarbon and fluorocarbon waxes using traditional methods of hot waxing, scraping to obtain a thin wax layer then followed by brushing. The fluorocarbon waxes, as expected, demonstrated higher levels of water repellency than the purely hydrocarbon waxes. The latter showed only small increases in contact angle compared to an untreated base.

Highly hydrophobic (144°) nano-sized particle filler was added to these previously tested ski waxes. These novel wax blends were tested but no improvement in hydrophobicity was evident. Whilst these nanoparticles are known to be highly hydrophobic, it is suggested that the wax coated the nanoparticles preventing their beneficial hydrophobic properties from being exhibited. Nano-sized particle fillers of a hydrophobic disposition also have the potential to add a particulate element to the wax, of a similar magnitude of dimension reported for the water film height. Control of this water film, towards a mixed lubrication regime, would be important in the attempt to reducing friction. It has been identified and reported by many authors that mixed lubrication regime, when the resulting water film is neither too thick (capillary drag), nor too thin (dry friction), demonstrates the lowest levels of friction. This is characterised by the Stribeck curve and any shift towards this 'ideal' where friction is extremely low on snow and ice (0.02) would therefore be beneficial.

To measure the effectiveness of the addition of nanoparticles to wax, a glide test method in an alpine environment was employed comparing a 'high level' hydrocarbon control against modified and unmodified fluorocarbon waxes. Due to the limited number of runs conducted, no confident inference could be drawn from a comparison of treated and untreated fluorocarbon waxes although these again showed improvement over the hydrocarbon control. Further testing would be needed to evaluate the effectiveness of adding nanoparticles to wax. Whilst, it was suggested that the wear mechanism experience on snow and ice could expose the surface of the nanoparticles rendering their beneficial properties useful in reducing water film height or reducing capillary drag, a greater range of testing conditions would need to be trialled in order to confirm this hypothesis. Highlighted in the section was the need to control the variability of surface structure at a microscopic and macroscopic level which could significantly affect measured contact angles and also sliding friction.

Surface modification of UHMW-PE was conducted. The ski base was physically structured using both traditional and novel abrasive methods. The contact angle was measured initially on untreated factory ski base sheet materials before various treatments were applied. Unlike the previous samples, these raw material samples did not include a stone ground structure, nor were they previously subjected to the wear mechanism on snow and ice or previous wax treatments. The surface was contact angle tested using the same methodology as the previous ski and base samples. When comparing the two sample sets, the untreated base material in its new factory state exhibits a significantly lower contact angle than that of a used state. This could be due to either the physical or chemical structure of the base, or both. The wax removal method utilised could not fully guarantee that all trace chemicals had been removed. The type of micro physical structure from abrasion of the surface, using the wax removal method may have also influenced contact angle measurements. There are several abrasive conditions a ski is subjected to, both whilst sliding and as a result of the preparation of the surface. Stone grinding, nylon treatments and wear were highlighted as possible influences in the contact angle tests of an untreated base. To investigate the effect of abrasive nylon surface refinement and simulated light abrasive wear caused by snow and ice, further experiments were conducted with 800 grit sander. Planing, skiving or scraping the surface was also reviewed and investigated. The effects of the treatment methods were examined using of scanning electron microscopy in order to observe the surface structures resulting from these treatments applied to the untreated factory base.

Initial abrasion using 'fine' 800 grit sandpaper showed a greater number of surface features or "hairs" when examined. It is known that traditional stone grinding treatments and the wear mechanism on abrasive snow causes these surface features to form. A light abrasive nylon treatment method has been traditionally used in an attempt to remove or reduce this effect. Scanning electron micrographs demonstrated that some of the larger features were removed, resulting in a visibly reduced surface roughness. Metal or plastic scraping is another traditional method of base preparation or wax removal. Whilst, these methods could have been included in the study, they have previously been investigated by other authors using SEM.

A novel glass scraping method was included which succeeded in removing even more surface features than the nylon treated surface. Skiving or planing the surface with a sharp edge is already used during manufacture to plane the desired thickness of a sintered cylindrical block. Taking into account the magnitude of the water film, it is suggested that smoother levels of surface refinement would be more beneficial. Certainly, a thin waxy sliding surface, as traditionally used, may have the effect of reducing asperity heights by filling in or coating these surface features, ultimately rendering the surface relatively smoother than an untreated base. The glass treatment method has been shown in these scanning electron micrographs to further reduce the visible surface roughness and feature heights additionally to that of a nylon treatment method alone. Suitable lubrication, longer strokes and fine pressure control may be explored in future which may reduce likelihood of creating marks in the surface, some of which were evident in the SEM images. This effect may also be in part due to the small sample area (10mm) which was treated.

This treatment method using glass as a material for scraping was chosen as it would be of similar hardness to the silica nanoparticles used for previous investigations, as indeed, they are both composed of silica. These nanoparticles were used to physically abrade the surface of the UHMW-PE. The resulting scanning electron micrographs would appear to present visual evidence of smaller surface abrasions created by this method in addition to a reduced number of large scale features. Certainly, texturing a base with micro to nano-scale features may be of future interest in the pursuit of controlling the size water film between ski base and snow. The variation of particle sizes at this level of magnitude may lead to finer control of the surface structure.

To render the nanoparticles safer to use in a practical environment and avoid potentially harmful inhalation, viscous PFPE was used to encapsulate them. This provided a physical structuring paste which was used on the base material but which, unfortunately, could not be observed using scanning electron microscopy. It did however provide an interesting additional sample for contact angle testing, static friction and glide testing.

Contact angle tests were conducted on untreated black and white UHMW-PE with additional treatments of abrasive nylon, glass and glass with silica and the novel paste wax, all after being subsequently abraded with 800 grit sandpaper. Interestingly, each consecutive treatment significantly increased the measured contact angle. There was also an obvious difference in contact angle results between black and white UHMW-PE. The highest measured contact angles were shown to be from a glass treated physical structure which was further improved by the chemical composition and physical features of the paste wax. There certainly seems to be a trend in smoother surface refinement and increasing hydrophobicity. Further testing, using an inclined plane friction ramp method sought to explore the relationship between the contact angle results and a defined coefficient of static friction.

The coefficient of static friction was again shown to vary quite substantially between black and white UHMW-PE, with black being lower. Both untreated and nylon treated black UHMW-PE samples were far superior to their white counterparts. Interestingly, with the glass and paste wax treatments, the measured coefficient of friction was improved more significantly on the white UHMW-PE, to a level well below that of black. In summary, the inclined plane method of testing was useful; however, the limited window to obtain results on real snow in the UK prevented a full range of temperatures from being explored. All of these tests were conducted in relatively wet and warm conditions. Testing using an inclined plane method measuring static friction may provide an insight into the performance in dynamic conditions because the water film size may be similar to that prevalent at higher speeds in colder conditions. The effect on dynamic friction was also explored for the paste wax using a glide testing method. This treatment was compared to traditionally waxed skis at downhill speeds. Although no confident inferences could be drawn due to the limited number of runs conducted. This investigation did show that an appropriate scale of physical structuring, at a nanoscale level, together with a hydrophobic chemical treatment, has the potential to closely match current high performance ski waxes at downhill speeds.

The last section 6.3 addressed bulk modification of the base material and the question as to whether it would be beneficial to modify the base material to improve sliding friction, even if subsequently, additional treatments are applied. Due to the wear mechanism on snow, even the most hard-wearing materials deteriorate during prolonged sliding, especially in abrasive conditions. Waxes or surface treatments therefore have a small performance window dependent on how quickly they are worn away. Waxes have been previously shown to improve the hydrophobicity of the surface; fluorocarbons more significantly than hydrocarbons. It seemed logical therefore to select known hydrophobic polymers and particle fillers for blending with UHMW-PE. Although, as with the previously investigated ski wax binder, a clustering effect was present with the particles tending group together to lower their surface energy by reducing the exposed area. The particles did however eventually disperse under prolonged heating and the incorporation of a wetting agent. UHMW-PE blended with nanoparticles produced brittle samples when high percentage weight of additive was used. The clustering effect was also observed in this investigation with UHMW-PE and the previously wax modified samples. The encapsulation of the nanoparticles, masking their beneficial chemical properties, was highlighted previously. This effect was also exhibited in the UHMW-PE samples with added nanoparticle fillers.

Due to the highly viscose nature of UHMW-PE, it was not surprising that compression moulding and sintering methods were found to be most effective at creating samples. A screw extrusion was trialled with PDMS due to the advertised benefits of lowering the melt viscosity when used as a masterbatch. However, this method created samples of poor quality as did loading with hydrophobic nanoparticle fillers. Perfluoropolyether, in contrast, was shown to be an effective polymer additive to UHMW-PE. Laboratory scale compression moulded blends were created at various levels of loading and tested using the same methods of investigation as conducted in the previous two sections namely; contact angle, SEM and inclined plane.

Two different molecular weights of PFPE were blended with UHMW-PE up to 10%. The PFPE samples of 2024x and A10-P were created using a small scale compression moulding process. The measured contact angles show a positive correlation with added percentage weight and increased hydrophobicity. At 8% loading level , the average contact angles recorded were 108° and 111°; and at 10% loading were 107° and 114° for 2024x and A10-P respectively. This is an improvement on the contact angle measured in section 6.1.1 for the two fluorocarbon waxes (103° and 110°) but also a 20° and 22° improvement on unmodified UHMW-PE measure at 91°. At lower levels of loading (5%) both blends demonstrate that they were as hydrophobic as traditional hydrocarbon waxes. All samples were abraded with nylon and theoretically could be further improved with glass treatment methods, as previous demonstrated in the surface modification section.

Friction was tested using the same inclined plane methodology. Both blends demonstrated a reduction in friction compared with an untreated base of the same colour (white). Over the duration of this investigation there was a rise in snow and air temperature; however, this was tracked by the use of a control sample. The sample containing the 5% 2024x additive would seem more beneficial than the higher levels of loading (8% and 10%). The A10-P samples were tested in the second series and showed the greatest lowering of friction compared to the control. It is suggested that there is a thicker water film present between snow and sample at warmer temperatures. However, not enough data is available to predict the frictional regime, characterised by the Stribeck curve, with all the variables taken into account. Although greater frictional reductions were exhibited between

A10-P and white UHMW-PE control in the second series it would not be advisable to draw conclusions at this stage between the two different molecular weight additives without further testing. Due to the physical properties of the raw blends, A10-P is a waxy solid and the 2024 is a viscous liquid, the latter was chosen simply for ease of use, in order for a limited number of Atomic 2013 Race Department Downhill skis to be manufactured for glide testing. The sintered base sheet material was professionally manufactured to include 2% and 5% levels of 2024x PFPE. Samples of this material were also examined using SEM and contact angle testing. The laboratory scale compression mould was beneficial in identifying PFPE as a favourable, friction-reducing, additive for UHMW-PE prior to glide testing.

The physical structure was investigated using scanning electron microscopy for comparison to unmodified UHMW-PE, previously investigated. It could be argued that only a limited amount of information can be gained from the resulting images. However, it may be of more interest that the 5% samples exhibited a resistant to the carbon coating procedure. The electro-static attraction of dirt and to the ski base has been highlighted as a significant factor which can increase friction. A base material which exhibits dirt repellent properties could be beneficial in reducing friction when sliding on old and dirty snow. Additionally, more hydrophobic surfaces tend to exhibit both dirt and water repellent properties. The contact angle was also measured on the sintered 2% and 5% base samples, untreated as well as surface textured, using previously tested methods for comparison. The 2% sample, predictability, was less effective than the 5% sample at increasing the measured contact angle. In comparison, the 5% blend was compared with the previously tested surface treatment methods; nylon and glass. The untreated 5% blend was on average more hydrophobic (+18°) and so was the glass treated (+6°) surface, when compared to white UHMW-PE (P-tex 4000) with the same surface treatment. The unmodified nylon treated UHMW-PE was recorded to be 3° higher than the 5% modified blend. The nylon treatment demonstrated the largest interquartile range consistent with surface asperities caused by this treatment method observed under the SEM, as did both the untreated blends. Evident on the 2% untreated SEM sample which did, carbon coat, were significant skiving marks cause by the industrial process. This irregularity of the surface would have the potential to cause variation in contact angle. However this physical change to surface texture should not be confused with the effect of the chemical treatment of the UHMW-PE polymer by the addition of 2024x. The smoother textured surfaces have largely demonstrated a narrower range of results which may be due to less irregularity in their surface structure. If the effect of the chemical treatment is to be measured then it would be advisable to focus on the treatment which imparts a regular structure with a narrow range of roughness on to the UHMW-PE surface. The glass treatment method succeeded in planing the surface smooth, although, still evident on the 2% SEM were features caused by the industrial manufacturing process on an untreated base. Therefore a 6% improvement in measure contact angle using this method would seek to advocate PFPE being used in future base bends at 5% levels of loading. Some large scale features on the glass scraped SEM did remain on 2% blend sample post- treatment, therefore this method is not without error in producing a more uniformly smooth surface at a micro-scale level. However, finer pressure control, lubrication, the use of fine abrasive particles and a large sample treatment area have been identified to reduce minimise this problem and enable the texture of the surface to a more defined with a smoother roughness which would increase the measured contact angle.

Measuring the static coefficient of friction using an incline plane method showed a significant reduction of friction when tested in conditions which tended towards the warm and wet. There was a large difference in measured friction between the white UHMW-PE and both 2% and 5% samples. Interestingly, there was only a comparatively small increase between the black UHMW-PE and the black additive blends. Glide testing was performed by *Atomic* on DH skis which were manufactured using the two base blends: 2% and 5% 2024x. When compared to the control, which was an unspecified blend of black UHWM-PE, the 5% demonstrated slightly slower times of descent. Comparison between blends shows that the blend containing a higher percentage weight of additive (5%) was consistently faster than the 2% blend. This series of glide tests comprised of six series of runs, each with all snow temperatures below freezing and series 1-4 conducted in -7 to -12°C conditions. Interestingly, the warmer conditions, just below freezing, in trials 5-6 did not show a significant improvement compared to that of trials conducted in colder conditions. Improvement can only be measured and compared against the black UHMW-PE control or between blends. However, this may not be ideal, as the black UHMW-PE could significantly reduce friction without modification with the investigated additive. Ideally, a comparison should be made using unmodified white UHMW-PE control or modified black blends with black control.

In summary, the beneficial fluorinated properties of the polymer additives used for bulk modification are currently already utilised in traditional wax technology as a temporary surface modifier although the beneficial properties of traditional waxes can diminish during prolonged sliding. Modifying the bulk material with fluorinated polymers may be beneficial at higher sliding speeds and warmer conditions when the water film is of a thicker magnitude. In old dirty snow such modified blends of base material may also be beneficial due to their resistance to electrostatic attraction of carbon. The resultant blends of UHMW-PE and PFPE used in this investigation have shown an increase in contact angle and reduction of friction using an inclined plane method. The material has been adhered to FIS Race level skis alpine DH skis and glide tested, although the effect of carbon black was not investigated. The absorption of solar radiation is a significant factor causing a possible temperature rise in the base in addition to frictional heating. Nearly all race skis are black for this reason. Further trials are planned to include carbon black in these blends for further testing. Certainly this technology shows promise towards the goal of manufacturing a ski base which does not need to be treated with additional post treatments and when worn, continues to expose the underlying material which has been confirmed to be of a more hydrophobic disposition than unmodified UHMW-PE. The combination of the blended base and the structuring treatment methods investigated in this thesis could also result in further frictional savings, although this needs to be confirmed with further testing. These blends have the potential to be the next generation of base material and provide racing success at the highest levels in alpine disciplines and potentially the wider snow sports industry.

Chapter [7]   Conclusions and outlook

UHMW-PE is a remarkable sliding material with a low coefficient of friction, a high wear resistance, and which is hydrophobic in nature. Current post-treatments aim to structure and chemically treat the base material in order to tailor the ski base/snow base interface to specific snow conditions. The performance gains achieved through post-treatment are relatively small and difficult to measure because of the variability of conditions at the interface.

Once a skier overcomes static friction, it is water, nature's 'natural lubricant', which is the primary cause of the low friction exhibited on snow and ice. Essentially, the skier is travelling on a nano-sized film of water, covering each ice grain or crystal, which has formed well below the bulk freezing temperature. Small increases in temperature or pressure will cause this water film to increase in magnitude. Flash heating, as the ski base slides over each grain, or small changes in the ambient conditions, will tip the balance from solid to liquid. It follows that the repellence to wetting and resistance to the negative effect of drag from the viscous resistance of the liquid water would be beneficial attributes of any base material. Plant and insect surfaces repel water in two ways: firstly, physically, as a result of a dual scale nano-structure and secondly, chemically by incorporating a wax-like coating. Current ski base treatments are not of the optimum structural size to be ideal for reducing friction. Until recently it was not considered possible to apply nanoscale structures to UHWPE without compromising other beneficial properties such as hydrophobicity.

Using hydrophobic fumed silica as a filler in waxes and in the raw UHMW-PE base has shown that there is a need for a wetting agent which prevents the clustering effect caused by the high surface to volume ratio of the silica nanoparticles. It is suggested that the difference in interfacial energy between particle and polymer chains may cause the particles to cluster together in an attempt to achieve thermodynamic equilibrium. In these investigations, ski wax was combined with fluorinated nanoparticles but wetted with acetone to lower the surface energy of the particles. This succeeded in achieving an adequate dispersal. The resulting hydrophobicity reflected in contact angle measurements, however, was not improved but was shown to decrease. It is suggested that this could be attributed to the wax polymer surrounding and encapsulating the nanoparticles. The wear experienced as a result of solid-solid interactions whilst sliding may serve to expose the surface of the nanoparticles. Glide testing at snow temperatures of -8± 0.5°C, humidity 17%, and air temperature of 2°C with humidity 30%, certainly showed no statistically significant advantage or disadvantage in using the nanoparticle wax compared to a conventional treatment. The performance window in terms of optimum snow conditions and subsequent water film height for the specific treatment has yet to be determined. This could be achieved by glide testing or tribometer testing in a variety of temperature and humidity ranges, as suggested as a future direction for work in this area.

Increasing the hydrophobicity of the ski base material was achieved as a result of blending a fluorinated polymer (PFPE) with UHMW-PE. Contact angle tests showed 12%, 16% and 18% improvement using blends of 5% and 8% and 10% of PFPE in UHMW-PE. The resulting samples also exhibited a 5%, 17% and 24% reduction in static friction on an artificial ski slope material. A full scale, sintered ski base is required to further assess the resulting mechanical properties of these blends. However, this novel material may provide a hydrophobic sliding surface comparable to that of traditional fluorinated wax treatments.

The water film parameter, based upon the thickness of the water film and the roughness of the ski base and the snow is known to be a key factor in the coefficient of friction. Therefore, the ski base should have a defined roughness to tailor the base to the particular snow conditions. Traditional stone grinding techniques provide a structure or roughness to the ski. However, there is some agreement that this structure is not of optimum magnitude and is in fact too rough. Nanoscale structuring of the ski base surface has been achieved with a novel glass scraping method combined with abrasive nanoparticles. Scanning electron microscopy of such a treated base demonstrated a smoother, isotropic and smaller scale textured surface compared with that of traditional ski base treatments. Combining the nanoparticles with PFPE allowed the creation of a hydrophobic cutting fluid encapsulating the nanoparticles to remove the health risks associated with inhalation of small particulates. PFPE is known to have beneficial sliding properties on snow so the fluid was tested in an alpine glide test. Glide testing at snow temperatures -11 to -12°C, showed no statistically significant advantage or disadvantage in using the nanoparticle wax compared with a conventional ski treatment. Future tests are required, however, to investigate this treatment in a variety of snow conditions.

The bulk modification of polyethylene has been explored with a view to modifying the base material to improve sliding friction. Initial investigations suggested that perfluoropolyether was an effective polymer additive to UHMW-PE. Two different molecular weights of PFPE were blended with UHMW-and samples, with a range of loading levels up to 10%, were created using a small scale compression moulding process. These samples demonstrated improvements in hydrophobicity and static friction compared to controls and there was a correlation between these properties and the percentage weight of additives. Sintered base material was professionally manufactured containing two different levels of one of the types of PFPE. This provided samples for further laboratory investigation and base material for *Atomic* to use for the manufacture of downhill skis and glide testing.

Ultimately the challenge in the preparation of skis solely for performance gain has to be practical one which is tailored meet a large variety of specific snow conditions. There is at present some uncertainty as to whether current post treatment methods optimally reduce friction based upon the science and current understanding of the tribological interaction between ski base and snow. However there are some promising indications that the use of nanoparticles in practical nano-structuring and combining nanoparticles to produce more hydrophobic blends of UHMWPE could lead to performance gains, although this has yet to be fully investigated in a wide range of snow conditions.

Chapter [8] Future Directions

Further glide testing should be undertaken on alpine snow, particularly in warmer and wetter environmental conditions. The high, sustained speeds of a downhill race of between 1 and 2 minutes duration at 60-100kmh^{-1} would be conducive to the formation of thicker water films. Thicker water films can also be found in warm and wet environmental conditions at slower gliding speeds. Testing in warmer conditions at lower speeds using shorter distances may provide a more accurate comparison to the sustained frictional heating during a downhill race. Further glide tests of sintered UHMW-PE polymer blends with PFPE would also be beneficial in these warmer conditions. During glide testing, comparison should be made to a white control if no carbon black is added to the PFPE blend. As black UHMW-PE has been found to have beneficial frictional properties it is suggested that further research on future blends should be with blends with carbon black added. Such new blends are being prepared by Atomic prior to glide testing during 2013/14. Other forms of PFPE in additiona to 2024x may also be found to promote sliding. A comparison of the mechanical properties of these blends, with unmodified UHMW-PE could also be undertaken.

Improving the accuracy of glide testing using instantaneous acceleration and velocity data could be achieved through the use of additional sensory devices such as an altitude heading reference system (AHRS). Measuring the time period between sections of a course, as per current methodology, only provides snapshots of information on which to draw conclusions. A possible future direction could be to attach AHRS and data recording devices to each skier. This would include the provision of instantaneous, GPS, vector speed and acceleration data. The measurement of the acceleration and the precise changes in slope gradient has the potential to improve the glide testing methodology. Alternatively, a tribometer could be used but at relatively high sliding speeds on real snow in alpine conditions; something which has not been previously achieved. Some preliminary trials were conducted as part the research for this thesis using the SBG systems IG 500N miniature altitude heading reference system (AHRA) and it is suggested that further work in this area would have considerable potential.

The structuring method involving the paste wax and surface planing using the novel glass method showed potential in creating a finely structured surface which was chemically and physically hydrophobic. The effects of the treatment of a ski using this method followed by the application hydrocarbon wax would certainly be worthy of investigation. An environmental SEM could be used to gain further insight into the surface structure and visible roughness, complimented by optical profilimetry. The effects of other treatments such as plastic/metal scraping, brushing and waxing have been previously investigated by other authors, mainly on cross country skis, however, an investigation to compare the effect each surface treatment in more detail may prove useful in enhancing post-treatment methods. Other sizes and types of nanoparticle could also prove effective at structuring the base material to defined small scale roughnesses which may link to their optimal performance in particular environmental conditions.

References

Ambach, W. (1958) On Determining the Melted Water Content of Snow by Dielectric Measurements. *Zeitschrift für Gletscherkunde Glazialgeologie*, 4(1)1-8.

Ambach, W. and Mayr, B. (1981) Ski Gliding and Water Film. *Cold Regions Science and Technology*, 5, 59-65.

Ashby, M.F. (1993) Criteria for Selecting the Components of Composites. *Acta Metallurgica et Materialia*. 4(1)1313-1335.

ASM International (2012) ASM International company website [online] Accessed 31th June 2013: http://www.asminternational.org

Atomic (2012) Atomic company website [online] Accessed 24th June 2013: http://www.atomic.com/

Barnes, P; Tabor, D and Walker, J.C.F. (1971) The Friction and Creep of Polycrystalline Ice. *Proceedings of the Royal Society of London: Series A, Mathematical and Physical Sciences*, 324(1557) 127-155.

Bäurle, L; Szabo, D; Fauve, M; Rhyner, H and Spencer, N. D. (2006) Sliding Friction of Polyethylene on Ice: Tribometer Measurements. *Tribology Letters*, 24(1)11–23.

Bäurle, L. (2006) Sliding Friction of Polyethylene on Snow and ice- A Dissertation submitted to the Swiss Federal Institute of Technology Zurich, nr 16517. [Online] Accessed 31th June 2013: http://e-collection.library.ethz.ch/eserv/eth:28803/eth-28803-02.pdf

Bäurle, L; Kaempfer, Th. U; Szabó, D and Spencer, N. D. (2007) Sliding friction of polyethylene on snow and ice: Contact area and modelling. *Cold Regions Science and Technology*, 2007. 47(3),276-289.

Bhushan, B (2002) Introduction to Tribology. USA. John Wiley and Sons, 1 Aug 2002

Bigler, H. P Dutsch, B. (1993) *Moveable plate assembly for ski binding support.* US Patent number: 5242188

Black, S (2003) Getting to the Core of Composite Laminates [Online] Accessed 18th June 2013: http://www.compositesworld.com/articles/getting-to-the-core-of-composite-laminates

Blossey, R. (2003) Self-cleaning Surfaces-Virtual Realities. *Nature Materials*, 2,301-306.

Boehm, A, P; Lehner, F; Messerschmidt, W. G. P. (1998) *Spacer plate arrangement for ski bindings*. US Patent number: 5746439

Bowden, F. P. and D. Tabor. (1964). The friction and lubrication of solids. Oxford University Press 149-158.

Bowden, F.P. & Tabor, D. (1950) The Friction and Lubrication of Solids Oxford University Press 87-89

Bowden, F.P. (1953) *Friction on Snow and Ice.* Cambridge University Press Series A, Cambridge, 217 (0)462-478.

Bowden, F.P. and Hughes, T.P. (1939) The Mechanism of Sliding on Ice and Snow. *Proceedings of the Royal Society of London*, 172(0)124-130.

Briscoe, B. J. and Sinha, S. K. (2002) Wear of polymers. Journal of Engineering Tribology, Proc. Instn. Mech. Engrs, Part J*: Journal of Engineering Tribology*, 216(0)401-413.

Brodie, M; Walmsley, A. and Page, W. (2008) Fusion Motion Capture: a Prototype System using Inertial Measurement Units and GPS for the Biomechanical Analysis of Ski Racing. *Sports Technology*, 1(1),17-28.

Brodie, M; Walmsley, A. and Page, W. (2008) Fusion Motion Capture: a Prototype System Using Inertial Measurement Units and GPS for the Biomechanical Analysis of Ski Racing. *Sports Technology*, 1(1),17-28.

Buhl, D; Fauve, M and Rhyner, H.U (2001). The kinetic friction of polyethylene on snow: the influence of the snow temperature and the load. *Cold Regions Science and Technology* 33(0)133-140.

Cann, P; Ioannides, E; Jacobson, B. and Lubrecht, A.A. (1994) The Lambda Ratio - a critical re-examination. *Wear*, 175(1-2),177-188.

Cheng, Y.T; Rodak, D.E; Wong, C.A. and Hayden, C. (2006) Effects of Micro and Nano-Structures on the Self-Cleaning Behaviour of Lotus Leaves. *Nanotechnology*, 5,1359-1362.

Colbeck, S. C. (1988) Kinetic Friction of Snow. *Journal of Glaciology*, 34(116)78-86.

Colbeck, S. C. (1992) A Review of the Processes that Control Snow Friction, *CRREL,* Hanover, NH.

Colbeck, S. C. (1994) A Review of the Friction of Snow Skis. *Journal of Sports Sciences*, 12(0)285-295.

Colbeck, S. C. (1995) Pressure Melting and Ice Skating. *American Journal of Physics*, 63(10)888-890.

Colbeck, S. C. (1996) Capillary Bonding to Wet Surfaces. *Surface & Coatings Technology*, 81(0)209-214.

Colbeck, S. C; Akitaya, E; Armstrong, R; Gubler, H; Lafeuille, J; Lied, K; McClung, D and Morris, E. (1990) The International Commission on Snow and Ice of the International Association of Scientific Hydrology. *International Commission on Snow and Ice (IAHS), World Data Centre A for Glaciology*, University of Colorado, Boulder, CO, USA.

Colbeck, S.C. (1994) Bottom Temperatures of Skating Skis on Snow. *Medicine and Science in Sports and Exercise*, 26(2)258-262.

Colbeck, S.C. (1986) A Review of the Metamorphism and Classification of Seasonal Snow Cover Crystals. in *Proceedings of the Davos Symposium*,

Colbeck, S.C. (1996) A Review of the Friction of Snow. *Physics of Sliding Friction*, 1996, 311(19)275-291.

Colbeck, S.C. and D.K. Perovich (2004) Temperature effects of black versus white polyethylene bases for snow skis. *Cold Regions Science and Technology*, 2004. 39(1)33-38.

Cottin-Bizonne, C; Barrat; J. L. Bocquet, L. and Charlaix, E. (2003) Low-friction flows of liquid at nanopatterned interfaces. *Nature Materials* 2, 237.

Coupe, R (2008) An Investigation Comparing the Efficacy of Different Lubricants for Skis on Artificial Snow. *Enquiry - The ACES Journal of Undergraduate Research*, 1(1) [online] Accessed 15th August 2009 at: http://research.shu.ac.uk/aces/enquiry/index.php/enquiry/article/view/10/16

Coupe, R. and Spells, S. (2009) Towards a Methodology for Comparing the Effectiveness of Different Alpine Ski Waxes. *Sports Engineering*, 12(2)55-62.

CPS (2012) CPS GmbH company website [online] Accessed 15th June 2013: http://www.cps-gmbh.net

Czichos, H Habig, K. H (2003) *Tribologie-Handbuch (Tribology handbook*), Vieweg Verlag, Wiesbaden, 2nd edition.

Czichos, H. (1978) Tribology a systems approach to the science and technology of friction, lubrication and wear. p400. *Tribology Series, 1*. Amsterdam: Elsevier.

Day, M. A. (1990) The No-Slip Condition of Fluid Dynamics. *Erkenntnis*, 33(3)285-296.

Desai, S. M. and Singh, R. P. (2004) Surface Modification of Polyethylene. *Advance polymer Science*, 169,231-293.

DHO (2012) Down Hill Only Ski Club website [online] Accessed 14th August 2012: http://www.downhillonly.com

Ekeland, A. Rødven, A. and Sulheim, S (2005) Injury Rates and Injury Types in Alpine Skiing, Telemarking, and Snowboarding. Skiing Trauma and Safety: Fifteenth International Symposium, ASTM STP 1464, R.J. Johnson, J. E. Shealy, and M. G. Ahlb umer Eds., *American Society for Testing and Materials*, West Conshohocken, PA, 31-39.

Engineers Edge (2012) Engineers Edge company website [online] Accessed 15th August 2012: http://www.engineersedge.com

Eriksson, R. (1955) Friction of runner on snow and ice (SIPRE Report TL 44, *Meddelande* 34-35,1-63

Evans, D. C. B; Nye, J. F; and Cheeseman, K. J. (1976) The Kinetic Friction of Ice. *Proceedings of the Royal Society of London*, 347(1651)493-521.

Fauve, M., et al. (2008) Putting Snow Knowledge into the Development of Winter Sports Equipment. *Sports Technology*, 1(2-3),145-151.

Federolf, P., Scheiber, P; Rauscher, E., Schwameder, H., Lu¨thi ,A.; Rhyner, H-U; Mu¨ller E. (2007) Impact of Skier Actions on the Gliding Times in Alpine Skiing. *Scandinavian Journal of Medicine & Science in Sports*, 18(6)790-797.

Fierz, C; Armstrong, R.L; Durand, Y; Etchevers, P; Greene, E; McClung, D.M; Nishimura, K; Satyawali, P.K; and Sokratov, S.A. (2009). The International Classification for Seasonal Snow on the Ground. IHP-VII Technical Documents in Hydrology N°83, IACS Contribution N°1, UNESCO-IHP, Paris.

FIS (2012) International Ski Federation website [online] Accessed 30th August 2012: http://www.fis-ski.com/

Fischer (2012) Fisher Sports company website [online] Accessed 15th August 2012: http://www.fischersports.com/en/Home

Fletcher N.H (1970) *The chemical physics of ice.* Cambridge University Press.

Formax (2012) Formax company website [online] Acessed 16th August 2012: http://www.formax.co.uk/

Frederolf, P. A. (2005) Finite Element Simulation of a Carving Snow Ski [Online], PhD, *Swiss Federal Institute of Technology, Zurich*. Accessed on 15th August 2009: http://e-collection.ethbib.ethz.ch/ecol-pool/diss/fulltext/eth16065.pdf

Fry, J (2006) *The Story of Modern Skiing.* University Press of New England

Giesbrecht, J. L; Smith, P; Tervoort, T. A. (2010) Polymers on snow: Towards skiing faster. *Journal of Polymer Science Part B: Polymer Physics* 48(13)1543–1551.

Glenne, B. (1987) Sliding Friction and Boundary Lubrication of Snow. *Journal of Tribology, Transactions of the ASME*, 109(4)614-617.

Gnanappa, A K; O'Murchu, C; Slattery, O; Peters, F; Aszalós-Kiss, B and Tofail, S. A. M. (2008) Effect of Annealing on Hydrophobic Stability of Plasma Deposited Fluoropolymer Coatings. *Polymer Degradation and Stability*, 93(12)2119-2126.

Golecki, L. and Jaccard, C. (1978) Intrinsic Surface Disorder in Ice Near the Melting Point. *Journal of Physics C: Solid State Physics,* 11(0)4229

Hamrock, B. J and Dowson, D. (1981) Ball Bearing Lubrication - the Elastohydrodynamica of Elliptical Contact. *Wiley-Interscience*, New York, 121-230

Harris, B. (1999) Engineering Composite Materials. *The Institute of Materials London*, [online] Accessed 15th August 2012: http://www.harribr.talktalk.net/Engineering%20Composites.pdf

Harvey, I (2000) How to use Toko wax. Pioneer Sports [online] http://www.skinnyski.com/notices/archives/Toko_1.html

Holmenkol Company (2012). Holmenkol company website [Online] Accessed on 15th August 2012: http://www.holmenkol.com

Howe, J (2001) *The New Skiing Mechanics*, McIntire Publishing, Waterford, ME, USA.

Hull, D. and Clyne, T.W (1996) *An Introduction to Composite Materials*. Cambridge University Press.

Jobwerx (2007) Silicones Give Ski Racing Wax Compatibility and Water Repellency. [Online] Accessed on 15th August 2009: http://www.jobwerx.com/news/Archives/ge_silicones_biz-id=947538_927.html

Kaempfer, T; Hopkins, M; and Perovich, D. (2007) A three dimensional microstructure-based photon-tracking model of radiative transfer in snow. *Journal of Geophysical Research*, 112(1)24-113.

Karlof, L; Smevold, T; Tretterud, O. B. and Zupan, M. (2007) *Swix* Test Protocol for Testing of Glide produce Technical Note #3-2007 [online] Accessed on 15th June 2013: http://www.*Swix*sport.com/dav/676d2c49ab.pdf

Karloff, L; Axell, L. T; Slotfeldt-Ellingsen, D. (2005) Why is Ice and Snow Slippery? The Tribo-physics of Skiing [Online] Accessed 15th August 2012: http://www.*Swix*sport.com/dav/babc49f803.pdf

Khedkar, J; Negulescu, I. and Meletis, E. I. (2002) Sliding Wear Behavior of PTFE Composites. *Wear*, 252(1),361-369.

Khorasani, M. T; Zaghiyan, M. and Mirzadeh, H. (2005) Ultra High Molecular Weight Polyethylene and Polydimethylsiloxane Blend as Acetabular Cup Material. *Colloids and Surfaces B: Biointerfaces*, 41(2–3)169-174

Kietzig, A.M; Hatzikiriakos, S.G. and Englezos, P. (2009) Ice Friction: The Effects of Surface Roughness, Structure, and Hydrophobicity. *Journal of Applied Physics*, 106(2)024303-7.

Kitzbühel Tourismus, (2013) [online] Accessed on 30th July 2013: http://www.kitzbuehel.com/en/sports_leisure/winter/skiing/strei

Krüger, A. and Edelmann-Nusser, J. (2009) Biomechanical Aanalysis in Freestyle Snowboarding: Application of a Full-Body Inertial Measurement System and a Bilateral Insole Measurement System. *Sports Technology*, 2(1-2)17-23.

Kuroiwa, D. (1977) The Kinetic Friction on Snow and Ice. *Journal of Glaciology*, 19(1)141-152.

Kurtz, S.M. (2004) The UHMWPE Handbook. Elsevier Academic Press, Boston, MA, USA.

Kustandi, T. S; Choo, J. H; Low, H. L and Sinha, S. K (2009) Texturing of UHMWPE surface via NIL for low friction and wear properties . *Journal of Physics D: Applied Physics*. 43(1)015301

Kuzmin, L. and Tinnsten, M. (2006) Dirt Absorption on the Ski Running Surface- Quantification and Influence on the Gliding Ability. *Sports Engineering*, 9(1)137-146.

Kuzmin, L. (2006) Investigation of the most essential factors influencing ski glide, in Department of Applied Physics and Mechanical Engineering. Luleå University of Technology.

Kuzmin, L. and Tinnsten, M. (2008) Hot Glide Wax Treatment and the Hardness of the Ski Running Surface. In Estivalet, M. and Brisson, P. (Eds.) *The Engineering of Sport 7*, 2(1)135-141

Kuzmin, L. (2010). Interfacial kinetic ski friction (Doctoral).[Online] Mid Sweden University. Accessed on 15th August 2012: http://miun.diva-portal.org/smash/get/diva2:319312/FULLTEXT01.

Lawin, L. R; Guire, P; Wen, J. and Taton, K. (2008) Nanotextured Super or Ultrahydrophobic Coating. [Online] US Patent Office. Accessed on 15th August 2009: http://www.faqs.org/patents/app/20080268233

Lind, D. and Sanders, S. P. (1996): *The physics of skiing: skiing at the triple point*. Springer Verlag, New York, 268.

Lorusso, A; Nassisi, V; Velardi, L; Raino, A. C; Torrisi, L; Margarone, D and Mezzaslma, A. (2008) Wettability modification of uhmwpe by laser beam irradiation. *Radiation Effects and Defects in Solids: Incorporating Plasma Science and Plasma Technology* 163(4-6)731-741

Lovett, R (2006) Skiing: From the stone age to Torino [Online] *National Geographic News*. Accessed 20th August 2012: http://news.nationalgeographic.com/news/2006/01/0131_060131_skiing.html

Lui, C; Ren, L; Arnell, R. D. and Tong, J. (1999) Abrasive Wear Behaviour of Particle Reinforced Ultrahigh Molecular Weight Polyethylene Composites. 225-229(1)199-204

Lund, M. and Masia, S. (2003) A Short History of Skis [Online] International Skiing History Association, ISHA resources. Accessed on 15th August 2009: http://www.skiinghistory.org/skishistory.html

Marmur, A. (2004) The Lotus Effect: Superhydrophobicity and Metastability. Langmuir, 20(9)3517-3519.

Masia, S (2004) Milestones and Detours in Ski Design, *Skiing Heritage Journal*, March 2004, 1(1)18-19

Masia, S (2005) The Evolution of Modern Ski Shape, *Skiing Heritage Journal*, September 2005, 1(1)33-37

Mathia, T.G; Zahouani, H. and Midol, A. (1992) Topography, Wear and Sliding Functions of Skis. International *Journal of Machine Tools and Manufacture*, 32(1-2)263-266.

MatWeb (2012) MatWeb company website [online] Accessed 27th August 2012: http://www.matweb.com/

Mayr, B. (1979) Ein Beitrag zur Physik des Schigletens: Elektronishche messung des wasserfilms beim gleitvorgang. Dissertation zur erlangung des Doktorgrades an des Naturwissenschaftlichen fakultat der Leopold-Franzens-Universitat Innsbruck (in German), 152p

McDonald, J; Duffy, D.C; Anderson, R. J; Chiu, T. D; Wu, H; Schueller, O. J. A. and Whitesides, G. M. (2010) Fabrication of Microfluidic Systems in Poly(dimethylsiloxane). *Electrophoresis*, 21(1)27–40.

Mellor, M. (1964) Properties of Snow. CRREL *Momograph* III-A1, p.105.

Miwa, M; Nakajima, A; Fujishima, A; Hashimoto, K and Watanabe, T. (2000) Effects of the surface roughness on sliding angles of water droplets on superhydrophobic surfaces. *Langmuir*. 16(1)5754–5760.

Mohan, R, D. (2003) Recent applications of viscoelastic damping for noise control in automobiles and commercial airplanes. *Journal of Sound and Vibration.* 262(3),457–474

Moldestad, D. A. (1999) Some Aspects of Ski Base Sliding Friction and Ski Base Structure. Unpublished doctoral dissertation submitted to the Norwegian University of Science and Technology N-7491, Trondheim, Norway.

Moore, D.F. (1975) *Principles and Applications of Tribology International Series on Materials Science and Technology*. Oxford ; New York Pergamon Press.

Morgan, A (2009) The 80 Year History of a Great Alpine Ski Race. *Kandahar Ski Club*

Nachbauer, W; Shhröcksnadel, P and Lackinger, B (1996) Effects of snow and air conditions on ski friction. Skiing Trauma and Safety; Tenth Volume, ASTM STP 1266, D. Mpte, Jr. Robert J. Johnson, Wolfhart Hauser, and Peter S. Schaff, Eds., *American Society for Testing and Materials*, 10(1266)178-185

NIST Database (2012) NIST Database website [online] Accessed 15th August 2012: http://webbook.nist.gov/chemistry/

Oksanen, P. and Keinonen, J. (1982) The Mechanism of Friction of Ice. *Journal of Wear*, 78,315-324.

Onda, T; Shibuichi, S; Satoh, N; and Tsujii, K (1996) Super-Water-Repellent Fractal Surfaces. Langmuir, 12,(9)2125-2127

Oshima, A; Tabata, Y; Kudoh, H; Seguchi, T; (1995) Radiation induced crosslinking of polytetrafluoroethylene. *Radiation Physics and Chemistry.* 45(1)269.

Oxtoby, D. W. (1999). Nucleation and surface melting of ice. *Ice physics and the natural environment*, 23-38. Vol. 56. Berlin: Springer-Verlag, Ed. Wettlaufer, J. S., Dash, J. G., and Untersteiner, N.

Patir, N and Cheng, H. S (1978) An Average Flow Model for Determining Effects of Three-Dimensional Roughness on Partial Hydrodynamic Lubrication ASME *Journal of Tribology*., 100(1)12–17.

Petrenko, V. F. and Colbeck S. C. (1995) Generation of Electric Fields by Ice and Snow Friction. *Journal of Applied Physics*, 77(9)4518-4521

Petrovic, J.J. (2003) Review Mechanical Properties of Ice and Snow, *Journal of Materials Science*, Vol 38 pp. 1-6.

Pikhala, P. and E. Spring (1986): Determination of the contact area between ski and snow using a simple thermal conductivity meter. Helsinki University, Department of Geophysics, Geophysics Report Series, 1(22)12-18

Quéré, D. (2005) Non-Sticking Drops. *Institute of Physics Publishing*, 68(1)2495-2532.

Quéré, D. and Callies, M. (2005) On Water Repellency. *Soft Matter*, 1(1)55-61.

Racewax (2012) Racewax company website [online] Accessed 15th August 2012: http://www.racewax.com/

Reynolds, O. (1901) *Papers on mechanical and physical Subjects*, 2(1)535-77 Cambridge University Press

Rossignol (2012) Rossignol company website [online] Accessed 20th August 2012: http://www.rossignol.com/GB/GB/

Ryan, K. J; Lupton, K. E; Pape, P. G and John, V, B (2000) Ultra-high-molecular-weight functional siloxane additives in polymers*. Effects on processing and properties journal of Vinyl and Additive Technology* 6(1)7–19.

Saito, N; Yamashita, S and Matsuda, T. (1997) Laser-irradiation induced surface graft polymerization method. *Journal of Polymer Science* Part A: Polymer Chemistry 35(1)747–754.

Scheve, I (2011) Norway Find Fast Skis and Controversy with Gallium Wax. [Online] Last Accessed 12th August 2012: http://fasterskier.com/2011/04/the-case-for-keeping-gallium-secret/ April 6th, 2011

Schulson, E. M (1999) The structure and mechanical behaviour of ice. *Journal of the Minerals, Metals and Materials Society* 51(2)21-27

Schultes, H. (1980) *The Alpine Ski* (R. Gammons, Ed.). Olin ski company, Middletown, Connecticut. Printed by Horton Printing, Meriden, Connecticut, 165 p

Scott, N. et al. (2007) Measurement of Ski Snow-Pressure Profiles. *Sports Engineering*, 10(3)145-156.

Sentmanat, M; Stamboulides, C. and Hatzikiriakos, S.G. (2009) A Novel Miniature Mixing Device for Polymeric Blends and Nanocomposites*. Polymer Engineering & Science*, 49(11)2092-2098.

Shafrin, E. G.; Zisman W. A. (1964) In Contact Angle, Wettability, and Adhesion; Advances in Chemistry Series; Fowkes, F. M., Ed.; *American Chemical Society*: Washington, DC, 1964; 43(1)145-167.

Shimbo, M (1971) Friction on Snow of Ski Soles, Unwaxed and Waxed. *Scientific Study of Skiing in Japan*, T.S.o.S. Science, Editor, Hitachi, Ltd: Tokyo Japan. p. 99-112

Sicomin (2012) Sicomin company website [online] Accessed 15th August 2012: http://www.sicomin.co.uk/

Ski Builders (2012) Skibuilders.com LLC website [online] Accessed 27th August 2012: http://skibuilders.com/

Skiwax.ca (2012) Skiwax.ca company website [online] Accessed 10th August 2012: http://skiwax.ca/

Slotfeldt -Ellingsen, D. and Torgersen, L. (1983) Water in Ice: Influence on Friction. *Journal of Physics*, 16(1)1715-1719.

Slotfeldt –Ellingsen. (1982) *Gliegenskaper til skisaler i polyetylen*. 1982 Oslo. p. 64.

Spring, E. (1988) A Method for Testing the Gliding Quality of Skis. *Tribologia*, 7(1)9-14.

Stein, H. L. (1998) *Ultrahigh molecular weight polyethylenes (UHMW-PE)*. Engineered Materials Handbook, 2(1)167–171. ASM International

Strausky, H; Krenn, J.R; Leitner, A. and Aussenegg, F.R. (1998) Sliding Plastics on Ice: Fluorescence Spectroscopic Studies on Interface Water Layers in the µm Thickness Regime. *Applied Physics B: Lasers and Optics,* 66(1)599-602.

Shimbo, M. (1971) Friction on Snow of Ski Soles, Unwaxed and Waxed, *Scientific Study of Skiing in Japan*, T.S.o.S. Science, Editor. 1971, Hitachi, Ltd: Tokyo,

Sturesson, P. (2008) Friction Characteristics Between Ski Base and Ice: Fundamental Lab Scale Tests and Practical Implications. UPTEC Q, Uppsala university pp. 1401-5773.

Sturm, M; Holmgren, J and Liston, G, E (1995) A Seasonal Snow Cover Classification Sysem for Local to Global Applications. American Meteorological Society

Styring, P. and Routh, A. F. (2007) Reduction of Friction on Artificial Ski Surfaces: Athlete- Surface Interactions. Proceedings of Science, Technology and Research into Sports Surfaces.

Suwanprateb, K (1998) Time-dependent hardness of particulate-filled composites. Journal of Materials Science, 33(1)4917-4921

Swix (2009) *Swix* company website [Online] Accessed on 15th August 2009: http://www.*Swix*sport.com/

Tang, Z; Wang, M; Zho, Y. and Wu, G. (2010) Tribological Properties of Radiation Cross-linked Polytetrafluoroethylene Sheets. *Journal of Wear*, 269(1)485–490.

Theile, T; Szabo, D; Luthi, A; Rhyner, H; Schneebeli, (2009) Mechanics of the Ski–Snow Contact. *Tribology Letters*. 36(3)223-231,

The Ski Lab (2012) The Ski Lab company website [online] Accessed 23th August 2012: http://www.skilab.com/

Tong, J; Ma, Y; Arnell, R. D; Ten, L. (2005) Free abrasive wear behavior of UHMWPE composites filled with wollastonite fibers. *Composites Part A: Applied Science and Manufacturing* 37(1)38–45

Tognar Toolworks (2012) Tognor Toolworks company website [online] last accessed 21th August 2012: http://www.tognar.com/

Toko (2009) Toko company website [Online], Last accessed on 15th August 2009: http://www.toko.ch

Torris, L; Gentile, C; Visco, A. M; Campo, N. (2003) Wetting modification on uhmw-pe surfaces induced by ion implantation. *Radiation Effects and Defects in Solids*, 158(10)731-741

Unal, H; Sen, U; Mimaroglu, A. (2005) *Abrasive wear behaviour of polymeric materials.* Materials & Design 26(8)705–710

Vola (2012) Vola company website [online] Accessed 21th August 2012: http://www.vola.fr/

Volkl (2012) Volkl company website [online] Accessed 10th August 2012: http://www.volkl.com/

Wang, S and Liang, L (2007) Definition of Superhydrophobic States. *Advanced Materials* 19(21)3423–3424

Werder, T; Walther, J. H; Jaffe, R. L and Koumoutsakos, P (2003). Water-Carbon Interactions: Potential Energy Calibration Using Experimental Data. Proceedings of *Nanotechnology Conference & Trade Show*. 2003. San Francisco, California, U.S.A. 3(1)546-548

Wettlaufer, J. S. (1999) Ice surfaces: Macroscopic Effects of Microscopic Structure. *Philosophical Transactions Royal Society London*, 357(1)3403-3425.

Wier, K. A. and McCarty, T. J. (2006) Condensation on Ultrahydrophobic Surfaces and Its Effect on Droplet Mobility: Ultrahydrophobic Surfaces Are Not Always Water Repellant. *Langmuir* 22(1)2433-2436.

Yang, W. and Ranby, B. (1999) Photoinitiation Performance of Some Ketones in the LDPE-Acrylic Acid Surface Photografting System. *European Polymer Journal*, 35(8)1557-1568.

Zhang, B; Huang, W. and Wang, X. (2012) Biomimetic Surface Design for Ultrahigh Molecular Weight Polyethylene to Improve the Tribological Properties. *Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology* 226(8)705-713

Zisman, W. A. (1964). Relation of equilibrium contact angle to liquid and solid constitution. In R. F. Gould, *Contact angle, wettability and adhesion, advances in chemical series*, Washington, DC: Amer. Chem. Soc. 43(1)1-51.

Appendix

To be inserted in paper copy [datasheet for GUR 4150]

Table 13: Mechanical properties of an epoxy resin commercially available from *Sicomin.*

SR 8500 / SD8603 Resin Mechanical properties			
Cure schedule	168h@23°C	24h@23°C + 24h@40°C	24h@23°C + 16h@60°C
Tensile			
Modulus of elasticity N/mm^2	3680	3620	3350
Maximum resistance N/mm^2	50	85	83
Resistance at break N/mm^2	50	83	81
Elongation at max. resistance %	1.3	3.6	3.6
Elongation at break %	1.3	3.9	4.6
Flexion			
Modulus of elasticity N/mm2	3650	3550	3280
Maximum resistance N/mm2	93	123	124
Elongation at max. resistance %	2.5	4.7	5.5
Elongation at break %	2.5	8.1	8.3
Compressive			
Compressive yield strength N/mm^2			114
Offset compressive yield %			10.2
Charpy impact strength KJ/m^2			
Resilience	15	27	30
Glass Transition / DSC °C			
Tg 1 °C	51	65	81
Tg1 max. °C			88

Table 14: Mechanical properties of SR 8500 with 15 layers of fibre glass reinforcement.

SR 8500/SD8503 Laminated Mechanical Properties		
Reinforcement material	E Glass, 2/2 Twill, 300 g/m^2	
Number of layers	15	
Method	Press	
Weight of reinforcement (Wf)	73	
Cure Schedule	24h@40 °C	16h@60°C
Flexural		
Modulus N/mm^2	25600	25900
Maximum resistance N/mm^2	675	665
Maximum elongation %	3.2	3.2
Bending delamination		
Shear load at break N/mm^2	56	56
Impact (Choc Charpy)		
Resilience KJ/m^2	205	210
Water Absorption % weight		
48 hr water distilled at 70°C	0.28	0.26
Glass Transition		
Tg 1 °C	68	84
Tg1 max. °C		91

Table 15: FIS competition rules 12/13

	Men (M) or Ladies (L)	SL	GS	SG	DH
Ski length (cms)	M	165	185	205 (210)	215 (218)
	L	155	180	200 (205)	210
Minimum Width (mm)		63	65	65	67 (65)
Minimum Width in front of binding (mm)	M		(98)	(95)	(95)
	L		(103)	(95)	(95)
Radius (m)	M		27 (35)	33	45
	F		23 (30)	33	45
Tip Height (mm)		50	50	30	30
Tail Height max (mm)		10	10	10	10

BETWEEN TREATMENTS (COLUMNS)

F>F critical therefore Reject Null Hypothesis

P value does not exceed 0.05 the observation is consistent with the alternative hypothesis.

There is a significant difference between waxes treatments and the hydrophobicity of the surface with 95% confidence.

BETWEEN TESTS (ROWS)

F<F critical therefore accept Null Hypothesis:

P value exceeds 0.05 the observation is consistent with the null hypothesis

There is no significant difference between contact angle tests conducted on each sample with 95% confidence.

Table 16: Two factor ANOVA analysis of the contact angles of manufactures waxes.

Anova: Two-Factor Without Replication with a 5% significance

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
1	5	512.2	102.44	36.4096
2	5	515.7	103.14	13.22815
3	5	514.44	102.888	5.27977
4	5	515.93	103.186	20.28533
5	5	519.31	103.862	17.00547
6	5	518.38	103.676	30.80723
7	5	520.8	104.16	22.514
8	5	520.44	104.088	4.79407
9	5	507.18	101.436	44.56143
10	5	510.2	102.04	33.05985
Untreated base	10	999.83	99.983	5.488223
Ch4	10	1006.8	100.68	11.10744
Universal	10	1010.68	101.068	4.661218
Cera Fluoro	10	1034.91	103.491	2.239277
HF Dibloc yellow	10	1102.36	110.236	3.280027

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	36.96747	9	4.107497	0.724788	0.683214	2.152607
Columns	707.7614	4	176.9403	31.22198	2.96E-11	2.633532
Error	204.0182	36	5.667173			
Total	948.7471	49				

HYPOTHESIS

Null hypothesis: There is no difference between left and right contact angles on each sample.

Hypothesis: There is a significant difference between left and right contact angles on each sample.

Table 17: Results of a Single factor ANOVA analysis conducted on each of the samples

Sample Number	*F*	*P-value*	*F crit*	*P>0.05*	*F>Fcrit*
11	1.170264	0.40228	3.020383	YES	NO
1	11.41115	0.00036	3.020383	NO	YES
8	6.965158	0.001755	2.853625	NO	YES
9	7.428415	0.002137	3.020383	NO	YES
10	1.487009	0.262098	2.853625	YES	NO

Table 18: Detailed Single Factor analysis on sample 10 and 11

Anova: Single Factor **Sample 10**

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Row 1	2	204.96	102.48	0.0002
Row 2	2	205.77	102.885	1.36125
Row 3	2	202.93	101.465	0.07605
Row 4	2	205.09	102.545	16.76205
Row 5	2	207.77	103.885	0.32805
Row 6	2	208.08	104.04	1.5488
Row 7	2	212.37	106.185	0.55125
Row 8	2	209.28	104.64	2.205
Row 9	2	209.84	104.92	6.1952
Row 10	2	203.72	101.86	0.3872
Row 11	2	206.981	103.4905	0.360401

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	40.25125	10	4.025125	1.487009	0.262098	2.853625
Within Groups	29.77545	11	2.706859			
Total	70.0267	21				

Anova: Single Factor **Sample 11**

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Row 1	2	195.76	97.88	1.0658
Row 2	2	201.87	100.935	4.89845
Row 3	2	204.4	102.2	2.6912
Row 4	2	204.31	102.155	7.33445
Row 5	2	204.15	102.075	11.37645
Row 6	2	197.1	98.55	4.9298
Row 7	2	196.94	98.47	60.5
Row 8	2	204.65	102.325	5E-05
Row 9	2	190.99	95.495	0.83205
Row 10	2	199.5	99.75	0.1058

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	98.7242	9	10.96936	1.170264	0.40228	3.020383
Within Groups	93.73405	10	9.373405			
Total	192.4583	19				

An analysis of Single Factor ANOVA indicates there is a difference between left and right contact angles recorded for samples 10 and 11 (untreated base and Cera Fluoro) because P>0.05. This possibly indicates the existence of outlying results between measured left and right angles which are highlighted. This is also indicated on the box and whisker plot (Figure 30) in section 6.1 with large outlining values (long tails) on both samples. Whether these results should be discounted from the data set was resolved by conducting a Z-Score which can highlight a high deviation from the statistical mean. The difference between left and right contact angles are all within three standard deviations of the mean and therefore not considered significant outliers. Additionally, the contact angles recorded on samples 11 and 10 were all within two standard deviations from the mean of the data set and are therefore not significant outliers. Using an average contact angle, between left and right, further normalised this data which was provided in the previous section.