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ADVANCED POLYMERIC MATERIALS FOR APPLICATIONS IN TECHNICAL EQUIPMENT FOR SNOW SPORTS

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a Francesca
e a Neva e Alfio

1 Introduction

Today, sports have become a very popular activity in our society with more people than ever practicing them. Furthermore due to the increased participation and interest from the general public, added to the extensive media coverage of sporting events worldwide, sport has evolved in a global business worth around US$600 billion in total. Overall the world sporting goods market is estimated at US$120 billion retail, which can be divided roughly in: footwear accounting for US$30 billion, apparel US$50 billion and equipment US$40 billion [1].

The optimum design of sports equipment requires the application of a number of disciplines, not only for enhanced performance but also to make the equipment as user-friendly as possible from the standpoint of injury avoidance and usage. In recent years the field of sports engineering has grown considerably bringing about great innovation for advances in equipment and understanding as how the tools of sport function and can be modified to move the resulting performance for the athlete up or down. Clearly, this field encompasses numerous different disciplines, such as materials science, mechanical engineering and physics. However, it also necessitates a knowledge of anatomy, physiology and biomechanics. Moreover in designing sports equipment, the various chemical and physical properties of materials must be considered. Among these important characteristics are strength, ductility, stiffness (modulus), temperature capability, damping, forgiveness (a collective term including fracture toughness, fatigue-crack growth rate, etc.) and density. For many high-performance applications, high cost can be accepted, although the level of acceptance depends upon the industry in question.

Over the past two decades technology has completely reshaped the sports industry, diversifying the offer in order to accommodate the different interests and needs of the athletes and also of the consumers in general. Millions of dollars have been spent by the companies on research and development of sport techniques and equipment with the goal of improving athletic performances, increasing revenues and opening new markets. The materials of choice for sports have shown a major evolution over the last 100 years, in fact prior to the mass commercialization and monetization of sports, most games were simply created for leisure using whatever goods and materials were readily available. This meant that early sports equipment was made from natural products such as wood, leather and other animal parts. Nowadays sports equipment uses almost every type of material imaginable, as athletes and designers leverage state-of-the-art materials to maximize human efficiency, performance, comfort and safety. High-technology metals, polymers and ceramics and synthetic-hybrid materials including composites and cellular concepts are easily found in everyday retail products [2]. Among these material classes polymers play a fundamental role due to their unique combination of properties. In fact they combine low density, easiness to manufacture even in complex shapes, durability, flexibility, cost and possibility to tune their properties to fulfil specific needs and requirements. In recent years many advanced polymeric materials found application in the sports industry. For example recently Burton Snowboards collaborated with Loughborough's Sports Technology Institute to develop new and innovative laser-sintering polymers for snowboard binding prototypes. The current state of commercially available laser sintering elastomeric materials were not meeting the requirements for the prototype needs. Based on this, the academic partnership resulted in a targeted polymer selection methodology to identify what makes a material suitable for the laser sintering process and furthermore the selection and testing of a material to address the requirements of the company [3]. Another interesting example of high-tech materials developed for the sports industry is Koroyd [4]. Koroyd is an engineered core with unrivalled consistency of production and performance. Originally developed for use in aerospace applications as a lightweight structural panel, is formed by tens of thousands of co-polymer extruded tubes, thermally welded to create an unparalleled consistent and fully engineered core, Figure 1.1. The inner core material presents a higher melting temperature, whereas the outer core has a lower melting temperature to allow a good thermal welding. The main application is energy absorption, in fact the combination of precise extrusion and unique thermal welding process leads to extremely efficient and consistent energy absorption properties. When impacted the cores crush in a completely controlled manner, decelerating and absorbing the energy from the impact and thus reducing the final trauma levels. Koroyd finds an application as a structural material for helmets and back protectors in different sport disciplines, from winter sports to cycling. Another possible application of Koroyd is its integration in the core of skis or snowboards thanks to its low density, better damping and increased vibration reduction capacity.

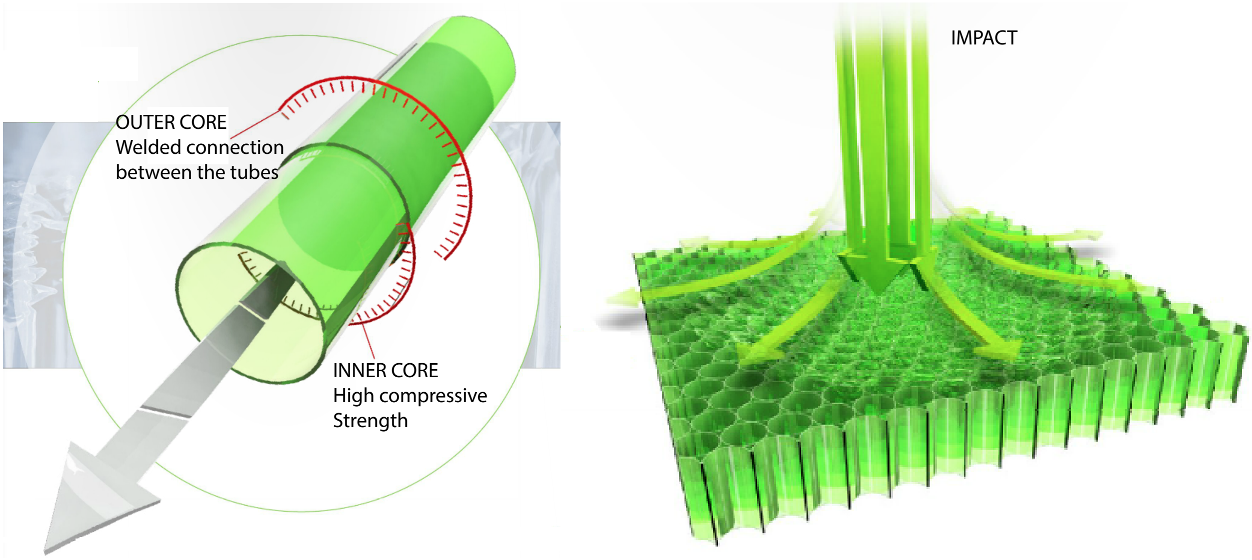

Figure 1.1: Koroyd structure and impact absorption

The introduction of new materials and technologies into equipment and apparel has brought sensible improvements and changes in sports, however recently the research is focused on multifunctional materials and adaptive technologies. One of the main topics is performance measurement and in particular real-time feedback. In 2012, the US sports brand Nike introduced on the market the Nike+ Sports Sensor, a system made from four different sensors inside the sole of the shoes which are strategically placed underneath your feet (big toe, heel, etc.) to spit out accurate readings. The sport sensor uses pressure data in combination with an accelerometer to calculate movement, that way Nike+ Sports Sensor can measure the height of the jump, speed and other information useful during training or performance analysis [5]. Moreover Kim et al, from the University of Illinois, have developed sensors able to monitor the bodily functions which are both stretchable and flexible to conform to the skin surface without breaking under deformation [6].

Snow sports have not seen a major influence of technology in the last thirty years. The construction of skis and snowboards is still based on the sandwich design first introduced by Head in the 1950s. Nevertheless the ski industry has seen some advances in the manufacturing technology and durability of the products during the years [7]. The materials used also have not changed much, besides the introduction of new fibers with low density and high stiffness, such as carbon and aramidic fibers. A similar situation can be found in the ski boot industry. In fact, also in this case carbon fiber finds some applications mainly limited to the ski mountaineering boots where lightness is of paramount importance. In all the other application thermoplastic polymers are still playing a fundamental role, with polyolefines, polyrethanes and nylons as the most commonly used. The reason for the longevity of these materials in the ski boot industry can be found in the limited cost, good impact resistance at low temperature, stiffness, low density and ease of manufacturing in complex shapes by injection moulding. The main technological advances are related to the customization of the shape of the boots and on the materials for the liners. In fact, in recent years, ski-boot producers have focused their attention on the development of new methods for the modification of the shape of the inner and outer part of the ski-boot to adapt to the shape of the skiers foot [8]. If the temperature of the shell and cuff is maintained between the melting temperature and the heat distortion temperature the plastic can be deformed using pressure. If the boot is then cooled to room temperature, the deformation can be permanently maintained. For this reason, new polymeric systems have been patented in order to obtain materials with an optimized softening temperature. Salomon has patented the use of a blend of polycaprolactone with polyurethane in order to decrease the softening temperature of polyurethanes. The DMTA curves in Figure 1.2 show that the polymer blends present a decreased softening point without significantly affecting the stiffness below $+40°C$ which depends on the amount of polycaprolactone added to the system.

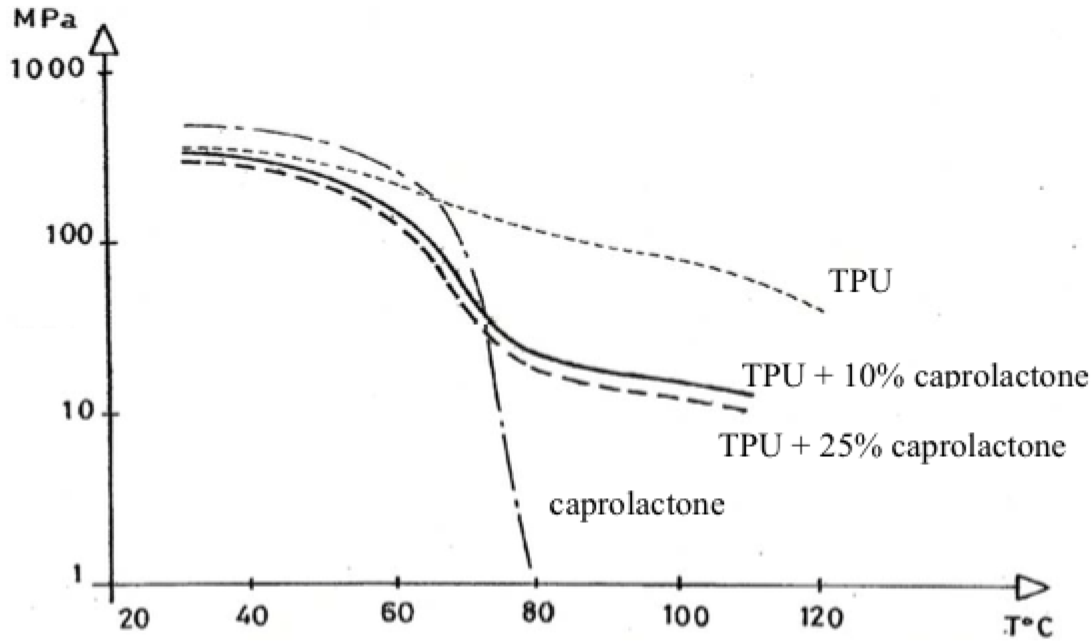

Figure 1.2: DMTA analysis of plastic for thermo-formable shell and cuff (adapted from USPat Appl 20080000109).

More recently, Fischer has patented a blend of nylon with a ionomer (polymer containing ionic groups) composed of a copolymer of ethylene and methacrylic acid (EMAA) to obtain a material very soft at $+80°C$ that could be shaped around a skiers feet applying an external pressure with a dedicated apparatus that involves a sealed bag to produce a pressure on the ski-boot after heating. The main difference between the two methods is in the pressure application. In fact in the Fischer's method the shell is adapted by external pressure on the skiers foot while in the method patented by Salomon it is the foot pressure that enlarges the shell.

Another part of the ski boot that has seen an evolution in the last years is the liner, also known as inner boot. The liner's main function is to provide thermal insulation, cushioning and comfort. The inner boots are generally formed of several parts glued or sewed. Traditional liners (Figure 1.3 a), are made of a mix of preformed ethylene vinyl acetate (EVA) and others foams with the upper layer made of polyethylene (PE) or polyvinyl chloride (PVC) and with the lower sole made of PVC. Recently a new kind of liner fully made of a mix of different density closed cell EVA foam partially cross-linked has been introduced (Figure 1.3 b). EVA has also the ability to be fitted by heating and formed on the shape of the skiers foot (thermo-formable liner) since it has a softening point of $+90°C$ (that can slightly change depending on the density and cross-linking) allowing changes in the shape of the foam and retaining these changes after cooling [8]. This new design has the advantage of improving the comfort of the wearer, thanks to the thermo-formability, as well as reducing the weight, due to the low density of EVA. Furthermore closed cell EVA liners have a higher thermal insulation with respect to open cell materials. However, the higher insulation is also combined with a lower permeability to moisture and therefore a higher humidity build-up inside the liner.

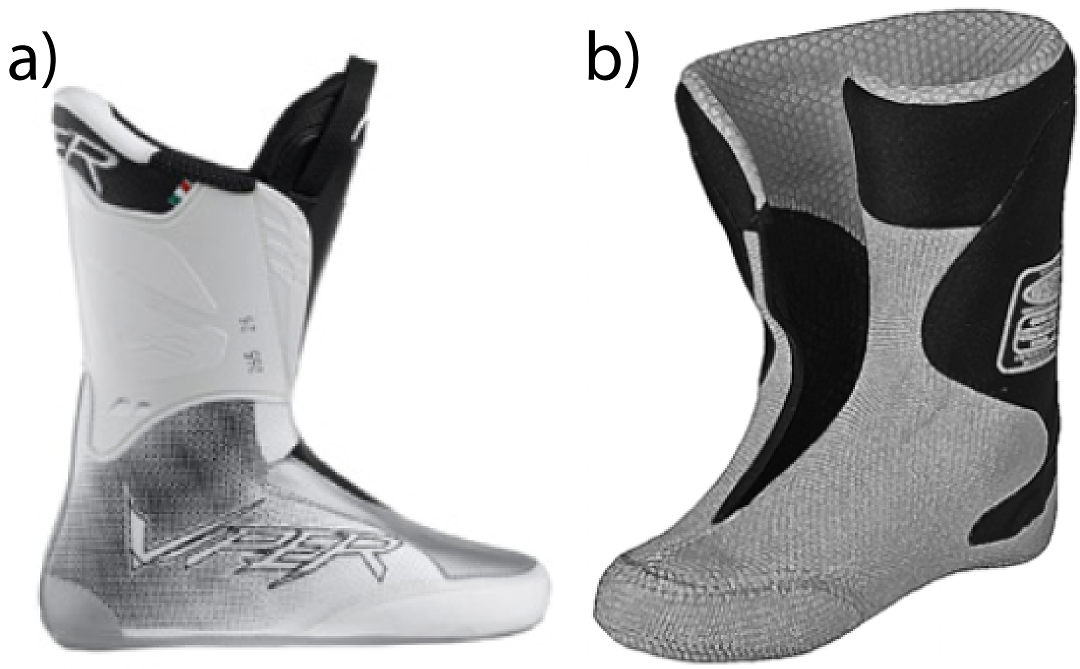

Figure 1.3: a) Traditional liner b) Liner made of closed cell EVA foam.

The main objective of this thesis is to introduce a scientific approach in the selection and development of new polymeric materials and technologies for snow sports. In particular the aim is to find a correlation between the physical and chemical properties of the materials used and the mechanical behaviour of the final products. This can be then used during the design process to reduce costs and time as well as improve performance. In fact the knowledge of the influence of the materials on the final products can lead to the development of specific and tailor made solutions for a certain application.

The thesis is divided in three chapters, each one covering one topic.

In the first chapter, the thermo-mechanical and impact properties of materials used for hard-shell and soft-shell back protectors have been analysed in order to understand the mechanism of action of the foams used for protective equipment. Dynamical mechanical analysis has shown that materials used for soft-shell protectors present frequency-sensitive properties that permit to have a soft response when stressed at low speed and a hard response when subjected to a high-speed impact. Furthermore, by means of drop weight impact tests, the shock absorbing characteristics of the materials have been investigated at two temperatures pointing out the differences between soft and hard-shell protectors; in addition it has been demonstrated that the materials used for soft-shell protectors maintain their protective properties after multi-impacts on the same point.

The second chapter covers the effect of the visco-elastic properties of the thermoplastic polymers on the flexural and rebound behaviours of ski boots for alpine skiing. Dynamic mechanical thermal analysis (DMTA) has been performed in a temperature range between $-30°C$ and $+50°C$. Also, the flexural and rebound behaviours of the boot have been tested using specially designed test benches. The DMTA analysis results and the flexural and rebound tests results were compared and a correlation between the visco-elastic properties and the flexural and rebound behaviour of ski boots was found. Therefore, DMTA analysis can be used in a knowledge based design process of new ski boots in order to improve on-snow performances. The same experimental methods were used to investigate the influence of the design of the ski boot on the flexural and rebound behaviour.

Finally in the third chapter the thermoplastic materials employed for the construction of ski boots soles used for alpine skiing have been characterized in terms of chemical composition, hardness, crystallinity, surface roughness and coefficient of friction (COF). The results obtained proved a relation between material hardness and grip, in particular softer materials provide more grip with respect to harder materials. On the contrary, the surface roughness has a negative effect on friction since the materials with the highest Sa (arithmetic mean high) have the lower coefficient of friction, because of the decrease in contact area. The measure of grip on inclined wet surfaces showed again a relation between hardness and grip, the softer materials having the best performances. The performance ranking of the different materials has been the same for the COF and for the slip angle tests, indicating that COF can be used as a parameter for the choice of the optimal material to be used for the soles of ski boots. The comparison of different sole treads indicates that the best results in terms of anti-slip behaviour are obtained with the soles that present the wider contact area with the ground.

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2 Thermo-mechanical and impact properties of polymeric foams used for snow sports protective equipment

The thermo-mechanical and impact properties of materials used for hard-shell and soft-shell back protectors have been analysed in order to understand the mechanism of action of the foams used for protective equipment. Dynamical mechanical analysis has shown that materials used for soft-shell protectors present frequency-sensitive properties that permit to have a soft response when stressed at low speed and a hard response when subjected to a high-speed impact. Furthermore, by means of drop weight impact tests, the shock absorbing characteristics of the materials have been investigated at two temperatures pointing out the differences between soft and hard-shell protectors; in addition it has been demonstrated that the materials used for soft-shell protectors maintain their protective properties after multi-impacts on the same point.

2.1 Introduction

Winter sports are very popular, performed by an estimated 200 million people in the world each year, including different sexes, ages and skill groups. This number is in constant growth thanks to the increasing development of new terrains together with an advance in materials and technology. The fact that winter sports are generally high-energy outdoor activities involving high velocity, jumps and acrobatic manoeuvres, coupled with an increasing congestion on ski slopes raises safety concerns. In particular about falls and collisions. These impacts produce significant traumatic injuries, with an average of around 1.5/1000 skiers/day [1]. The statistics of the distribution of these injuries over the body have discording results depending on the country taken into exam [2, 3]. Nevertheless, all the studies agree that the most affected areas are head and brain, shoulders, spine, neck and knees. Due to the high healthcare expenses connected with these injuries and a constant risk of death and permanent damage, there is a strong interest in prevention. This can be done on different levels, from regulation of ski slope activities to the development of more efficient protective equipment such as helmets and back protectors. A first step towards reducing skier's risk of injury depends on the risk-taking behaviour and the knowledge of proper ski behaviour [4]. With the goal of promoting safe skiing the International Ski Federation introduced rules in 1967 that apply to all skiers and snowboarders and are given significant weight in legal proceedings. Furthermore the improvement of protective equipment can play an important role in prevention, in fact it has been demonstrated that wearing helmets reduces the occurence of head injuries, minimizing the damage to the head [5]. The energy absorbing material inside the helmet accomplishes its protective function by compressing during the impact and slowly restoring to its original shape. The compression and restoration prolongs the duration of the collision and absorbs part of the force, reducing the total momentum transferred to the head [6]. Nevertheless helmets are currently not generally accepted as an integral part of ski and snowboard equipment and just a few countries (i.e. Italy, Austria and Croatia) have made helmet use for children compulsory [7]. The usage statistics and specific studies on back protectors are very limited. An analysis of the changes in the behaviour of wearing protective equipment by alpine skiers and snowboarders after injury showed an increase from 14.3% to 23.8% with a doubling of the wearing rate for the skiers [8]. Michel et al [9] have conducted an overview of the potential protective effects of back protectors combining an athlete survey with experimental performance tests (free falling impact testing). A total of 3263 athletes participated in the survey, partly through personal interviews on the slopes and partly through an on-line survery. The final results showed that back protectors are considered a very important piece of protection from severe spinal injuries. Despite the protective expectations of the skiers and snowboarders there is no specific performance standard related to snow sports. The industry is currently using motorcycling standards to test impact performances [10, 11] and market their products. The laboratory test was conducted in accordance with the EN 1621-2 standard; the norm specifies the minimum coverage to be provided by the back protector as well as the requirements for the protectors under impact and the test methodology [11]. Two levels of protection are defined, based on the measurement of the transmitted force through the protector when hit by a falling mass with an energy of 50 J. The highest level of protection being level 2, when the average force measured in the five tests required is below 9 kN with no individual measure exceeding 12 kN; and the lowest being level 1 for an average force below 18 kN with no individual value exceeding 24 kN. A total of twelve back protectors with different designs, materials and covered body regions were investigated. Ten out of twelve passed the protection level 1, fulfilling the minimum protection requirements; from these ten just six passed the protection level 2. The authors question the suitability of the loading scenario to the context of skiing and the customers expectation. In fact back protectors do not protect the spinal column when an axial force is applied (i.e. head-on impact) being design for a force applied perpendicularly to the device (i.e. fall on a curb side or crash barrier on the side of the road). In addition the back protectors have little influence over the torsional movements of the trunk [9]. Further studies by the same group [12], performed using the same approach of combining surveys with laboratory testing, confirmed the inappropriacy of the current testing standards with respect to snow sports. Further studies on the mechanism of spinal injuries to get a better biomechanical understanding were suggested. On the same topic Engsberg et al [13] designed and developed a device, called SCIBITS, able to protect against both spinal cord and brain injuries. The basic idea is a head shield with a plastic foam lining mounted on a thoracic jacket, where the protective concept lays in the transfer of the impact loads from the head shield to the trunk via the structural members connecting the head shield to the vest. The SCIBITS has not been made to be worn by humans, but just as a test structure to be used as part of the development of a testing method for this kind of injuries. All the laboratory experiments lead to the demonstration of the effectiveness of the protective concept.

Free fall testing is a common technique in the assessment of the shock absorbing properties and has been applied in different fields (i.e. sports, military, health care). Verdejo in her doctoral thesis studied how the ageing mechanisms affect the thermal and mechanical properties of EVA foams used in running shoes [14], focusing on the macroscopic characterization performed by means of dynamic mechanical thermal analysis and impact testing. Typical results obtained are shown in Fig. 2.1, where the force-displacement behaviour for the 1st impact for three EVA is reported, all medium density foams (≈ 150 kg/m^3) with different amount of blowing agent.

It can be seen that EVA 146 and EVA 151 have a similar behaviour with a yield point slightly above that of EVA 152, with the densification occurring at larger strain values. This implies their peak force, for the same displacement, is lower than the one of EVA 152, absorbing more energy than the EVA 152. Therefore, these two foams are better shock absorbers. Moreover the behaviour of the foams over a large number of impacts has been investigated. The samples were struck up to 100 times, with data collected every 25 cycle. An example of the results is reported in Fig. 2.2.

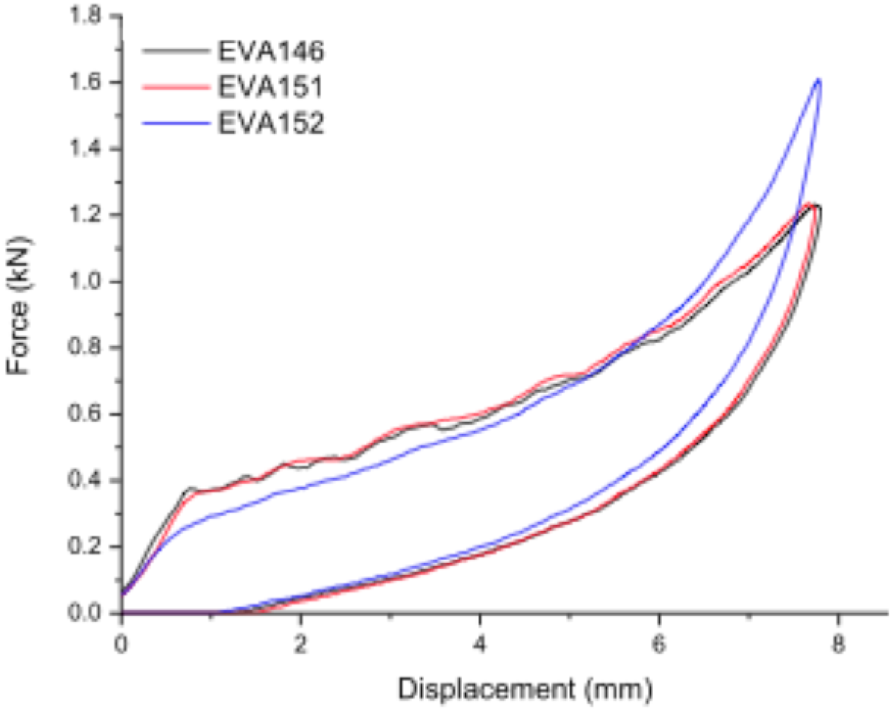

Figure 2.1: Force-displacement behaviour for the 1^{st} impact

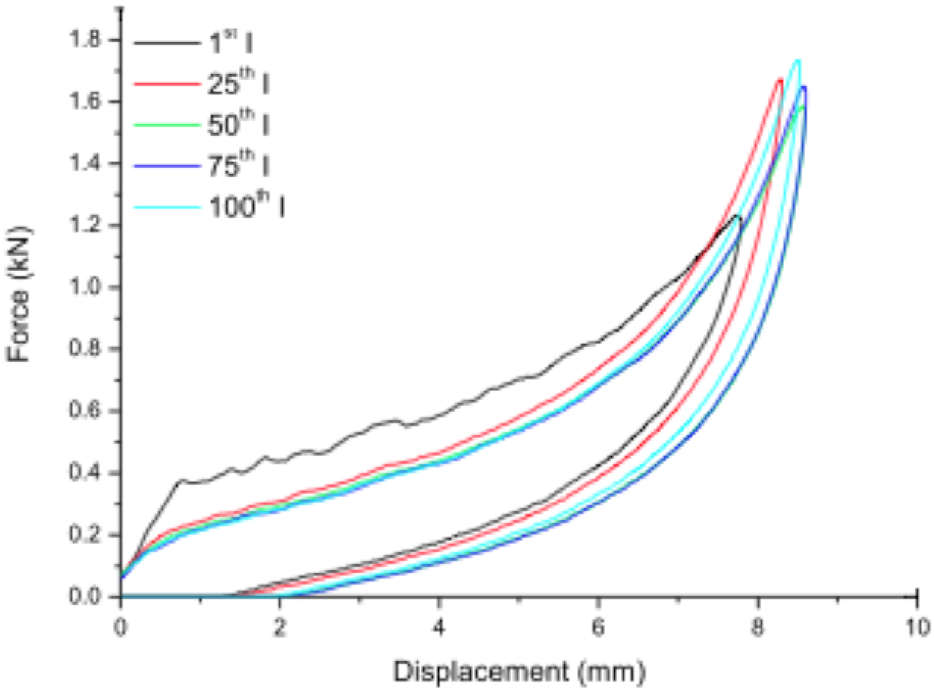

Figure 2.2: Force-displacement of EVA 146 over 100 impacts

The first impact curve shows a clear elastic region after which a constant slope of plastic deformation takes place, the typical behaviour of viscoelastic foams. This behaviour is maintained also in the following impacts but with a lower yield point and an increase of the peak deflection and force. In a different study Bulat et al [15] tryed to determine if the protective properties change in different types of hip protectors after repeated, simulated falls. A total of five models, including hard plastic shell, soft foam pads and hybrid pads were tested in a vertical impact testing tower. The results showed that the protective properties diminish after multiple impacts for all the samples. However in most cases the mean force that passes through the protective pad was below the hip fracture threshold of 3100 N.

In order to get a good understanding of the curves an explanation of the energy absorption mechanisms of foams under compressive loading is needed. Polymeric foams are two phase materials, made up by a solid cellular structure with a fluid phase dispersed in it. Thanks to this structure polymeric foams can undergo large compressive deformations and absorb considerable amounts of energy. This behaviour can be explained with the bending, and subsequent compression of the fluid in the cells, followed by buckling or fracture of the cells that constitute the foam's structure. Three regions are clearly visible in a compressive stress strain curve: linear elasticity, plateau and densification [16]. For small strains it is clearly visible a linear elastic behaviour, with the slope equal to the Youngs modulus of the foam. This region is controlled by cell walls bending and stretching. As the load increases there is a plateau where the deformation is elastic but not linear. This region is controlled by elastic buckling in elastic foams, plastic yielding in plastic foams and brittle crushing in brittle foams. The transition between the elastic region and the plateau is the yield point. The behaviour changes once the opposite walls meet and touch (collapse), a process known as densification which lads to a sharp increase of the stress. Although structural properties are different a very similar behaviour is shown by soft polymeric foams, and the same features can also be observed in a force-displacement diagram. Moreover thanks to the flat and long plateau of the stress-strain curve the force does not reach high values, thus, resulting in non-dangerous decelerations on the body. In Fig. 2.3 a typical compressive stress-strain curve for a polymeric foam is shown.

Manufacturers of protective gear for winter sports (i.e. back, hip, elbow or chest protectors) have been focused, in recent years, on the development of new soft shock adsorbing materials based on polymeric foams, thanks to their superior impact absorption properties. Historically, all the protectors had a hard-shell construction consisting of a hard outer shell of thermoplastic material (i.e. polypropylene) with an inner soft padding foam and some textiles, forming the lining. In these products the shock attenuation technology, coming from the motorcycling industry, is based on the concept of distributing the force

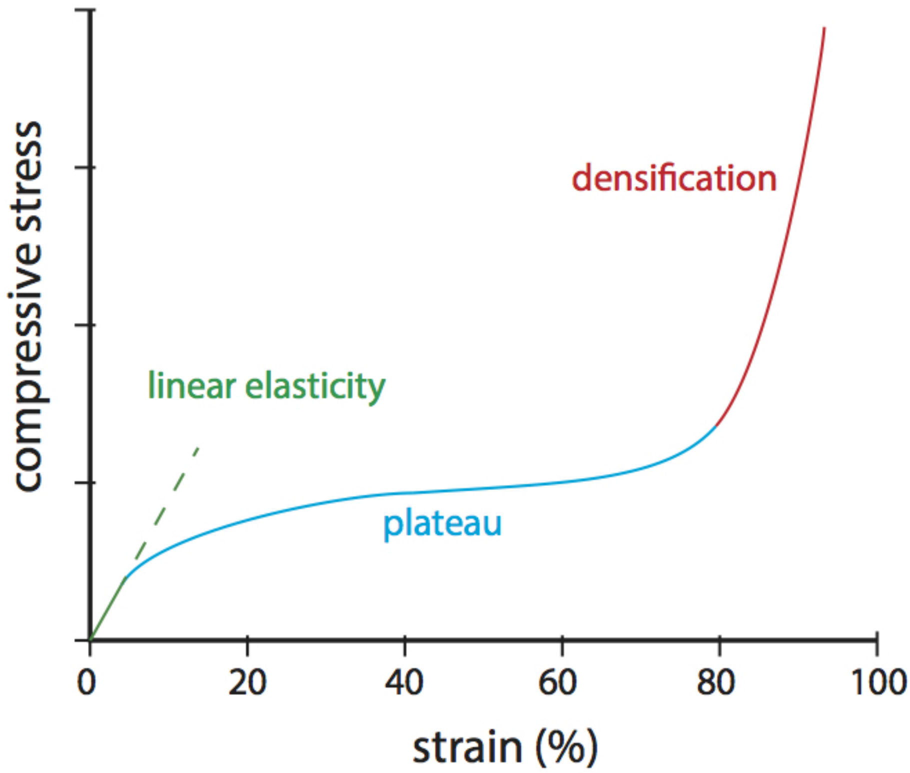

Figure 2.3: Typical compressive stress-strain curve

of the impact over a wider area using a rigid material. The hard armour back protectors are designed to resist abrasive and puncture injuries. The main disadvantage of this construction is not allowing a good air flow and thus increasing the temperature and sweating on the back resulting in a poor thermal comfort. Besides the poor thermal comfort, even the ergonomic comfort is low, in fact the rigidity of the outer shell does not allow complete freedom of movements and can lead to compression of the contact zones with the body, resulting in pain or discomfort. To overcome these problems, recently the market has seen an increasing number of products based on the new soft-shell technology adopting soft polymeric foams. As explained previously, in these materials the protection is given by the fact that the foam dissipates energy to deform the structure of its walls and time to compress the fluid within the foam cells. Resulting in an increase of the impact time or impulse of the collision. Trauma to the body is prevented by three methods: shock absorption (impact energy absorption), delay (increased time of transmission of the shock) and dissipation (dissipation of the impact over larger areas of the body). The pseudo dilatant nature of the polymeric foams ensures an adaptive behaviour, reacting like hard and rigid materials when exposed to a high deformation rate, such as those induced by an impact, and like soft viscous materials at low rate of deformation [17]. This behaviour enables a high level of protection in case of crash as well as a good flexibility and comfort during movements. Indeed, the new soft polymeric foams have higher comfort both from an ergonomic (due to the softness of the material) and thermal (since the production processes and the material characteristics allow to obtain breathable perforated structures) points of views. Furthermore the low density of the materials allows the production of lightweight protectors with a limited thickness, increasing the anatomical and ergonomical comfort. Usually the protector elements are enclosed in a high resistance stretch fabric vest which adheres perfectly to the body and retains the correct position of the protector element during a crash.

The goal of the present study was to investigate the properties, in terms of visco-elastic and impact behaviour, of materials used for commercially available back protectors, and to identify the effect of multi-impacts and temperature on the shock absorption properties, correlating the differences with the characteristics of the materials used.

2.2 Materials and Methods

2.2.1 Materials

In this work a total of five back protectors have been tested, the samples are shown in Fig. 2.4. All the samples are commercially available products in size L, no modification has been performed.

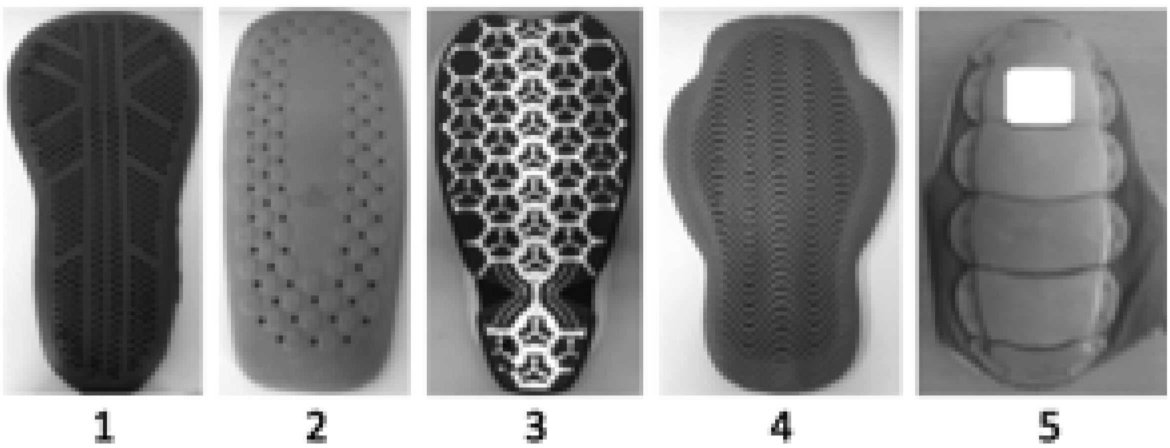

Figure 2.4: Commercial back protectors tested

Protectors 1, 2, 3 and 4 are based on the "soft-shell" technology, whereas protector 5 is a "hard-shell" motorcycling back protector consisting of a hard outer shell of thermoplastic material with multiple layers of inner soft padding foams. According to the manufacturers protector 1, 2, 4 and 5 have a certified protection level of 2, and protector 3 has a level

1. The certification is based on the European standard EN 1621-2. No tests have been performed to confirm the protection level stated by the manufacturers. Table 2.1 reports the characteristics of the protectors tested in this work. The density goes from 0.15 g/cm^3 of protector 1, being the lightest, to 0.35 g/cm^3 of protectors 2 and 4. The density of protector 5 is not reported since it is composed of multiple materials. Finally there is a significant difference in thickness between the "soft-shell" and "hard shell" technologies. In fact protector 1 and 3 are 16 mm thick, protector 2 is 19 mm thick and protector 4 is 18 mm. On the other hand protector 5 has a thickness of 30 mm. Furthermore protector 5 is not flat, but presents a curvature, which will affect the impact testing results.

Protector	**Construction**	**Protection level** $(EN1621-2)$	**Mass** $[g]$	**Density** $[g/cm^3]$	**Thickness** $[mm]$
1	Soft-shell	2	283	0.15	16
2	Soft-shell	2	657	0.35	19
3	Soft-shell	1	325	0.22	16
4	Soft-shell	2	472	0.35	18
5	Hard-shell	2	525	n/a	30

Table 2.1: Characteristics of the protectors tested

2.2.2 Methods

Fourier Transform Infrared Spectroscopy (FT-IR)

A common method to detect the chemical composition of polymers is based on infrared spectroscopy. In general an IR spectrum is obtained by scanning a sample with IR radiation and detecting the transmitted light. When the frequency of the incident IR beam is the same as the vibrational frequency of a molecular bond, absorption occurs. Consequently each peak in the spectrum corresponds to a functional group present in the molecule. In Fig. 2.5 a typical spectrum is reported with peaks corresponding to the most common functional groups. The graph reports the IR light absorbance on the y axis and the wave numbers (number of waves per unit distance) on the x axis.

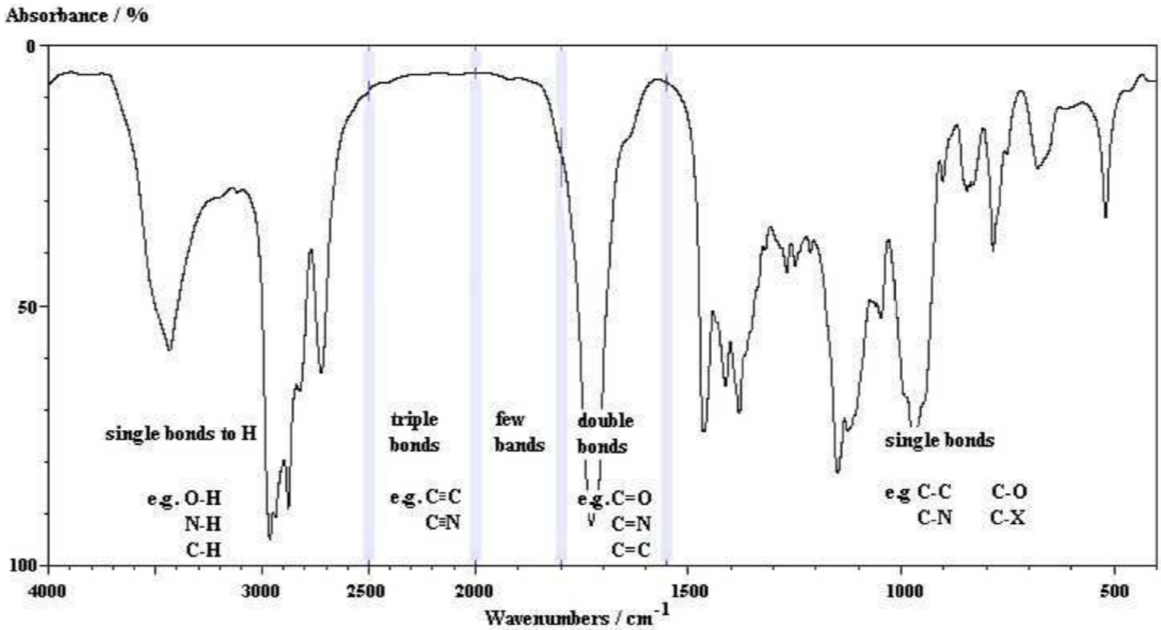

Figure 2.5: IR spectra reporting the peaks of the typical functional groups

Although IR spectroscopy is used to analyse a wide range of materials, it often requires some sort of sample preparation in order to obtain a good quality spectrum. In the case of a solid the preparation consists in grinding the material to a fine powder and dispersing it in a matrix. The mull obtained is then spread in the form of a thin film between two mid-infrared transparent windows (e.g. NaCl, KBr) and placed in the spectrometer. The complexity of the sample preparation leads to reproducibility issues and to overcome these problems in recent years a new technique has been developed: Attenuated Total Reflectance. In this method an IR beam is directed onto an optically dense crystal with a high refractive index, creating an evanescent wave due to the high internal refractance. This wave extends beyond the surface of the crystal for a few microns into the sample held in contact with the crystal. The evanescent wave will be attenuated or altered in the regions of the IR spectrum where the sample absorbs energy. At the end exits from the opposite side of the crystal and is passed to the detector of the IR spectrometer. A schematic of the FT-IR ATR system is shown in Fig. 2.6.

The chemical composition has been determined by Fourier transform infrared spectroscopy (FT-IR) with a Perkin Elmer Spectrum One instrument, using an Attenuated Total Reflectance (ATR) detector. Wavelength range varies between 4000 and 650 cm^{-1}, each spectrum is the result of 32 scans with a resolution of 4 cm^{-1}.

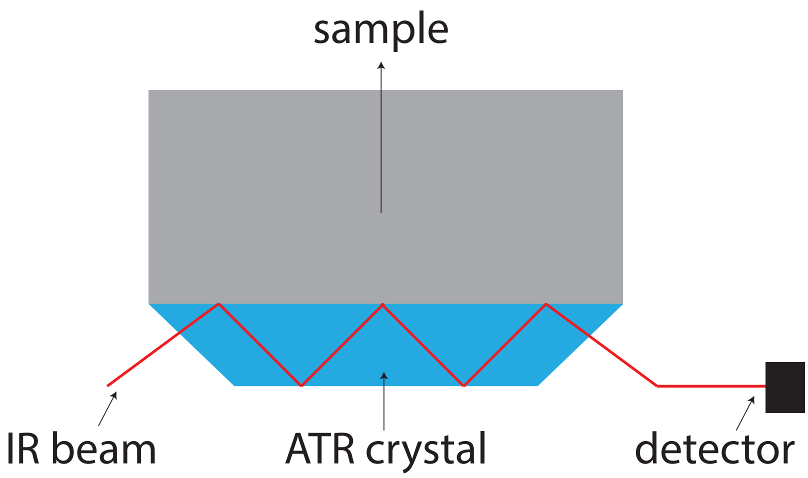

Figure 2.6: FT-IR ATR system

Hardness testing

Hardness measurements were performed using a Hildebrand Shore A durometer at 23°C according to the specification of the norm ISO 868. In this method a specified indenter is forced into the sample and the depth of the penetration after 15 sec is measured. The hardness is inversely related to the penetration and is correlated with the elastic modulus of the material. Die-cutted samples with size 10x10 cm were directly obtained from the protectors, maintaing the original thickness of the protectors. For each sample a total of five measurements were preformed and the from the results the mean values were calculated.

Scanning Electron Microscopy (SEM)

The scanning electron microscope (SEM) forms high resolution images of the surface of an object by scanning it with a focused beam of electrons. The electrons interact with a thin layer of the surface and generate a variety of signals which can give information about the sample external morphology, chemical composition, crystalline structure and orientation. The high spacial resolution of the SEM makes it a powerful tool to characterise a wide range of specimens at the nanometre to micrometre length scales.

Non-conductive samples tend to charge when scanned by the electron beam causing scanning faults and other image artefacts. To avoid this problem they are usually coated with and ultrathin coating of conduction material, i.e. gold, in a process known as gold sputter coating. In this process the samples, mounted on a sample holder or stub, are positioned in a cylindrical chamber under a gold foil. First of all vacuum is created in the chamber and maintained throughout the whole experiment. The purpose of the vacuum is to evacuate atmospheric gases and eliminate all the gases and vapours from the samples. The chamber is then filled with argon in order to further clean the environment and the surface of the samples. This is done to avoid any oxidation and thus damaging of the gold foil during the metallization. At this point a potential difference is applied between the sample holder and the gold foil provoking the oxidation of the argon inside the chamber. The argon ions are accelerated by the electric field towards the gold foil and upon impact cause the separation of gold particles. These particles due to gravity fall on the samples creating the conductive layer. The instrument is equipped with a crystal able to detect the thickness of the layer, which usually is set at 10 nm.

Cross-sections of the foams were obtained by fracturing the protectors at low temperature, after immersion in liquid nitrogen. The samples were examined using a Nova NanoSEM 450 scanning microscope.

Dynamic Mechanical Thermal Analysis (DMTA)

Dynamic Mechanical Thermal Analysis (DMTA) is a powerful tool used for the characterization of polymers and polymeric foams [18]. This technique is performed applying an oscillatory force to a sample and analyzing the material's response to that force. Due to the visco-elastic nature of the material, the oscillatory force will cause a sinusoidal stress to be applied on the material, which generates a sinusoidal strain with the same frequency but out of phase by a phase angle δ. This is valid if the material is kept within its linear viscoelastic region, i.e. low stress. A schematic view of the behaviour is given in Fig. 2.7. The phase lag is due to the excess time necessary for molecular motion and relaxation to occur.

For any point on the curve the stress applied can be determined as

$$\sigma = \sigma_0 sin(\omega t) \tag{2.1}$$

where σ_0 is the maximum stress, ω is the frequency of the oscillation and t is the time. The elastic response at any time for a visco-elastic material will be

$$\begin{aligned} \varepsilon &= \varepsilon_0 sin(\omega t + \delta) \\ &= \varepsilon_0 [sin(\omega t) cos\delta + cos(\omega t) sin\delta] \end{aligned}$$

This equation can be then braked in the in-phase and out-of-fase strains

$$\varepsilon' = \varepsilon_0 sin(\delta) \qquad \varepsilon" = \varepsilon_0 cos(\delta) \tag{2.2}$$

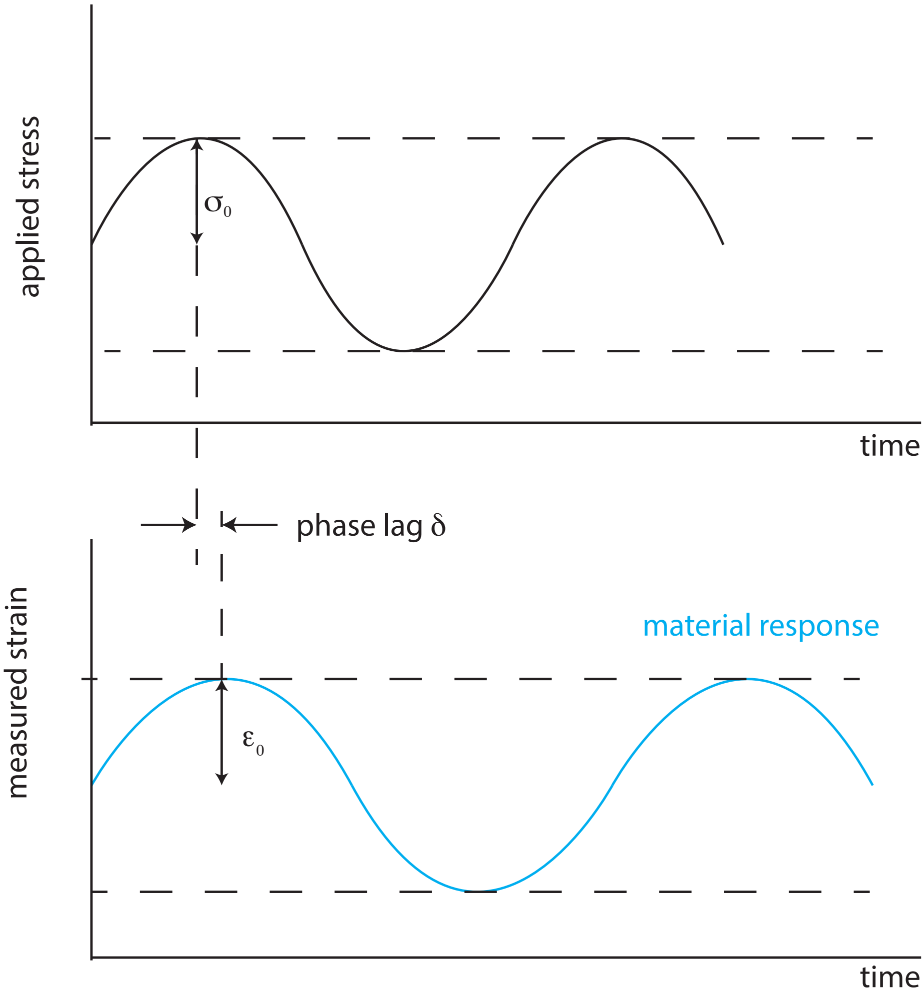

Figure 2.7: Sinusoidal stress applied during DMTA induces a sinusoidal strain out of phase

and the vector sum of these two components gives the complex strain of the sample

$$\varepsilon* = \varepsilon' + \varepsilon" \quad (2.3)$$

From these data is possible to calculate:

- The storage or elastic modulus (E')

$$E' = \frac{\sigma_0}{\varepsilon_0} cos(\delta) \quad (2.4)$$

  which is a measure of the elastic behaviour of the material and can be related to the energy stored during the deformation and then recovered. Furthermore for low and medium damping can be considered equivalent to the Young's modulus and thus give information on the stiffness of the material

- The loss modulus (E")

$$E' = \frac{\sigma_0}{\varepsilon_0} sin(\delta) \quad (2.5)$$

  which is a measure of the viscous behaviour of the material and can be related to the dissipated energy in the form of heat during deformation

- The loss tangent or damping (tan δ)

$$tan\delta = \frac{E"}{E'} = \frac{\varepsilon"}{\varepsilon'} \quad (2.6)$$

  which is a measure of how efficiently the material loses energy to molecular rearrangements and internal frictions. Being the ratio of the storage to loss modulus is independent of geometry effects

DMTA tests have been performed with a Rheometrics Dynamic mechanic thermal analyser DMTA 3E model, using a single cantilever bending geometry and applying a strain of 0.1%. The samples with dimensions 20x8x4 mm were die-cut directly from the protectors. In order to obtain a complete understanding of the materials' properties and their variation with frequency and temperature, three frequencies were used (1 Hz, 10 Hz and 50 Hz) in a temperature range between $-50°C$ and $+50°C$ (heating rate of $3°C/min$)).

Impact testing

Polymeric foams are often used as shock absorbers, mainly to minimize the kinetic energy produced by an impact. For this reason the main engineering parameter is the amount of energy that the material can absorb. To measure the shock absorbing properties falling weight impact testing can be performed resulting in force-displacement curves. The absorbed energy (E_a) can be calculated as $E_a = E_i + E_r$ where E_i is the impact energy (loading energy) and E_r is the recovery energy (unloading energy). These parameters are calculated by integrating the force against the displacement, Fig. 2.8.

$$E_i = \int_0^{xm} F \, \mathrm{d}x \tag{2.7}$$

$$E_r = \int_{xm}^{xf} F \, \mathrm{d}x \tag{2.8}$$

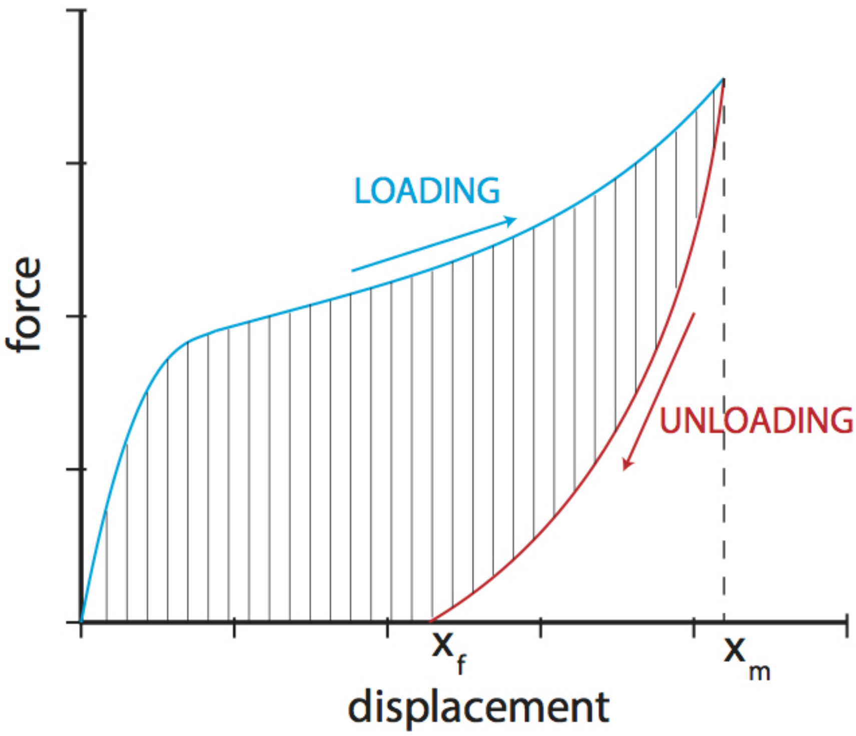

Figure 2.8: Force-displacement curve; E_a vertical lines

Furthermore impact protection is provided by increasing the time of impact and decreasing the peak force. In this way the energy transfer rate to the body is reduced, resulting in a less traumatic impact event. For these reasons a good impact protector will have a low peak impact force distributed over a longer time [19]. Elastomeric foams can achieve this effect by using energy to deform the structure of its walls and compress the fluid within the cells.

Impact tests have been performed using an Instron Dynatup 9250 HV drop weight impact testing machine. This setup is a gravity driven test instrument that is used to test the impact characteristics of an extensive variety of materials.

The basic assembly is illustrated in Fig. 2.9 and can be described as follows [20]:

- Drop weight and tup: the drop weight is formed by a frame bolted to two bearing housings that run on the tower columns. The frame contains two threaded studs that locate the weights that may be added to the drop weight to adjust its overall weight. On the bottom of the drop weight is fixed an instrumented tup that measures the loads generated during the impact test. The tup consists of two parts: the load cell for measuring the impact force (sampling rate 500 Hz) and the impactor which is the component that strikes the sample. For this study a flat circular impact head with a diameter of 4.5 cm was used

- Velocity flag and detector: the velocity detector is mounted inside the tower enclosure and works in conjunction with a flag mounted on the drop weight. By adjusting the position of the velocity detector is possible to measure the velocity of the drop weight immediately before the impact and trigger the data acquisition

- Drop tower framework: the framework is a rigid rectangular frame consisting of a steel table plate, aluminium top plate and two steel side columns. The frame is then further enclosed in a clear polycarbonate box with a door on the front, it provides protection from flying debris and prevents entry in the test area. On the steel table plate are usually fixed anvils that hold the specimen during the testing. Many different shapes of anvils are available to accommodate various test specifications and techniques. For this study a flat aluminum anvil was used, with the specimens fixed on it by double sided tape

To avoid the influence of the curvature of the protectors the impacts have been performed only on flat sections; a total of two tests per sample have been performed to ensure the consistency of the results. The samples have been tested at $20°C$ and after being kept at $-5°C$ for 24 hours. The total testing time was below 30 seconds, so it can be assumed that the samples maintained their temperature during the tests. All the samples were impacted using a mass of 5 kg dropped from a height of 1 meter, to ensure an impact energy of 50 J, with a sampling rate of 600 Hz. From the data set recorded during the test the software was able to calculate the deflection of the sample using the load-time curve and the impact velocity. Furthermore the energy absorbed by the sample has been derived from the area under the load-deflection curve. This type of tests provide a more complete information set (impact time and force, depth of penetration, etc.) on the material properties compared to the EN 1621-2 norm, which only measures the transmitted force [11].

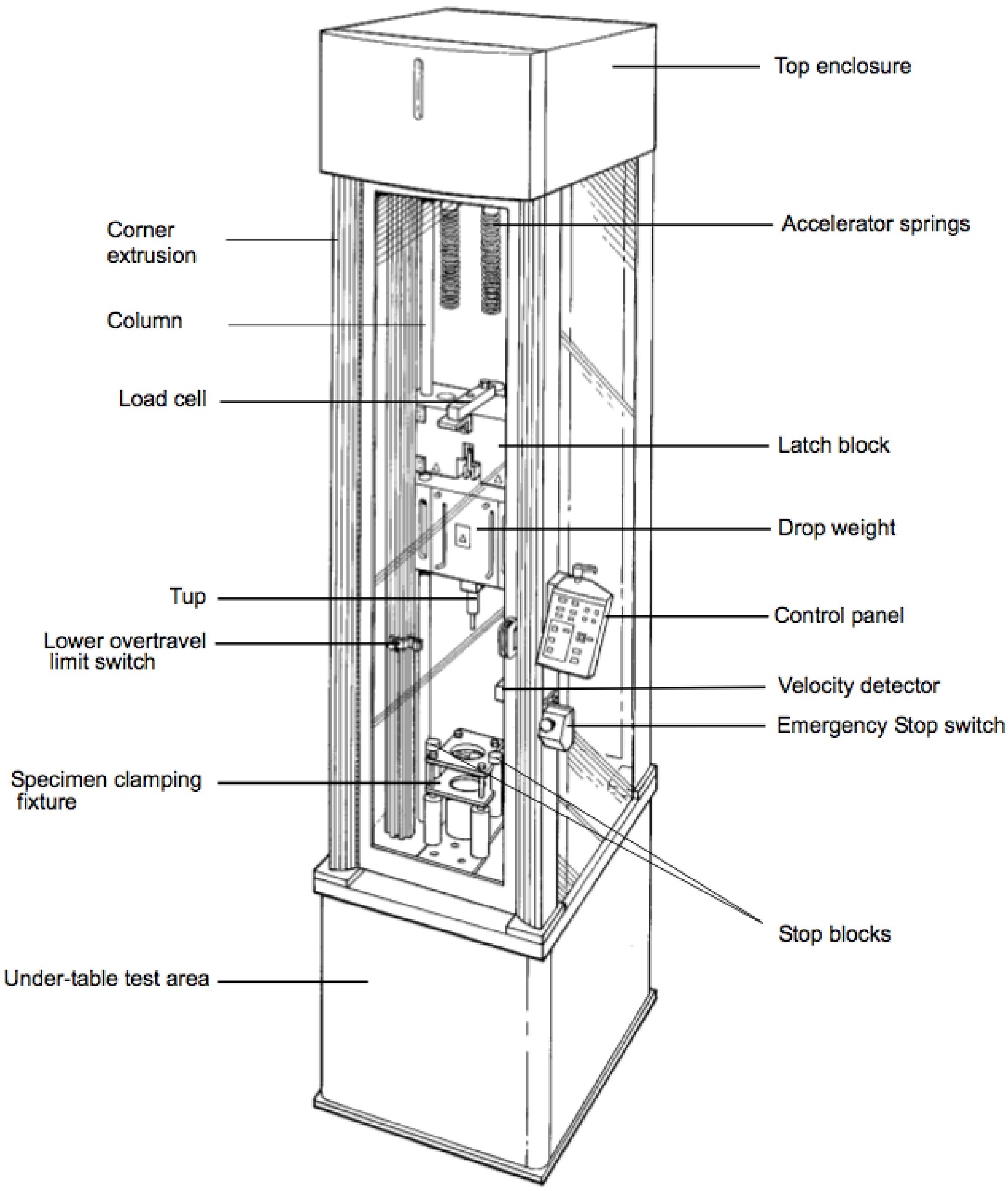

Figure 2.9: Instron Dynatup 9250HV drop weight impact testing machine

2.3 Results

In this section the results obtained during the study are presented. Starting from a characterization of the materials from a chemical point of view and microstructural, investigated with SEM imaging. Followed by the DMTA analysis of the influence of temperature and frequency on the visco-elastic properties of the materials, in particular on the elastic modulus and damping. And finally the impact absorption testing, in terms of single impacts at ambient and low temperature and multiple impacts.

2.3.1 Chemical composition (FT-IR) and Hardness testing

The materials have been characterized by FT-IR analysis in order to determine their chemical composition. The comparison with a database of polymeric foams shows that protectors 1, 2 and 3 are made of a blend of polyvinyl acetate, ethylene vinyl acetate (EVA) and nitrile butadiene rubber. Protector 4 is made of a polyurethane blend containing polydimethylsiloxane. Protector 5 has a sandwich structure consisting of a hard polypropylene exterior shell with a foam of polyolefines based elastomers.

In Table 2.2 the hardness of all the samples are reported.

Protector	**Construction**	**Hardness** $[ShoreA]$
1	Soft-shell	33
2	Soft-shell	23
3	Soft-shell	15
4	Soft-shell	14
5	Hard-shell	85

Table 2.2: Hardness of the protectors tested

2.3.2 Microstructure (SEM)

From an analysis of the SEM images it has been possible to determine the microstructure of the soft-shell protectors. SEM imaging of the hard-shell protector has not been performed due to the known structure of polyolefines.

A qualitative analysis of the micrograph reveals a closed cell structure for all the protectors, with cell dimensions and wall thickness that depend on the density and chemical composition of the foams, in particular:

- Protector 1: cell dimensions non-homogeneous, varying between 90 μm and 19 μm; thin cell walls throughout the whole sample, Fig. 2.10
- Protector 2: cell dimensions homogeneous, around 57 μm; thick cell walls throughout the whole sample, Fig. 2.11
- Protector 3: cell dimensions homogeneous, around 230 μm; medium sized cell walls throughout the whole sample, Fig. 2.12
- Protector 4: spherical cells with radius around 80 μm; wall thickness variable with position, Fig. 2.13

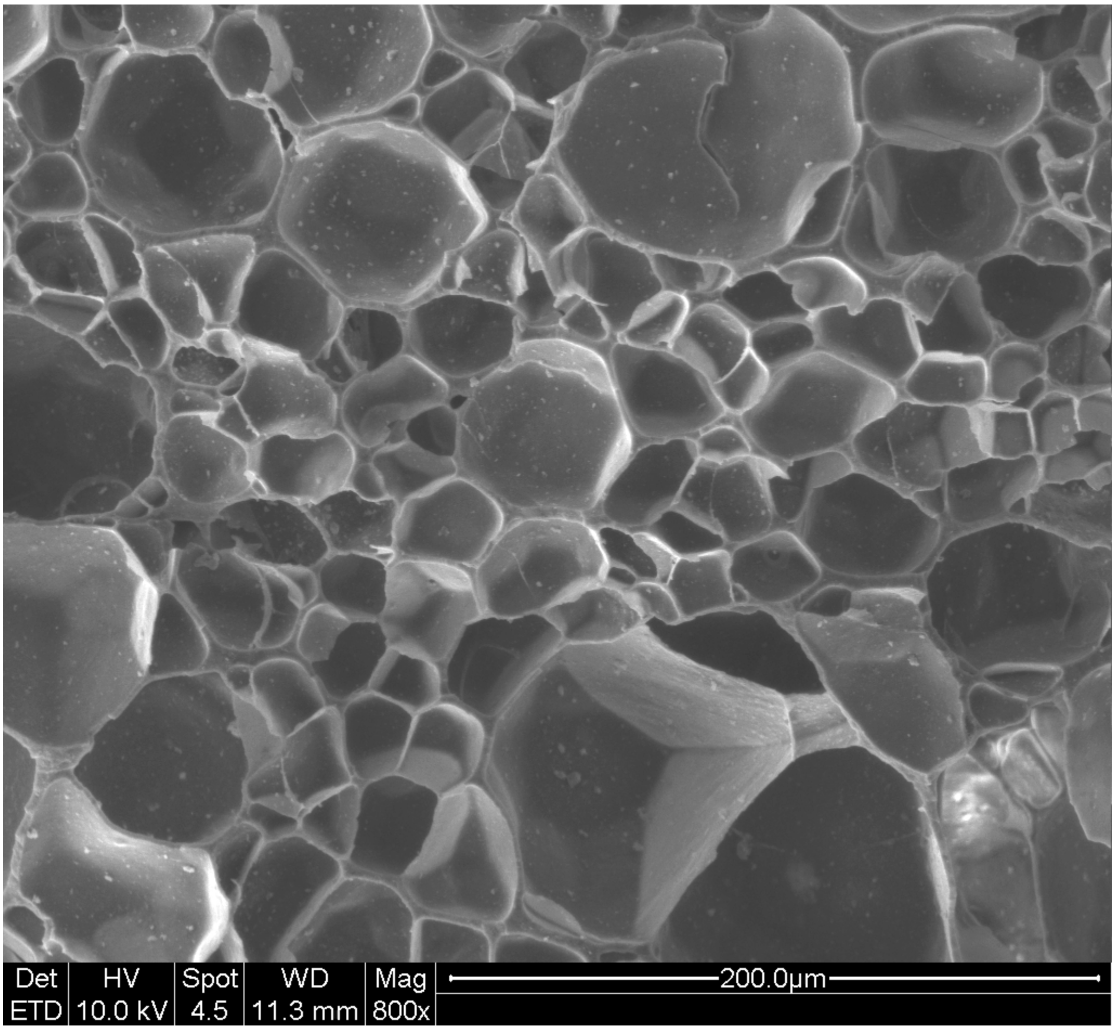

Figure 2.10: Scanning electron microscope image of protector 1

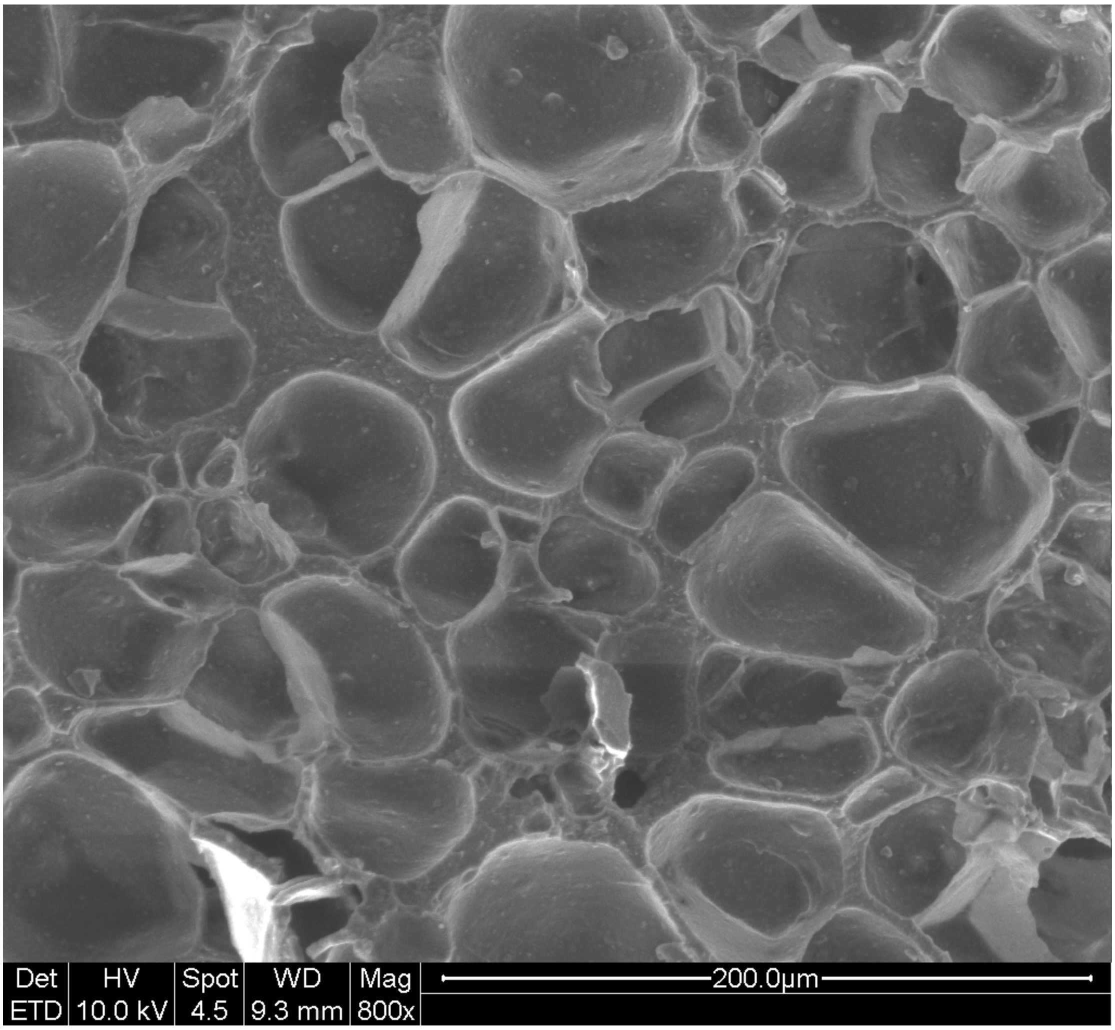

Figure 2.11: Scanning electron microscope image of protector 2

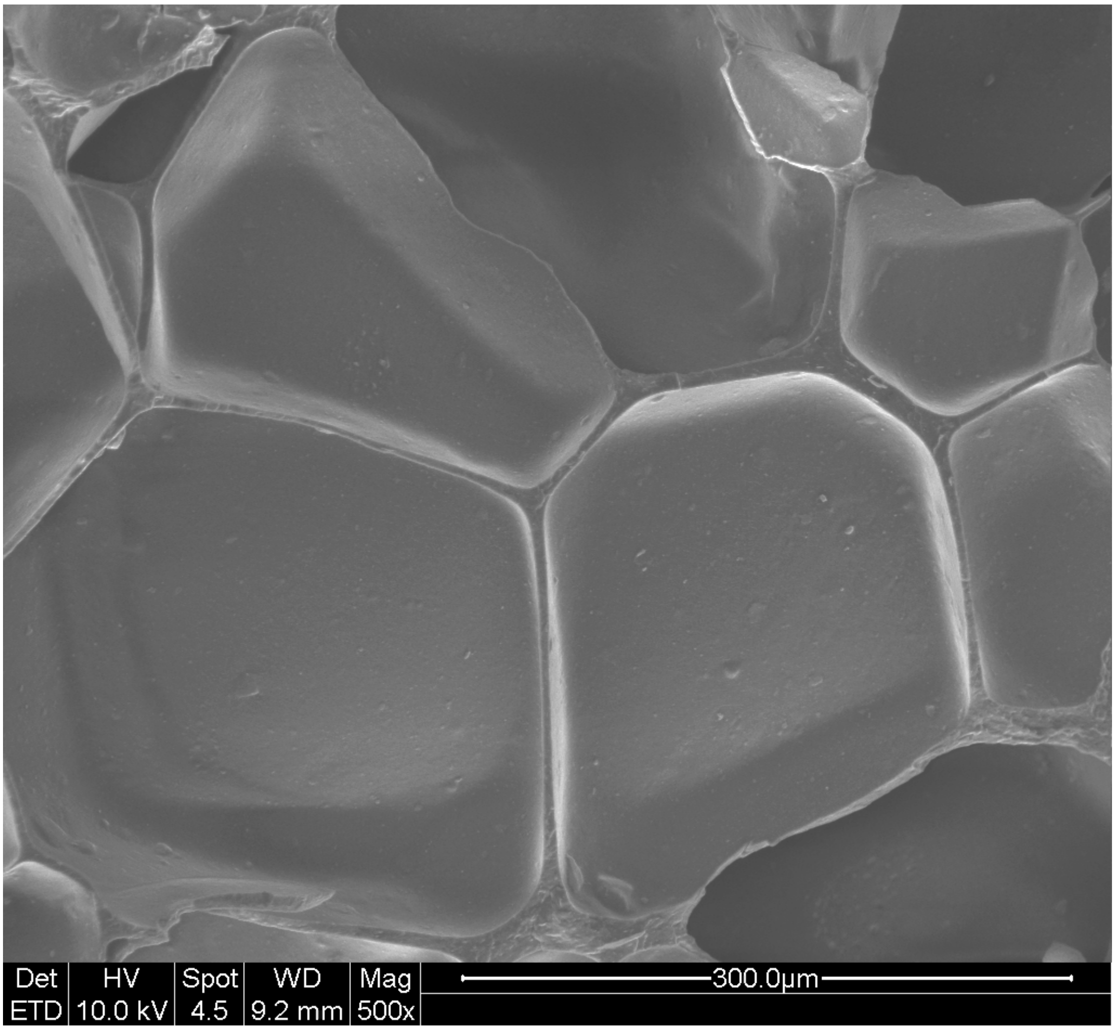

Figure 2.12: Scanning electron microscope image of protector 3

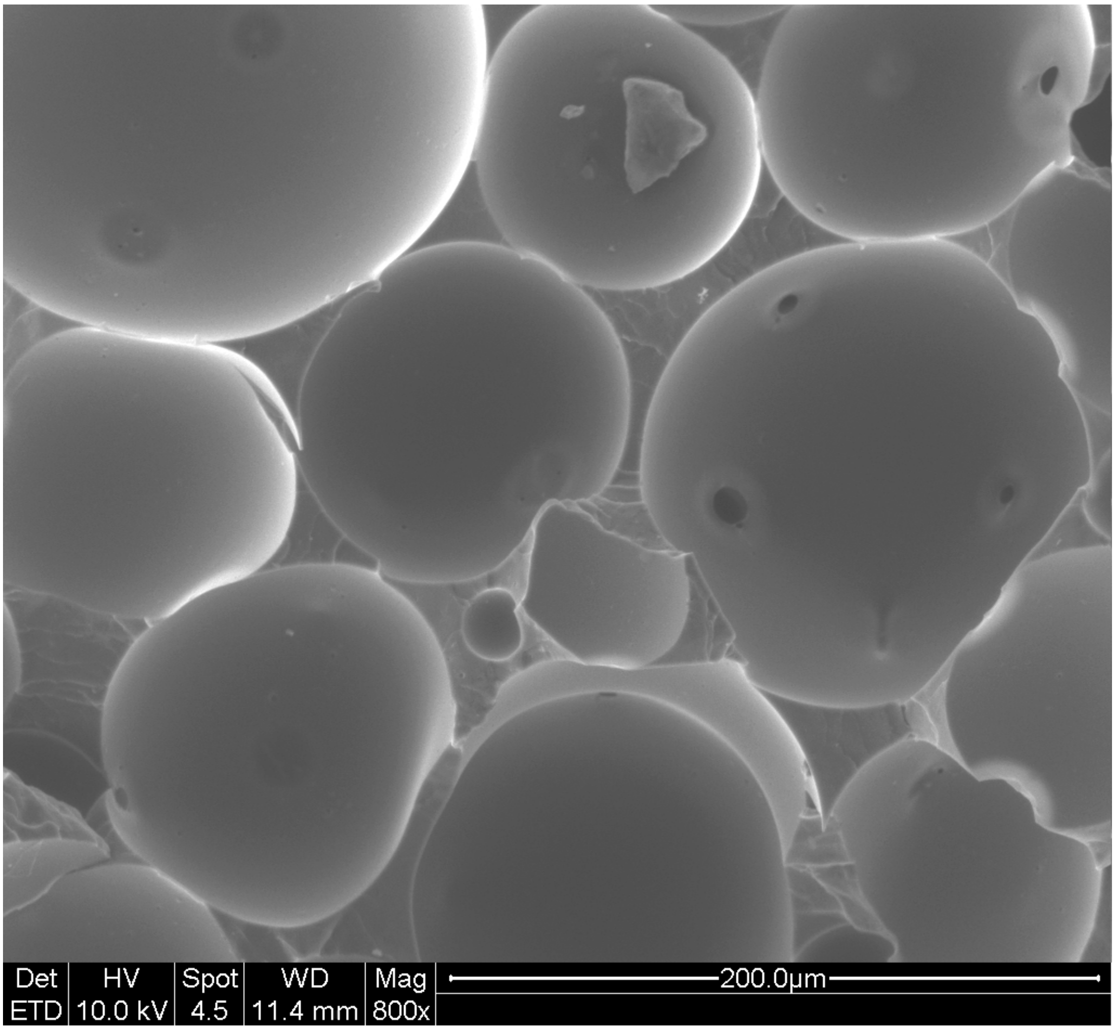

Figure 2.13: Scanning electron microscope image of protector 4

2.3.3 Dynamic Mechanical Thermal Analysis (DMTA)

In this study the influence of temperature and frequency on the visco-elastic properties of the materials used for ski protectors has been investigated by DMTA analysis.

A total of three frequencies were applied to the samples (1 Hz, 10 Hz and 50 Hz) in a temperature range between $-50°C$ and $+50°C$ (heating rate of $3°C/min$). This kind of analysis gives a broad overview on the properties of the materials in different conditions simulating the conditions of use of the final product.

Temperature influence

The influence of temperature on the visco-elastic properties for the materials used for ski back protectors has been measured by DMTA analysis . All the "soft-shell" samples have been scanned from $-50°C$ to $+50°C$ with an applied frequency of 1 Hz. The samples with dimensions 20x8x4 mm were die-cut directly from the protectors. Protector 5 has not been tested since it was not possible to cut a sample suitable for DMTA analysis directly from the protector.

The results of the DMTA analysis for the elastic modulus are reported in Fig. 2.14 and Table 2.3. All sample present the characteristic, for all polymeric materials, decrease of the elastic modulus with increasing temperature. It is evident that the elastic modulus of protector 1 has the smallest variation in the temperature range investigated with a 97.7 % decrease. Whereas protector 4 is the most affected by temperature, having the highest elastic modulus at low temperature and the lowest at high temperature. This kind of behaviour is not desirable in a material used in winter sport applications.

Protector	**Elastic Modulus** $[MPa]$		
	$-40°C$	$0°C$	$+40°C$
1	13.4	9.1	0.3
2	44.2	19.9	0.07
3	31.8	18.6	0.1
4	76.2	45.2	0.07

Table 2.3: Influence of the temperature on the elastic modulus E' measured at 1 Hz

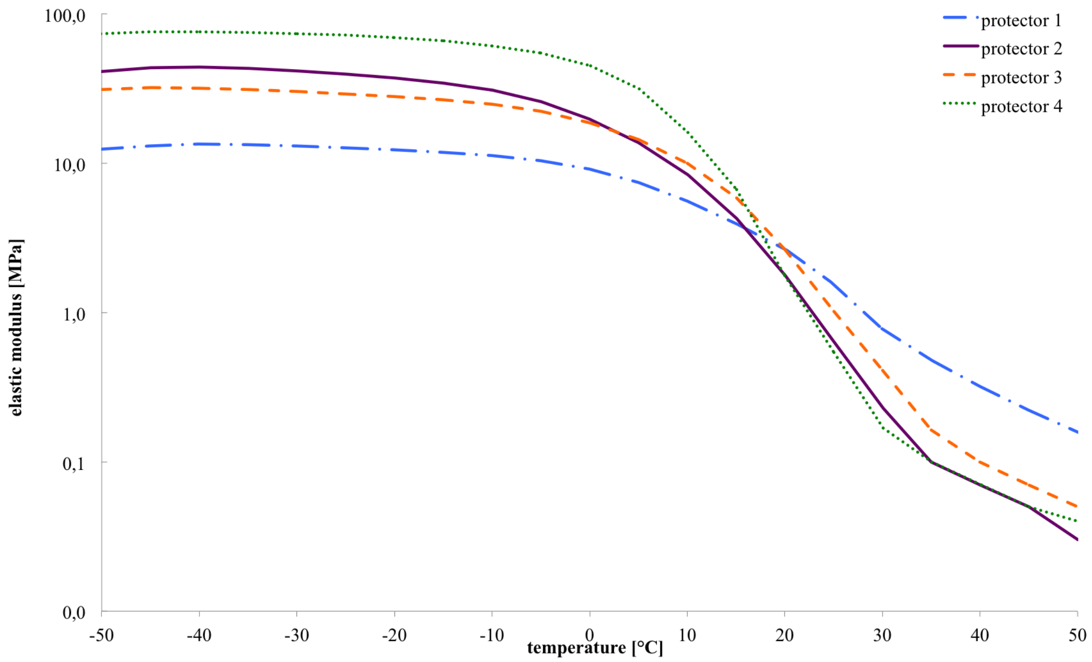

Figure 2.14: Elastic modulus measured at 1 Hz in the temperature range $-50°C$ to $+50°C$

Moreover in Fig. 2.15 and Table 2.4 the influence of temperature on the damping behaviour, tan δ, is shown. All the samples present a similar bahaviour with temperature.

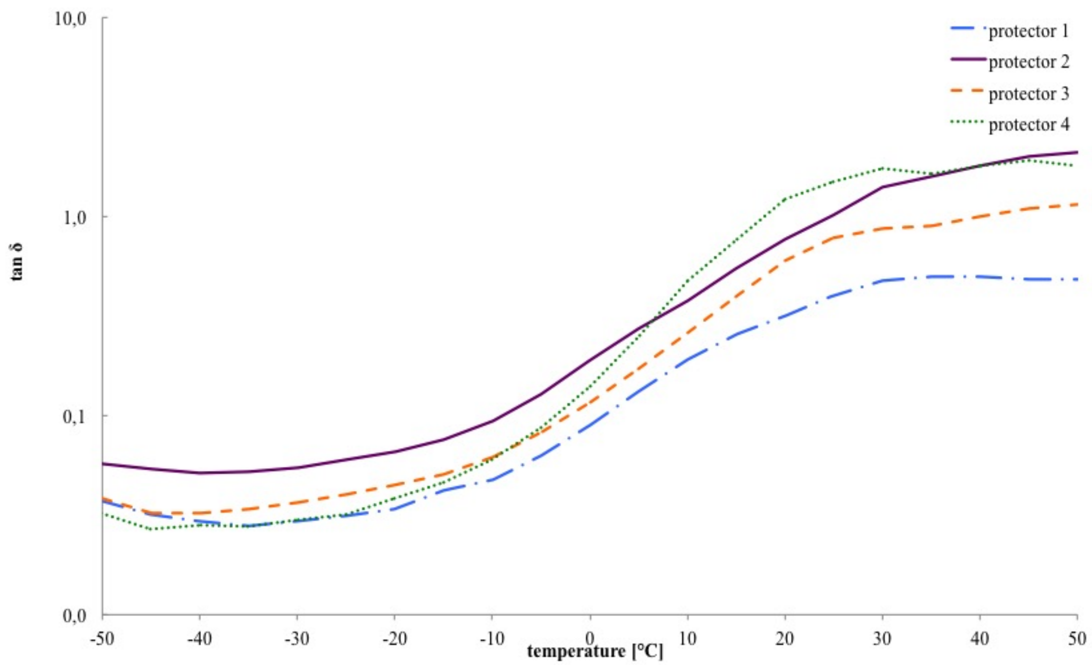

Figure 2.15: Tan δ measured at 1 Hz in the temperature range $-50°C$ to $+50°C$

Protector	**tan δ**		
	$-40°C$	$0°C$	$+40°C$
1	0.02	0.09	0.49
2	0.05	0.19	1.8
3	0.03	0.12	1
4	0.02	0.14	1.8

Table 2.4: Influence of the temperature on the tan δ measured at 1 Hz

Frequency influence

Furthermore the influence of frequency on the visco-elastic properties has been investigated, in Fig. 2.16 and Fig. 2.17 the behaviour of E' and tan δ is shown for protector 1 in the temperature range between $-50°C$ and $+50°C$. The other foams have a similar behaviour so are not presented graphically. However the values of the elastic modulus for the different materials at $+20°C$ are reported in Table 2.5 and the tan δ values in Table 2.6. All the soft-shell materials present an increase of the elastic modulus when increasing the frequency, which is more intense for temperatures above $0°C$. It is clear that the frequency of the applied force has an important effect on the material stiffness. For example, a 8-fold increase can be observed for protector 4 moving from 1 Hz to 50 Hz. This frequency-sensitive pseudo-dilatant behaviour is responsible for the particular properties of soft foams used for protective equipment. The materials have a lower elastic modulus, and thus are softer, when subjected to a low strain rate and therefore provide a good ergonomic comfort. On the contrary, when a high strain rate is applied (e.g. an impact during a fall) the material behaves as a rigid material, distributing the impact over a wider surface. The materials used for soft-shell protectors present high tan δ values ranging, at 1 Hz, from 0.32 to 1.2, indicating a strong damping behaviour of the materials. The tan δ values decrease by increasing the frequency of the stress. Thermoplastic polyolefines, such as the material used for protector 5, generally have tan δ values significantly lower compared to those of the foams used for soft-shell protectors [21].

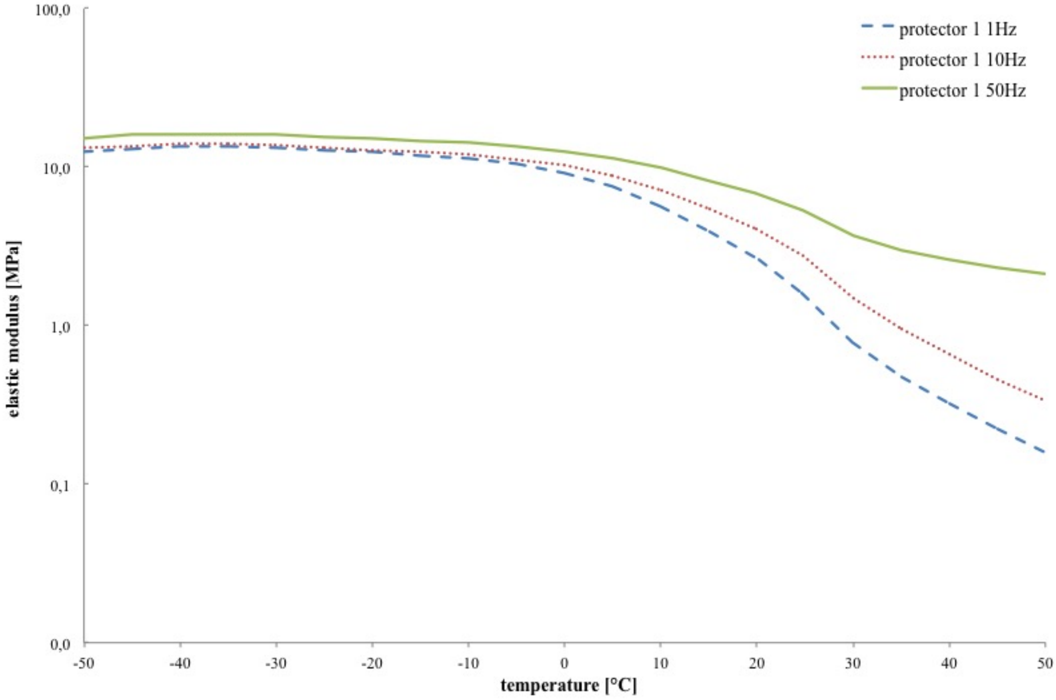

Figure 2.16: Effect of frequency on elastic modulus measured for protector 1

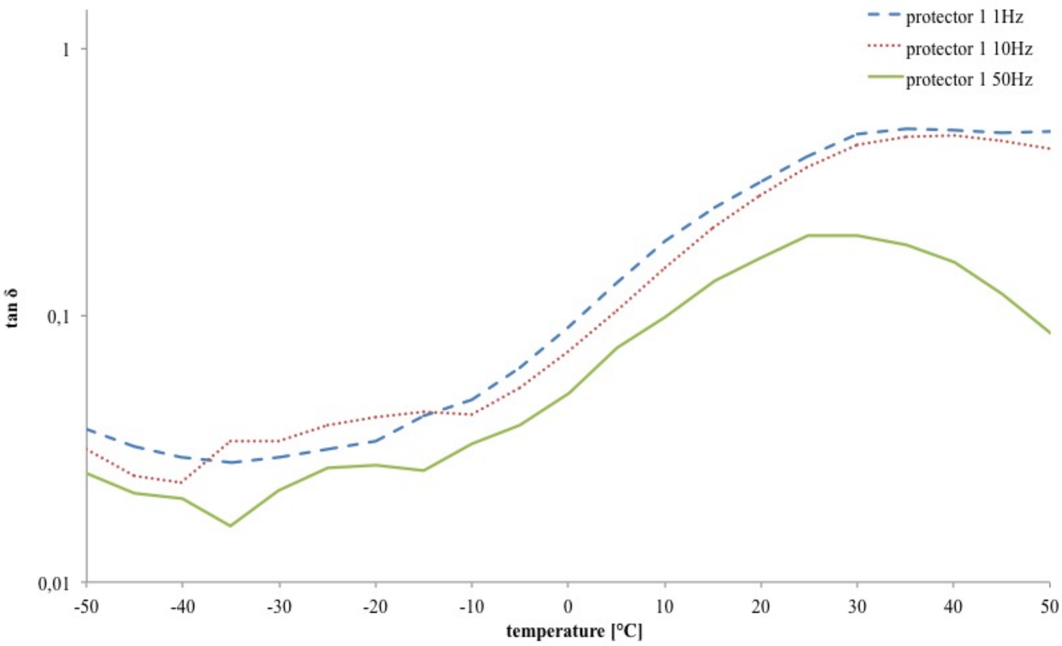

Figure 2.17: Effect of frequency on tan δ measured for protector 1

Frequency	**Elastic Modulus** $[MPa]$			
	Protector 1	Protector 2	Protector 3	Protector 4
1 Hz	2.6	1.8	2.6	1.8
10 Hz	4.1	4.6	5.6	6.9
50 Hz	6.8	10.1	10.8	14.7

Table 2.5: Influence of the frequency on the elastic modulus E' at $+20°C$

Frequency	**tan** δ			
	Protector 1	Protector 2	Protector 3	Protector 4
1 Hz	0.32	0.77	0.60	1.20
10 Hz	0.28	0.58	0.46	0.78
50 Hz	0.16	0.34	0.26	0.47

Table 2.6: Influence of the frequency on the tan δ at $+20°C$

2.3.4 Impact testing

The shock absorbing properties of the materials have been tested using a drop weight impact testing machine which resulted in force-displacement curves. Initially, single impacts have been performed at two different temperatures: $+20°C$ and $-5°C$. In this way it is possible to have an assessment of the influence of temperature on the shock absorbing properties. From the same tests, it is possible to obtain the penetration of the impactor in the sample. Finally the behaviour of the samples after multiple impacts has been tested at $+20°C$.

Single impact

The impact tests have been performed with an impact energy of 50 J. The results of the impact force over time, tested at $+20°C$, are reported in Fig. 2.18. In general a good shock absorbing material should present a low impact force spread over a longer time, resulting in a reduced energy transfer rate and thus to a smaller probability of injury. All the soft-shell protectors present the same impact behaviour in different parts of the protector while for the hard-shell protector (protector 5) the properties strongly depend on the point of impact.

The soft-shell protectors present three regions in the impact curve, typical of visco-elastic foams. On the other hand the hard-shell sample behaves as a typical rigid polymer with a high impact force concentrated in a short time.

All the results obtained at $+20°C$ are summarized in Table 2.7. In particular the maximum impact force (F_{max}), the time-to-peak, the absorbed energy (E_a) and the energy absorbed per unit thickness (E_a/thickness) are reported. It is of particular interest the absorbed energy versus thickness parameter, which can be considered as the "efficiency" of the material. Protector 3 has the highest value, with 2.8 J/mm, although having a lower certified level of protection (level 1 EN 1621-2), which is reflected with the high value of the maximum impact force and absorbed energy. Overall protector 1 has the best combination of values: low maximum impact force, high absorbed energy and time-to-peak, offering the best impact absorbing properties. The fact that the peak, measured for protector 5, is shifted at 7 ms is due to the geometry of the product. In fact the protector has a curved shape, thus during the first part of the impact, up to 5 ms, the protector is being compressed until it gets flat against the anvil. Once it is flat the impact force raises very quickly to the maximum.

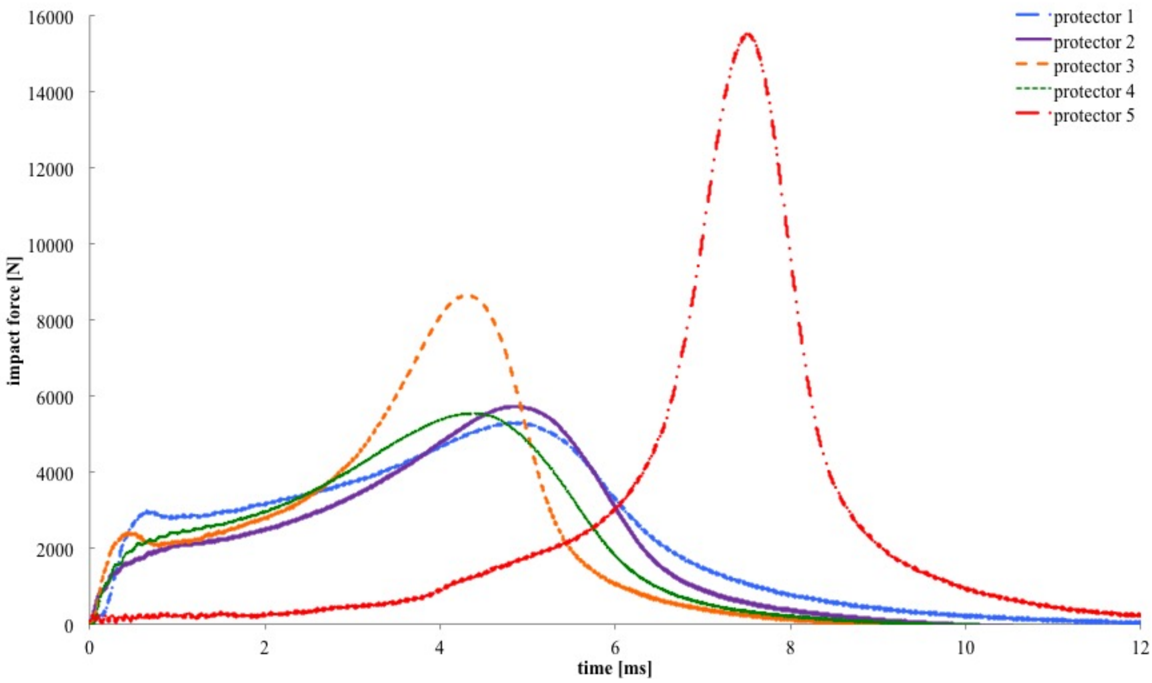

Figure 2.18: Impact force as function of impact time at +20°C

Protector	$\mathbf{F}_{max}$ $[N]$	**time-to-peak** $[ms]$	$\mathbf{E}_a$ $[J]$	$\mathbf{E}_a$**/thickness** $[J/mm]$
1	5301	4.8	45.7	2.8
2	5728	4.8	46.2	2.4
3	8644	4.3	45.4	2.8
4	5549	4.3	46.3	2.6
5	15537	7.9	41.2	1.4

Table 2.7: Results of impact testing at +20°C

As demonstrated by the DMTA analysis soft materials are strongly temperature dependent. Therefore a second set of testing with an impact energy of 50 J has been performed at $-5°C$, the results are shown in Fig. 2.19 and Table 2.8. At low temperature all the soft-shell protectors present an increase of the first part of the impact absorption process (hard behaviour) with respect to the behaviour at $+20°C$, since the material is more rigid due to the reduced motions of polymer segments at low temperature, with the result of an increase of the yield point. The second part of the impact curve after the yielding point is not anymore present since, as measured by DMTA analysis, the soft materials have a sharp decrease of tan δ values below $0°C$, and therefore have lost most of their viscous behaviour. In particular protectors 2 and 4 show the largest increase of the peak impact force, with a behaviour similar to the hard-shell protector, i.e. high impact force spread in a short time. These variations at low temperature are well predicted by the DMTA analysis, the change in impact behaviour that can be connected with the largest modulus increase showed by DMTA analysis in Fig. 2.14. On the contrary, the hard-shell protector does not present a significant change at low temperature since the mechanism of impact protection is performed by energy dissipation over a wider area, without a viscous absorption of the impact. However, fractures in the outer part have been observed at low temperature for protector 5 and therefore a not efficient multi-impact behaviour is expected.

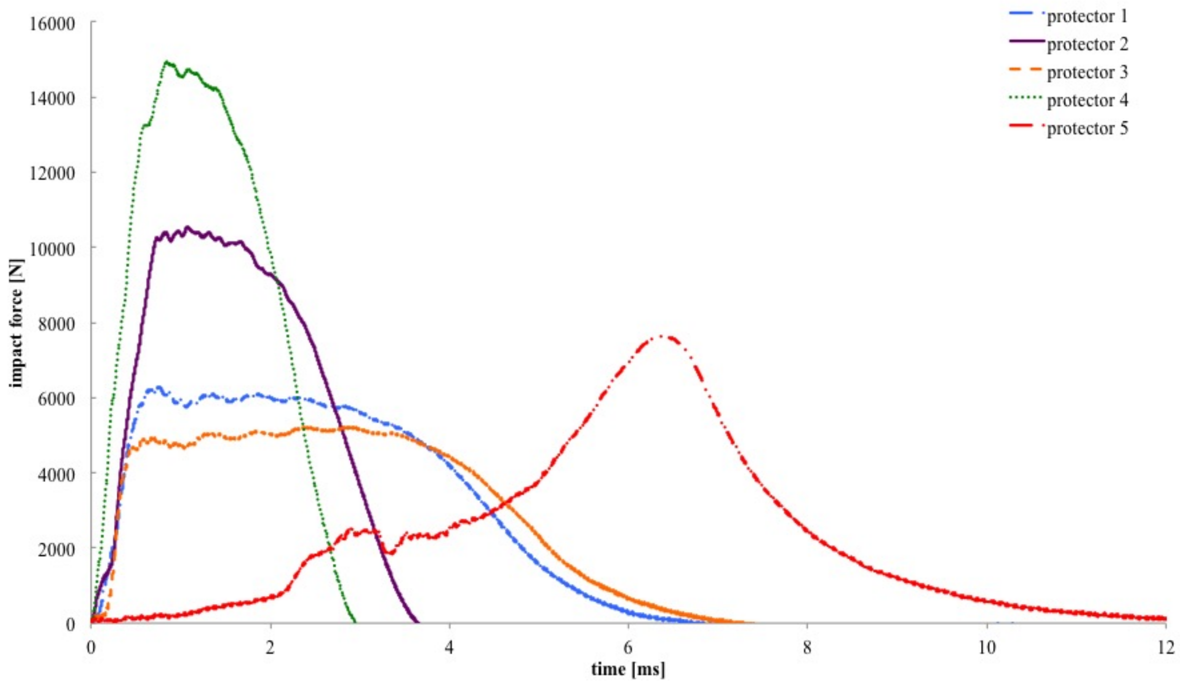

Figure 2.19: Impact force as function of impact at $-5°C$

Protector	**F**$_{max}$ $[N]$	**time-to-peak** $[ms]$	**E**$_a$ $[J]$	**E**$_a$**/thickness** $[J/mm]$
1	6292	0.7	44.0	2.8
2	11196	1.7	44.3	2.3
3	5220	2.9	45.5	2.8
4	15534	0.8	40.7	2.3
5	7644	6.3	44.0	1.5

Table 2.8: Results of impact testing at $-5°C$

Moreover in Fig. 2.20 and Fig. 2.21 the penetrations of the impactor inside the samples during the impact are reported both at $+20°C$ and $-5°C$, and the results are summarized in Table 2.9. It is important to note that none of the samples has bottomed out. For all the soft-shell protectors the penetration corresponds to the compression of the polymeric foam. On the other hand the high value of penetration for the hard-shell protector 5 is not completely due to the compression of the soft lining on the inner side of the sample. In fact due to the curved shape of the rigid external shell the sample was not laying flat on the anvil and thus when impacted the impactor cause a first flattening followed by compression of the lining. This effect is confirmed by the high penetration at low temperature, confirming the limited influence of the temperature on the material properties.

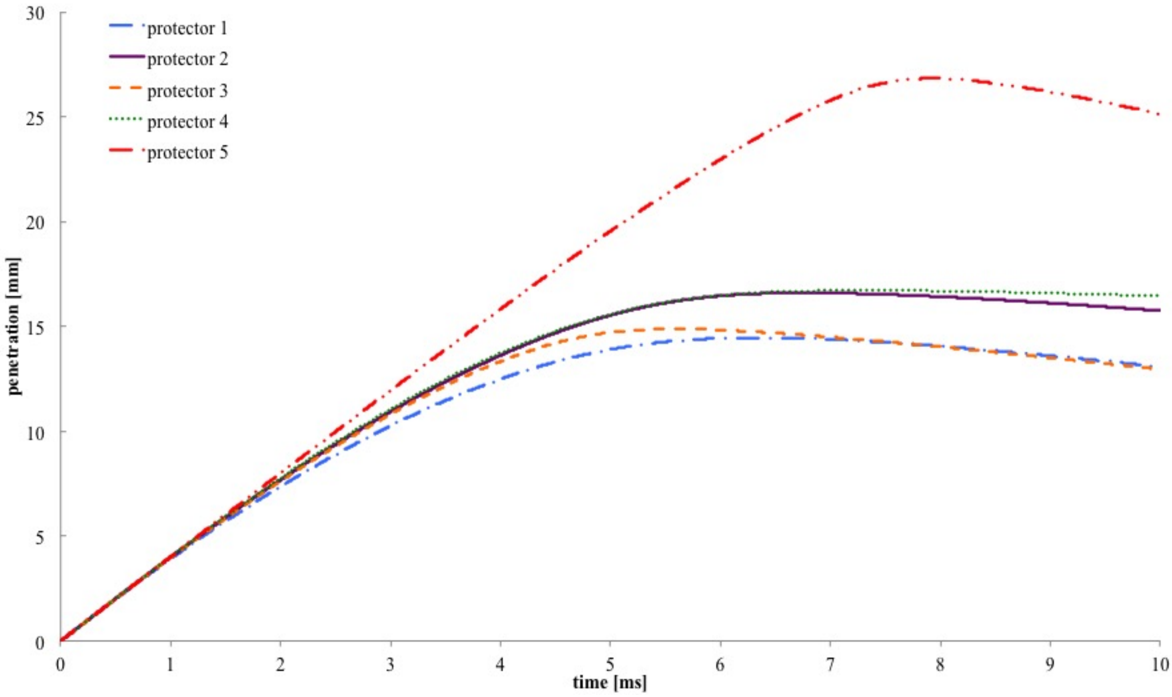

Figure 2.20: Penetration of the impactor inside the sample for testing at $+20°C$

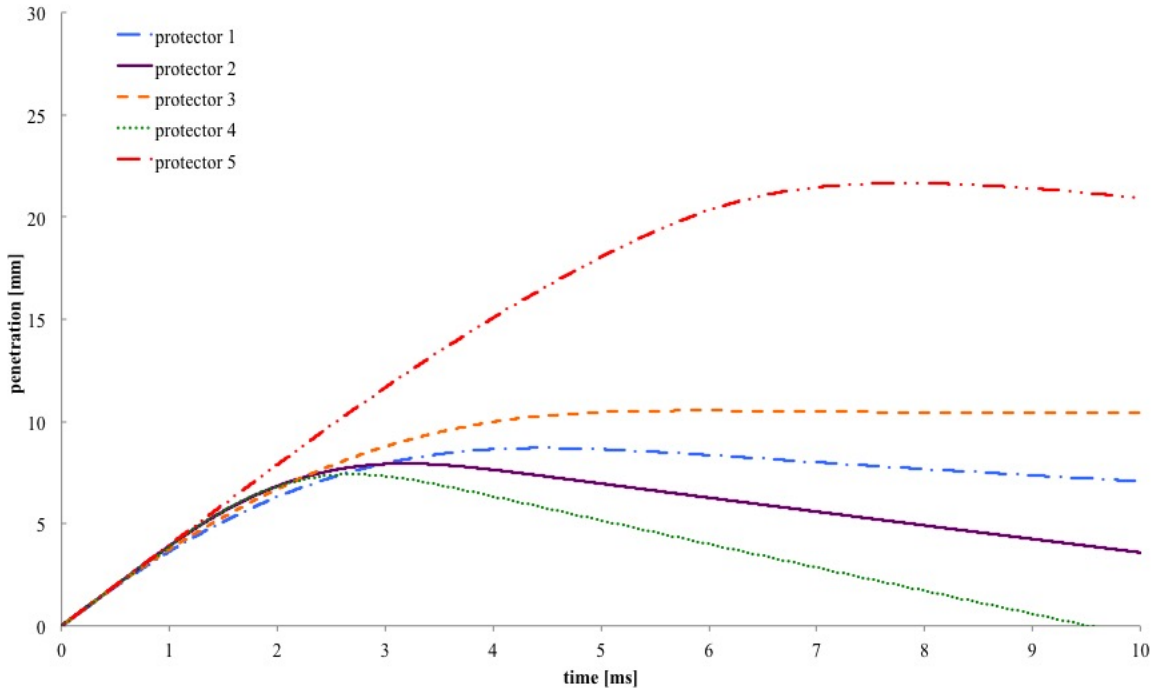

Figure 2.21: Penetration of the impactor inside the sample for testing at $-5°C$

Protector	**Thickness**	**Penetration** $+20°C$	**Penetration** $-5°C$
	$[mm]$	$[mm]$	$[mm]$
1	16	14.6	8.7
2	19	15.0	7.9
3	16	13.7	10.9
4	18	14.2	7.4
5	30	26.8	21.7

Table 2.9: Penetration of the impactor at $+20°C$ and $-5°C$

Multiple impacts

The behaviour of the samples after multiple impacts has been tested by repeating the impact for five times consecutively in the same area of the sample, with a time between impacts of 1 minute. All the testing has been conducted at the temperature of $+20°C$. The results are shown in Fig. 2.22 and Table 2.10 for a soft-shell protector (protector 2), and in Fig. 2.23 and Table 2.11 for the hard-shell one (protector 5). The other soft-shell protectors presented behaviours similar to that of protector 2, for this reason the results are not reported in the present work. From Fig. 2.23 it is clear how the hard-shell protector has a sensible increase in the peak impact force after multiple impacts due to the yielding effect that the impacts have on the hard material. Moreover, some damages (permanent compressions and fractures) were present on protector 5 after the first impact and therefore the impact is distributed over a smaller area with a reduced width of the protector (that is responsible of the reduced time-to-peak after the first impact). On the other hand, the soft-shell materials present a negligible increase of the peak impact force. The first impact curve shows a clear elastic region followed by a plateau of deformation (controlled by non-linear elastic buckling). This behaviour is still observed in the following impacts but with a lower yield point and an increase time-to-peak.

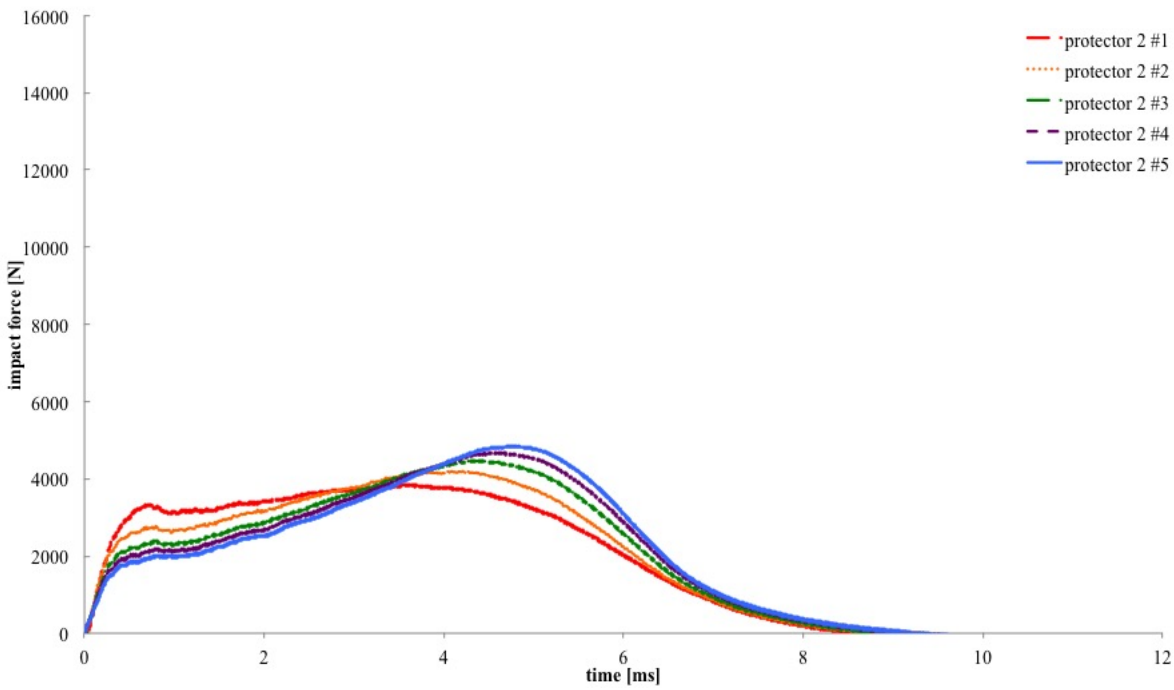

Figure 2.22: Multi-impact behaviour for soft-shell protector 2

Impact nr	$\mathbf{F}_{max}$ $[N]$	**time-to-peak** $[ms]$	$\mathbf{E}_a$ $[J]$	**Penetration** $[mm]$
1	4381	3.19	45.4	13.2
2	5345	4.15	44.9	14.2
3	6236	4.45	44.0	14.8
4	7854	4.49	44.4	15.1
5	9578	4.50	44.4	15.3

Table 2.10: Results of multiple impacts testing for soft-shell protector 2

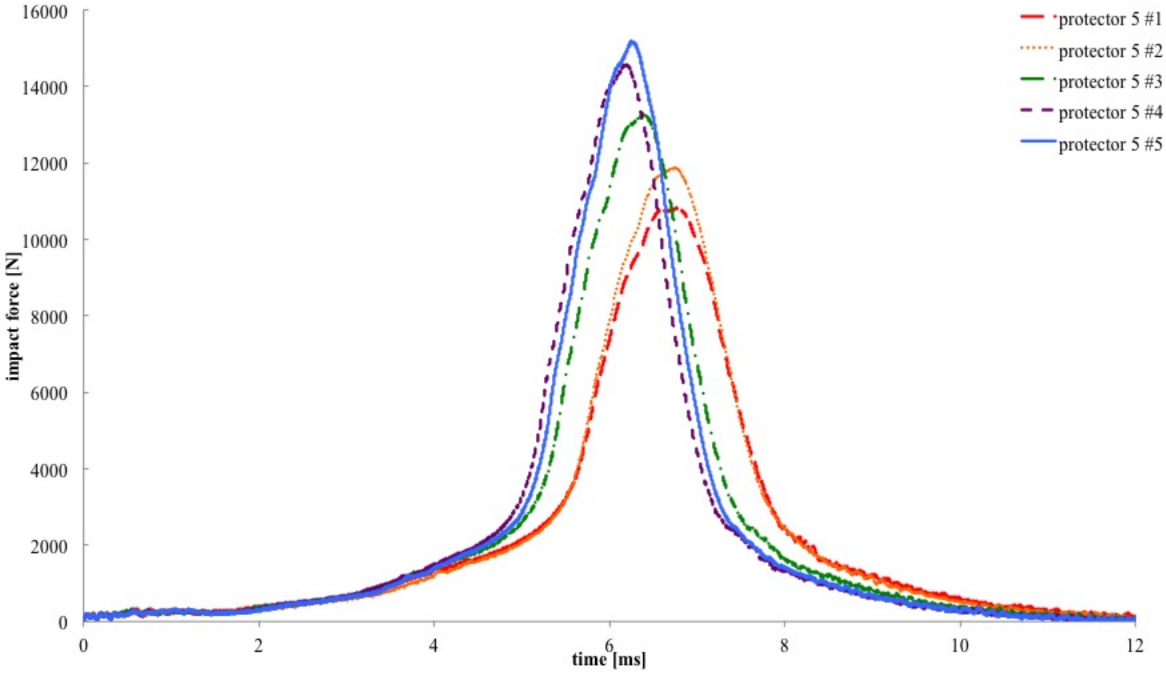

Figure 2.23: Multi-impact behaviour for hard-shell protector 5

Impact nr	**F**$_{max}$ $[N]$	**time-to-peak** $[ms]$	**E**$_a$ $[J]$	**Penetration** $[mm]$
1	5666	5.60	44.3	29.1
2	7305	6.18	46.3	26.0
3	9160	6.52	47.2	25.4
4	9688	6.59	46.1	24.5
5	10456	6.42	46.42	24.1

Table 2.11: Results of multiple impacts testing for hard-shell protector 5

2.4 Discussion

In this chapter a complete characterization of the typical materials used for the production of back protectors has been carried out, focusing on the new generation soft materials but also considering the hard-shell technology coming from the motorcycling sector.

These new materials are polymeric foams made by blends of EVA or polyurethane. From the SEM analysis of the microstructure it emerged that all the samples present a closed cell structure with cell dimensions and wall thicknesses that depend on the density and chemical composition.

The influence of temperature on the visco-elastic properties for the materials has been measured by DMTA analysis. This parameter is of relevant importance since this kind of equipment is subjected to large temperature changes during use and storage. A minor influence of temperature on the visco-elastic properties is desirable in a material for ski back protectors allowing a constant performance, both in terms of impact absorption and flexibility. Although DMTA is a low strain technique compared with the high strains during impacts, it permits to highlight the influence of temperature and frequency on the material properties [22]. From the results obtained protector 1 showed the smallest variation of the elastic modulus in the temperature range investigated, while protector 4 was the sample mostly affected by temperature. Furthermore the influence of frequency on the visco-elastic properties has been investigated with DMTA analysis. In a similar way as temperature, also the frequency of the applied stress plays an important role on the performance of the final product. In fact a back protector is subjected to both low frequency stress, e.g. body movements, and high frequency stress, e.g. high speed falls or impacts. The results pointed out that all the soft-shell materials present an increase of the elastic modulus when increasing the frequency, especially for temperatures above $0°C$. For example, a 8-fold increase can be observed for protector 4 moving from 1 Hz to 50 Hz. This frequency-sensitive pseudo-dilatant behaviour is typical of the soft foams used for protective equipment. In fact these materials have a lower elastic modulus, and thus are softer, when subjected to a low strain rate and therefore provide a good ergonomic comfort. On the contrary, when a high strain rate is applied (e.g. an impact during a fall) the material behaves as a rigid material, distributing the impact over a wider surface. Moreover the tanδ values are ranging, at 1 Hz, from 0.32 to 1.2, indicating a strong damping behaviour.

In a back protector the shock absorbing properties play a fundamental role. For this reason drop weight impact testing has been carried out using an Instron Dynatup 9250 HV testing machine. All the soft-shell protectors present three regions in the impact curve, typical of visco-elastic foams. A first linear elastic region (controlled by cell wall bending and stretching) followed by a plateau of deformation (controlled by non-linear elastic buckling). These two regions are separated by a clear yield point. Finally, there is a densification area where the force increases sharply (controlled by collapse of cell walls). On the other hand the hard-shell sample behaves as a typical rigid polymer with a high impact force concentrated in a short time. Overall protector 1 has the best combination of values: low maximum impact force, high absorbed energy and time-to-peak, offering the best impact absorbing properties. As demonstrated by the DMTA analysis soft materials are strongly temperature dependent, therefore a second set of testing has been performed at $-5°C$. The temperature decrease reduces the motions of the polymer segments resulting in a more rigid material. This translates in a increase of the first part of the impact absorption process (hard behaviour) with respect to the behaviour at $+20°C$. Furthermore the second part of the impact curve after the yielding point is not anymore present since, as measured by DMTA analysis, the soft materials have a sharp decrease of tan δ values below $0°C$, and therefore have lost most of their viscous behaviour. In particular protectors 2 and 4 show the largest increase of the peak impact force, with a behaviour similar to the hard-shell protector, i.e. high impact force spread in a short time. The low temperature impact behaviour is well predicted by the DMTA analysis, in fact the difference can be connected with the increase of the elastic modulus showed by DMTA analysis. On the contrary, the hard-shell protector does not present a significant change at low temperature since the mechanism of impact protection is performed by energy dissipation over a wider area, without a viscous absorption of the impact. However, fractures in the outer part have been observed at low temperature for protector 5. Impact testing provided information also on the penetration of the impactor inside the samples. None of the soft-shell samples has bottomed out and the penetration corresponds to the compression on the foam. On the other hand for the hard-shell sample the penetration measure is initially connected to the flattening of the sample, followed by the limited compression of the lining.

Finally the behaviour of the samples after multiple impacts has been assessed. The hard shell protector presents a clear deterioration of the shock absorbing properties expressed by the increase of the peak impact force and due to the yielding effect that the impacts have on the hard material and to the damages of the external shell. On the other hand the soft-shell materials are not greatly affected by multiple impacts. There is just a lower yield point and an increase in the time-to-peak. The explanation of the decrease of the yield point can be connected to the damage that some regions of the structure have received during the first impact, which leads to a softening of the foam structure [23]; such damage remains in the structure making the foams easier to deform.

2.5 Conclusions

The study of the impact and thermo-mechanical properties of the materials used for back protectors indicates that the materials used for soft-shell protectors present a shear-sensitive behaviour. In fact the visco-elastic properties, both elastic modulus and damping, depend on the frequency of the applied stress. Thanks to this behaviour the materials are soft for low speed deformations and rigid when subjected to high speed impacts. Thus, the resulting protector will have a good ergonomic comfort, allowing freedom of movements during skiing, but protecting the body in the event of a fall or collision.

On the other hand the hard-shell protector exhibits a longer time-to-peak due to its curved shape, does not change the impact properties at low temperature but presents a low resistance to multiple impacts. Mainly due to the damages suffered during the first impact. On the contrary, soft-shell protectors have good multi-impact properties and are more sensible to temperature.

The analysis performed for this chapter can be used as a protocol during the design and development of new body protectors in order to select the best performing materials and geometries. And thus bring a reduction of the cost and time of the development process.

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3 Ski Boots for alpine skiing: design, materials and testing procedures

The flexural behaviour and elastic rebound are the main parameters that determine the global performance of a ski boot during skiing. These two parameters are related to the visco-elastic properties of the polymeric materials used. For this reason, the visco-elastic properties of the materials most utilized for the production of ski boots (polyurethanes and polyolefines) have been studied using dynamic mechanical thermal analysis (DMTA) in a temperature range between $-30°C$ and $+50°C$. Also, the flexural and rebound behaviours of the boot have also been tested using specially designed test benches. The DMTA analysis results and the flexural and rebound tests results were compared and a correlation between the visco-elastic properties and the flexural and rebound behaviour of ski boots was found. Therefore, DMTA analysis can be used in a knowledge based design process of new ski boots in order to improve on-snow performances. Furthermore the influence of the design of the ski boot on the flexural and rebound behaviour has been investigated.

3.1 Introduction

In the last 50 years the materials used for ski boots have significantly changed, passing from leather to thermo-plastic polymers. The first attempt to stiffen ski boots was made by Robert Lange, who incorporated fiberglass reinforced epoxy resin in 1947 [1]. This prototype allowed Lange to acquire knowledge about the use of reinforced epoxy resin, and lead to the production of the first ski boot made completely in plastic in 1960. The boot was built from acrylonitrile-butadiene-styrene (ABS) polymers [1] and went under the trade name Royalite from Uniroyal. After testing, the boot showed to have poor impact resistance at low temperature, which, gave rise to several mechanical failures. In 1965, to solve the problems connected with ABS plastic, boot makers began using Adiprene, a thermoplastic polyurethane manufactured by Dupont. With this new material it was possible to produce ski boots by injection moulding. The mass production of plastic ski boots started in 1966 with Lange that commercialized ski boots with an overlap design, made of two parts, the lower part called shell and the upper part called cuff. In the same year the production was also started by Nordica in Montebelluna (Italy) in collaboration with API Plastic, using a polyurethane made by Bayer for aerospace applications (Desmopan) [2]. In 1972, Hanson introduced the rear entry design that was then used by Nordica and Salomon. However, after a first commercial success, this type of design has suffered a contraction of use and is nowadays almost not produced anymore. The last important innovation in ski boot design was made in 1979 by a former NASA engineer, Eric Giese. Taking inspiration from the joints of spacesuits, he designed a ski boot with a plastic tongue able to control the flex of the boot. This construction was named Flexon design and now is also known as 3-pieces design or cabrio design. In the last few years, several new designs have been introduced to the market, however the main construction designs have always been related to the overlap and to the 3-pieces designs (Fig. 3.1). A market analysis of commercial ski-boots shows that the most common design is the overlap design with respect to 3-pieces. In particular, Salomon and Head brands offer just ski-boots with overlap design, while Nordica has 56% of the models with overlap and Dalbello just 43%, the rest being 3-pieces.

The overlap designed boot is composed of a lower part (shell) connected by metallic screws to the upper part (cuff). The forward flex of the boot is controlled by the bending of the upper-back part of the shell (spine) and by compression of the lower front part of the cuff on the shell. The latter interaction could cause the undesired enlargement of the instep of the shell if the boot is not properly designed. This design provides the best fit in the front part of the shell since the two parts of the shell overlap, and therefore the tightening of the buckles decreases the internal volume providing a tight and precise fit. Moreover, it provides a fast power transmission from the skier to the ski edge. That is why the overlap design is the only one currently used in World Cup racing ski boots. On the other hand it could sometimes give rise to problems in entry and exit of the foot from the boot in cold weather, especially if stiff plastics are used.

3-pieces is less used than overlap, although it actually is the preferred design for some producers (Dalbello and Full Tilt, as reported in their websites) and for some skiing disciplines (freestyle and mogul skiing). 3-pieces does not use friction to resist the flex. Instead, it uses a separate piece of plastic (tongue) that acts as a spring [3], yielding

Figure 3.1: 3-pieces design (left) and overlap design (right) ski boots

two advantages: first of all a gradual application of force, and, in second place, the boot returns to its original position when the level of force is lowered. In order to ensure that the flexing force remains under control even under extreme bending, the plastic is formed into the same bellows-like shape used in spacesuits. The result is a smoother flex that starts off soft and gradually stiffens [3]. When tightened, the mid buckle pulls the foot rearward, which helps keeping the ankle in the rear pocket of the boot [3]. The gradual increase of the flex makes this type of ski boots very efficient in adsorbing shocks during landings or skiing in moguls and for this reason is the design of choice for freestyle and off-piste disciplines. Moreover, the possibility to move the tongue makes for an easier entry and exit of the foot from the shell with respect to overlap. The main drawback of this design concerns the difficulty to adapt the shell shape to the skiers foot when closing the buckles, affecting negatively the control of the edges with the front part of the boot. That is why this type of boots is no longer used in World Cup races. However thermo-formable liners allow to employ shells with a narrower Last, without compromising comfort and granting a more precise edge control. Moreover, since the flex of 3-pieces boots is mainly governed by the tongue, flex stiffness can be easily modified by replacing the tongue with another made of a stiffer plastic. On the contrary, it is more difficult to change the flex of an overlap boot, as it requires different materials for the cuff and/or the shell. The results of the XXII Olympic Winter games show that for freestyle disciplines (i.e. slopestyle, moguls, aerials and halfpipe) 59% of the medalists used 3-pieces designed boots while all the medals of alpine racing skiers have been obtained by skiers using the overlap design. Therefore, it is clear that the different use of the two designs should be connected with the different performances. Recently, a combination of the two designs was developed, with an 3-pieces tongue and an overlap structure in the front part. This new design combines the precise fit and edge control of the overlap with the flex progressivity of the 3-pieces

Regarding the materials used for the production of ski boots, nowadays, plastic boots cover the full range of skiers needs, from amateurs to world cup athletes. According to ski boots producers [3], the main classes of materials used for ski boots are thermoplastic polyurethanes (TPU), polyolefines copolymers (PO) based on polyethylene and polypropylene (Figure 3.2), Nylon 12 and polyamide-polyether block copolymers (Pebax). These classes of materials possess a sufficient impact resistance at low temperature that permits their application in the production of ski boots that do not become brittle during the use at temperatures above $-30°C$.

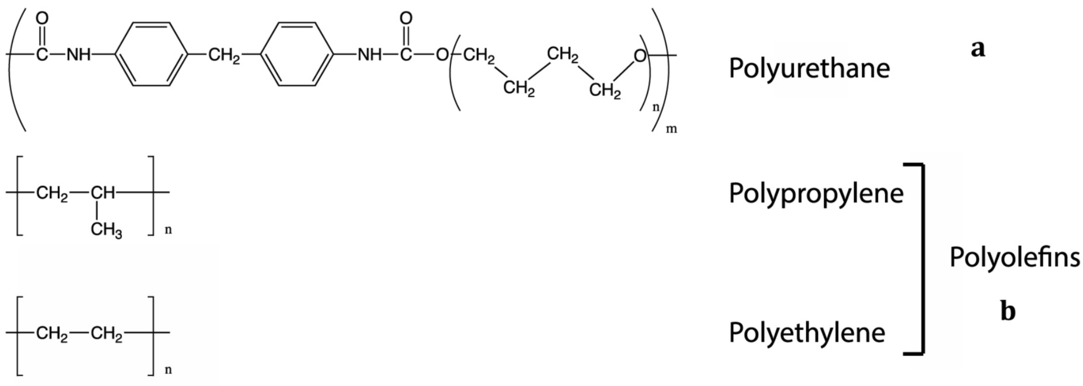

Figure 3.2: Chemical structures of polyether based polyurethane (a) and polyolefines (b)

A statistical analysis of the plastics used for the models present in the catalogue of one of the largest ski boots producers worldwide (Salomon [3]) indicates that polyurethanes and polyolefines are the most utilized materials. In particular, 74% of the male models are made of polyurethanes, 11% of polyolefines, 11% of a combination of polyurethanes and polyolefines and the remaining 4% of Nylon [3]. These data have been confirmed by the Fourier transform infrared analysis (FT-IR) of the ski boots of another major worldwide producer (Calzaturificio Dalbello) [3] that indicates that 72% of male ski boots models are made of polyurethanes, 25% of polyolefines and the remaining 3% of Pebax. For both producers (Dalbello and Salomon) the models made of polyamides (Nylon and Pebax) are commercialized as ski-mountaineering boots and are provided with a ski-walk mechanism and a rubber sole. Ski-mountaineering is known worldwide as the combination of skiing and mountaineering. In this discipline the skier also climbs the mountain with the skis by means of climbing skins and specially designed bindings, therefore lightweight equipment is preferred. Polyamide based materials are used in ski-mountaineering due to their low density (1.01 g/cm^3) that permits to obtain boots with lower weight with respect to those made of TPU (density 1.18 g/cm^3) [3]. However, due to the high costs of polyamides with respect to TPUs and POs [3], these materials are not widely used for the production of recreational and racing boots for alpine skiing. For this reason, in the present study we have focused our attention only on the analysis of polyurethane and polyolefines based ski boots. Looking in detail inside the models designed for different skiing disciplines, it can be observed that all the alpine-ski racing models of the analysed producers (Salomon and Dalbello) are made in TPU while most of the models for intermediate and beginner skiers are made of polyolefines. Moreover, a larger number of models made of polyolefines are used for women and junior ski boots. Women models produced completely or partially in polyolefines were recorded to be 57% for Salomon and 52% for Dalbello while junior ski boots were recorded to be 82% for Salomon and 88% for Dalbello [3]. These differences should therefore be connected with the viscoelastic and physical properties of the plastics used.

Ski boot performances are ruled by two main characteristics: the forward flex and the elastic rebound. The forward flex is the moment needed to bend the boot to a certain angle. Generally, ski boots are sold with a Nominal Flex Index (NFI) value [4] that describes the moment needed to bend the boot to a certain angle from the neutral position. Unfortunately, there are no ISO or ASTM standards to unify the way to measure the flex index [4]. The forward flex moment has a significant effect on skiing performances since the transmission of the forces from the skiers to the ski is controlled by the ski boot flexion. If the ski boot is stiff, the loads are rapidly transferred from the skier to the ski, resulting in a fast control of the trajectory. However, a stiff ski boot is not able to transmit the action smoothly to the ski and therefore the edge grip can be affected. In addition, a stiff boot does not allow the skier to easily adapt his body position to the variations of the skiing slope and to absorb the possible slope roughness: therefore this type of boots is used by racers and high level skiers that have skills and strength to bend the ski boot to adapt the skiers position to the shape of the skiing surface. Moreover, racers prefer a stiffer boot to avoid losing their balance at high speeds due to excessive forward bending of the boot under load. For the same reasons, intermediate and beginner skiers (especially if lightweight) prefer soft boots that permit a more confortable control of the skis with less effort.

The elastic rebound represents how fast the boot returns from a certain angle of inclination to its neutral position. It can strongly influence the ability of the boot to adapt and adsorb the variations of the slopes. If the elastic rebound is too fast it can cause a backward loss of balance of the skier, while if it is too slow it will require an additional effort to return to the initial position for the next turn.

The increase in stiffness at low temperatures and the visco-elastic behaviour of the materials used have a significant effect on the flexural and rebound properties of ski boots during the skiing action. Indeed, a more elastic material should provide a faster rebound. Moreover, a minor influence of temperature on the flexural stiffness is desirable in order to have a constant performance in the different climatic conditions that can be encountered during skiing.

Several factors have a significant effect on the flexural and rebound behaviour of ski boots. First of all, the design and the type of thermoplastic polymers are responsible of the overall performances of ski boots. Material properties are significantly affected by temperature, humidity and strain rate; therefore, these parameters should be considered in order to define the optimal type of materials to be used. In particular, it is well known that the strain rate has an effect on the properties of polymeric materials that possess a strain-sensitive behaviour and the practice of skiing involves the application of forces from the skier to the ski boot at different rates. In particular, the rate of application of the forces depends on the type of skiing disciplines. For example, faster impulses are requested by slalom racing skiers for more control during high-speed events. On the other hand, slower and smoother impulses are requested by off-piste skiers to prevent the sinking of the tips of the ski in low density snow.

Other important factors that can influence the flexural and rebound behaviours are the force needed to close the buckles and the dimension of the foot. Both factors can cause a change in the pressure between the different parts that compose the external shell of the ski boot and therefore affect the flexural behaviour. Another important factor to be taken into account is the effect of the binding that applies a localized force at the interface between the boot and the binding and affects the flexural behaviour of the boot.

Also, it is important to consider that the moulds used for the injection moulding process of ski boots are very expensive components. Therefore, once the boot design is completed, it is more convenient for ski boot manufacturers to change the material properties than to modify the moulds and change the local thicknesses of the boot, obtaining variations in the flex. For this reason, the visco-elastic properties of the polymeric materials used for the preparation of ski boots shell and cuff are a key factor in order to tailor the final flexural and rebound properties of ski boots.

Over the years, a number of scientific papers have been published on ski boots [5], but few have studied the flexural behaviour. Petrone et al [6] have evaluated the effect of an aluminium boot board on stiffness, torsional and bending moment of ski boots in laboratory and field tests. The same authors have also investigated the effect of boot stiffness on the flexural behaviour of alpine ski boots, combining on-snow testing of flexion angles with laboratory cyclic bending tests [4]. This testing results in a new parameter for the measure of the flex called effective flex index (eFI), which is the value of the bending moment (expressed in Nm) to obtain a forward leaning angle of 10° from the neutral position. Kuipers et al [7, 8, 9] have studied the influence of a modified ski boot in the prevention of injuries in mogul skiing. A ski boot with an increased forward-lean flex was prepared in order to obtain a reduced boot induced anterior drawer (BIAD) that is responsible for some types of knee injuries. The smoother flex was obtained by cutting parts of the cuff and of the shell close to the instep. Although the moment needed to bend the boot was lower compared to that of a traditional ski boot, the skier did not perceive any problem apart a slight decrease in speed control and balance. On the contrary, shock absorption and forward flex were increased. Reichel et al [10] have developed a test bench for the measure of the stiffness of ski boots reporting for the first time in the literature the bending moment curve of a ski boot. However, no specific information about the plastic used for the ski boots tested has been provided and no correlation between the materials used and the final properties has been reported in any of the cited papers.

Parisotto et al [11] have presented a procedure for the design of telemark ski boots developed through experimental tests on materials, that focused on their behaviour in terms of elasticity, viscosity, temperature dependence and degradation. Recently, Natali at al have published two papers [12, 13] with a detailed study of the mechanical properties of Pebax, using mechanical and dynamic mechanical thermal analysis (DMTA) tests. The authors have also investigated the effect of weathering on the mechanical properties and have used the data to build a FEM model in order to predict the flexural behaviour of telemark ski boots. DMTA tests have been performed on degraded and non-degraded samples at different frequencies in a temperature range from $-20°C$ to $+20°C$. However, all the ski boots studied in that work were made of Pebax and there was no comparison with other materials. Also, DMTA analysis was used to determine the dampening of skis [14]. The reported results show that the behaviour of skis is strongly influenced by the polymeric top-sheet used. In particular, materials with higher tan δ values at $0°C$ (measured by DMTA analysis) provide the best damping behaviour [14]. The effect of different frequencies has also been analysed and a finite element analysis has been conducted with good correlation between experimental and DMTA data.

Based on previous works and ski boot producers selection of specific polymeric materials, it can be supposed that the mechanical behaviour of ski-boots (flex and rebound) is correlated to the intrinsic visco-elastic properties of the polymeric materials used for their construction. DMTA analysis is able to measure the visco-elastic response of materials subjected to cyclic loads, similar to those occurring during normal skiing. Cyclic loads are applied to the boot to transfer the impulse to the ski and control the trajectory and the speed. Moreover, DMTA analysis can be performed with varying temperature, which is a critical feature for material characterization for equipment used in winter sports, being performed in specific environmental conditions. However, no correlation between DMTA data and flex or rebound behaviour of ski boots has ever been reported in the literature. For this reason, the aim of this work is to study the affect of visco-elastic properties of the polymers, obtained through DMTA analysis, on the mechanical properties of the finished products, and establish a protocol to predict and test the behaviour of ski boots on the basis of the visco-elastic properties of the plastic materials used for their production. As stated above, several factors have a significant affect on flexural and rebound performances and therefore, a multi-factorial approach is necessary. The main focus of this study is on material properties and on the affect of temperature and several of these parameters will be kept constant including design type, strain rate, closure force of buckles and binding influence. Furthermore, to have a better understanding of the mechanical behaviour of ski boots, in the second part of the chapter the correlation between the design and construction of the ski-boot and its rebound and flexion properties has been investigated. The results, both from the materials as well as from the design point of view, can be used during the development of new products to adjust the boot properties to the final destination of use.

3.2 Materials and Methods

3.2.1 Materials

For the analysis of the influence of the materials and their visco-elastic properties on the flexural behaviour and rebound response two boots of the same model (Dalbello Aerro, size 26.5 Mondopoint) were used. According to the ski-boot producer, each boot was produced using a single material, both for the shell (lower part) and cuff (upper part). The ski boot in TPU was named Boot-1 while the one in PO was named Boot-2. The parts in different colours have been co-injected with materials (according to the ski boot producer) having the same chemical composition and only with different colours. Both boots have an overlap design with four buckles, as shown in Fig. 3.3. This setup, using the same boot model but in produced using different materials, avoids any influence of the boot design.

Figure 3.3: Image of the ski boot model used for the flexural and rebound testing

Furthermore for the analysis of the influence of the design of the ski boot on the flexural behaviour and on the rebound response two different ski-boot models have been selected:

- 3-pieces: Dalbello Kr2 Pro (NFI 130). The boot is commercialized with two tongues made with different materials and two inserts to modify the flex, Fig. 3.4; model year 2013

- Overlap: Dalbello Scorpion 130 (NFI 130) and Dalbello Scorpion 110 (NFI 110) with the same design and with only different base materials; model year 2013

Figure 3.4: Insert and tongues used to modify the stiffness in the 3-pieces ski boot

3.2.2 Methods

Fourier Transform Infrared Spectroscopy (FT-IR) and Hardness testing

The chemical composition was determined via Fourier transform infrared spectroscopy (FT-IR) (2.2.2) using a Perkin Elmer Spectrum One spectrometer equipped with an attenuated total reflectance (ATR) detector.

The Shore D hardness of the materials was measured according to ISO 878 at $+23°C$ (2.2.2).

Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) is an experimental technique that monitors heat effects associated with phase transitions or chemical reactions as a function of temperature. The difference in heat flow to the sample and a reference at the same temperature, is recorded during a temperature scan at constant rate. Since the pressure is constant the heat flow is equivalent to enthalpy changes:

$$(\frac{dq}{dt})_p = \frac{dH}{dt} \tag{3.1}$$

The heat flow difference between the sample and the reference is:

$$\Delta\frac{dH}{dt} = (\frac{dH}{dt})_{sample} - (\frac{dH}{dt})_{reference} \tag{3.2}$$

This heat flow difference can be both positive, for endothermic processes such as most phase transitions, and negative, for exothermic processes such as crystallization or cross-linking. The calorimeter consists of a sample holder and a reference holder, both constructed of platinum to withstand high temperatures. The sample is sealed into a small aluminium pan, usually around 10 mg of material. Whereas the reference is an enpty pan and cover. Under each holder there is resistance heater and a temperature sensor. The difference in the power to the two holders, necessary to maintain the holders at the same temperature, is used to calculate $\Delta dH/dT$. Furthermore a flow of nitrogen is maintained over the sample to create a reproducible and dry atmosphere and also to eliminate air oxidation of the sampler at high temperatures.

In Fig. 3.5 a typical DSC scan is reported, where each peak corresponds to a heat effect associated with a specific process, such as crystallization or melting. From a DSC curve is possible to know the temperature at which a certain process occurs and the peak temperature corresponds to the temperature at which maximum reaction rate occurs.

Furthermore it is possible to obtain the enthalpy change associated with a certain process by a simple integration of the area under the corresponding peaks. A special case is the temperature associated with an important phase transition for polymers, the glass transition temperature, T_g. For amorphous, non-crystalline polymers this temperature sets the separation between the brittle, glasslike form, to the rubbery, flexible form. In fact below the glass transition temperature certain segmental motions are hindered by the interaction with neighbouring chains. For this reason T_g is not a true phase transition but one that involves a change in the local degree of freedom. In the DSC experiment the glass transition is defined by a rapid change in the base line, corresponding to a change in heat capacity. Since it is not associated with an enthalpy change , being a second order transition, the effect is weak and is observable only with a sensitive instrument.

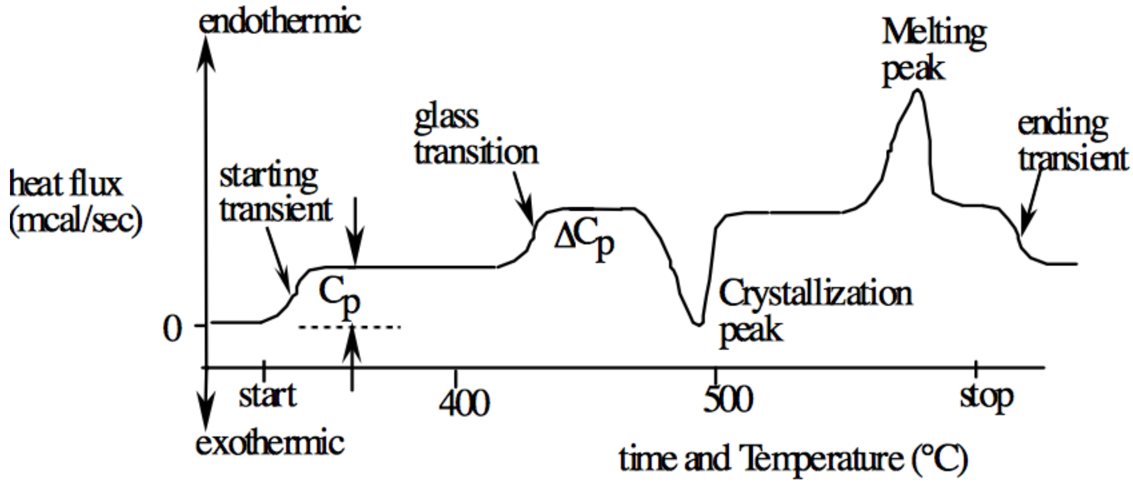

Figure 3.5: Typical DSC curve; crystallization is a typical exothermic process and melting a typical endothermic process

Calorimetric measurements have been carried out using a Perkin Elmer DSC7 instrument calibrated with high purity standards. Weighted samples of approximately 10 mg were encapsulated in aluminium pans. Temperature scans were performed with a heating and cooling rate of $20°C$/min from $0°C$ to $+250°C$ (heating scan) and from $+250°C$ to $0°C$ (cooling scan).

Dynamic Mechanical Thermal Analysis (DMTA)

The visco-elastic properties as a function of temperature were determined via DMTA (2.2.2) using a Rheometrics dynamic mechanic thermal analyser DMTA 3E model with a single cantilever bending geometry on samples of 25x2x6 mm. In all the tests a single frequency of 10 Hz has been used, with a strain of 0.1%. Temperature scans were performed in a temperature range from $-30°C$ to $+50°C$ and with a scan rate of 3°/min.

The samples analysed by DMTA have been prepared in a lab-size injection moulding apparatus from pieces cut directly from the boots previously analysed on the flexural test bench. The temperatures used in the lab moulding were the same as the ones used during the standard industrial production moulding cycle. All the samples for DMTA analysis and the ski boots tested have been conditioned at $70°C$ for 24 hours in order to release any internal stress due to the injection process.

Ski Boot Flexural Test Bench

The flexural behaviour of ski boots was measured using a purpose-built test bench (Figure 3.6) similar to the one used by Reichel et al [10]. In this setup the boot is fixed to a steel base frame and flexed by a pneumatic arm connected to an aluminium leg prosthesis inserted in the boot. The pneumatic arm is equipped with a load cell to measure the applied moment and a position sensor to measure the actuator displacement. The load cell is a quartz force sensor integrated in a link, designed for measuring compression to 22 kN and tension to 4 kN, with a 0-10 V linear output. The position sensor is a draw wire sensor with a range up to 1250 mm and a 0-10 V linear output. Both sensors have been calibrated properly prior to use and connected to a personal computer through a National Instrument DAQCard, allowing a sampling rate of 100 Hz.

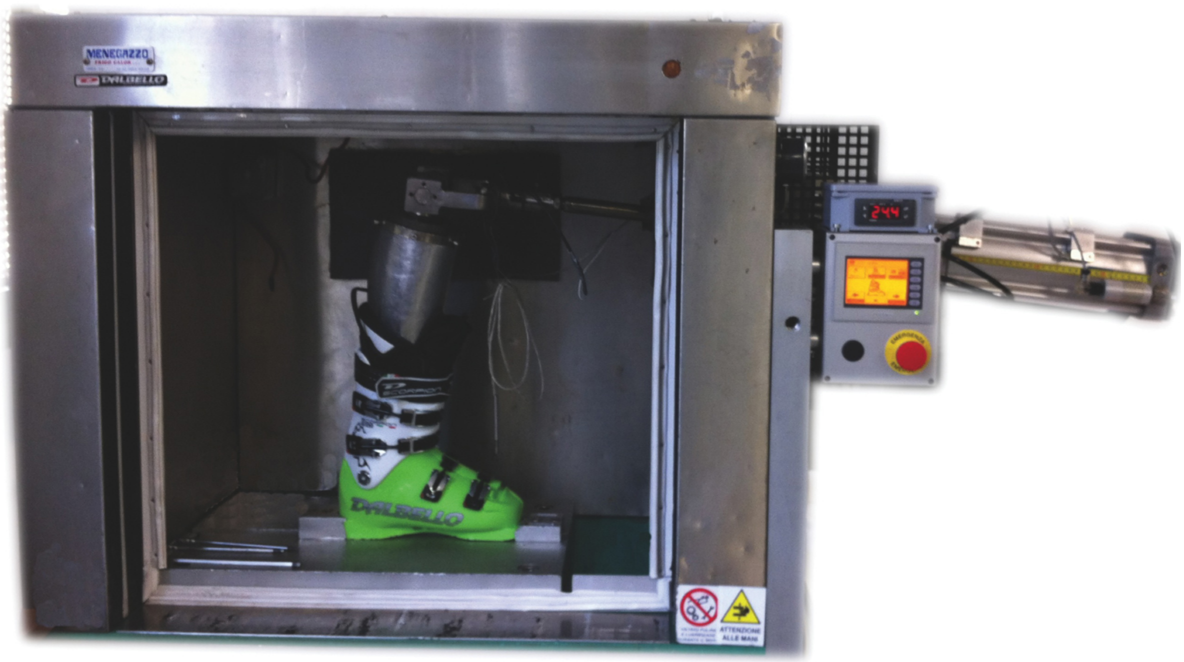

Figure 3.6: Ski boot flexural test bench

Therefore, the angle measured is the flexion angle between the prosthetic tibia and the shell, which corresponds to the shell-tibia angle reported in reference [4]. Furthermore the system is enclosed in a climate chamber, in this way it is possible to perform tests also at low temperatures, going down to $-30°C$. The data acquisition was done through a personal computer connected to the test bench, using a National Instrument Labview software written specifically for this application.

All the tests were performed at the same velocity (20 cycles/min) and in an angular range between $-5°$ and $+17°$ from the neutral position [4]. The flexural speed was 14.7/s that is similar to that previously reported in the literature (16.6°/s) by Petrone et al [4]. To investigate the influence of temperature on the flexural behaviour, the tests were performed at three temperatures ($+12°C$, $-2°C$ and $-12°C$). It was observed that after the first 10 cycles the flexural behaviour became constant (Figure 3.7), which is due to a stabilization of the system during the flexion (foams of the liner, buckles, pivot points). Consequently, the first cycles were not considered during the analysis and the 10th cycle was used in all the tests for the evaluation of the flexural behaviour.

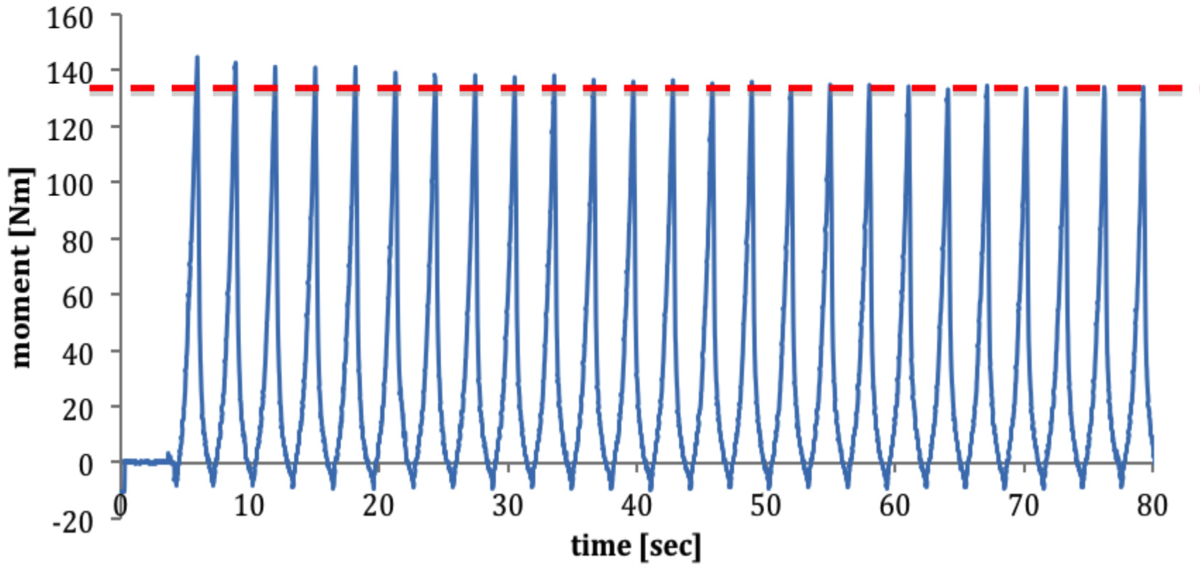

Figure 3.7: Stabilization of the flexural behaviour

Boot-2 was tested two times at $+12°C$ in order to verify the reproducibility of the method. The results in Figure 3.8 show a good reproducibility.

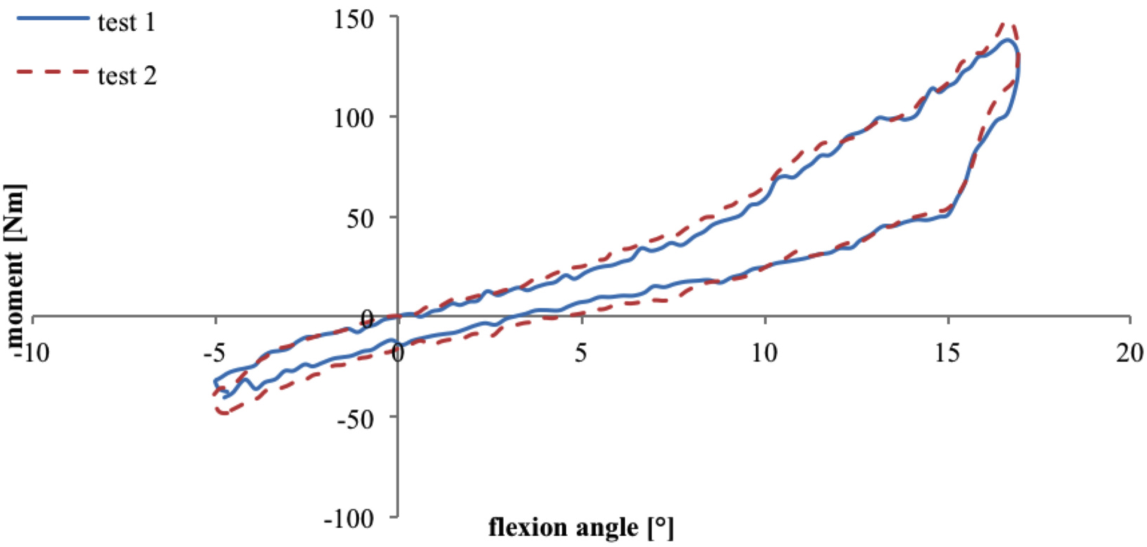

Figure 3.8: Reproducibility of the flexion moment as a function of prosthesis flexion angle for Boot-2 at $+12°C$

During all the tests the same commercial liner has been used, to avoid any influence of the liner construction and properties on the results. Furthermore the buckles have been closed in all tests at the same point of the rack to provide the same closure force.

Ski Boot Rebound Test Bench

The rebound response of ski boots has been measured using a purpose-built test bench. In this setup the boot is fixed to a steel base frame and flexed forward to +17° from the neutral position. Once flexed the boot is held in position with a quick-release carabineer. In this way any influence of the operator during the release is avoide. A draw wire sensor, attached on the higher part of the prosthetic leg, allows the measurement of the rebound time and the total displacement of the cuff (Figure 3.9). The data acquisition was done through a personal computer connected to the test bench through a National Instrument DAQCard, allowing a sampling rate of 100 Hz, and using a National Instrument Labview software written specifically for this application. The tests have been repeated for 10 times and the results averaged.

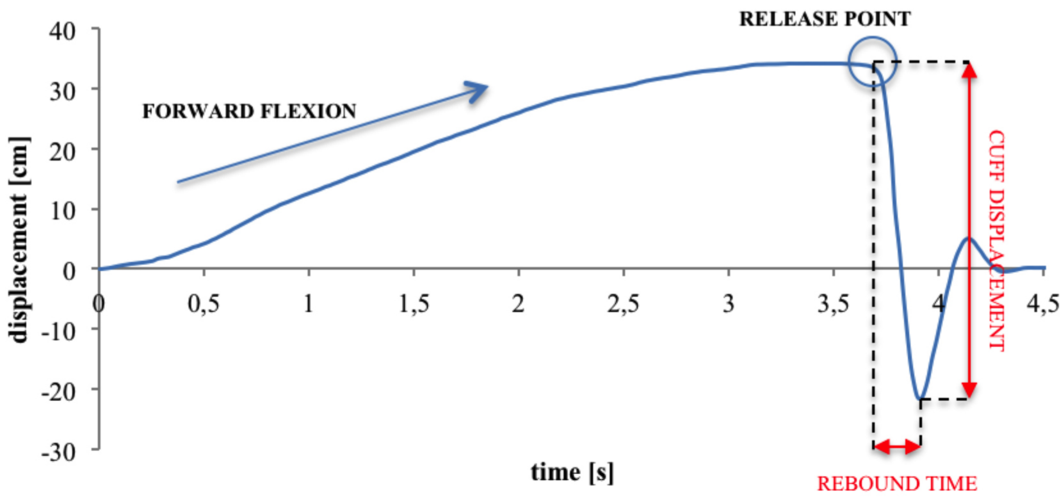

Figure 3.9: Typical rebound curve showing the displacement of the cuff versus rebound time

3.3 Results

In this section the results obtained during the study are presented. Starting from the investigation of the influence of the materials used in the production of ski boots on the final flexural and rebound behaviours. The flexural and rebound test have been correlated with the visco-elastic properties obtained by means of DMTA analysis. Furthermore the influence of the design and construction of the boots has been studied leading to a complete understanding of all the parameters involved in the definition of the overall performances of the ski boots.

3.3.1 Influence of Materials for Structural Parts

Chemical composition (FT-IR), Hardness testing and Differential Scanning Calorimetry (DSC)

The chemical composition of Boot-1 and Boot-2 has been detected by FT-IR analysis (Figure 3.10). The resulting FT-IR spectra were compared to a database of known polymeric materials resulting that Boot-1 was composed of a polyether based polyurethane (obtained using MDI as isocyanate precursor) and Boot-2 was composed of a polyolefin blend containing SBR rubber. In particular, the peaks at 1699 and 1727 cm^{-1} were used to identify the polyurethane based materials, the peaks at 1456 and 1439 cm^{-1} were used to identify polyolefin based materials. Moreover, the analysis indicates for each boot, the cuff and the shell are made of the same material. Finally, the white and black parts of the same boot present the same chemical composition. The results are in accordance with the information provided by the producer.

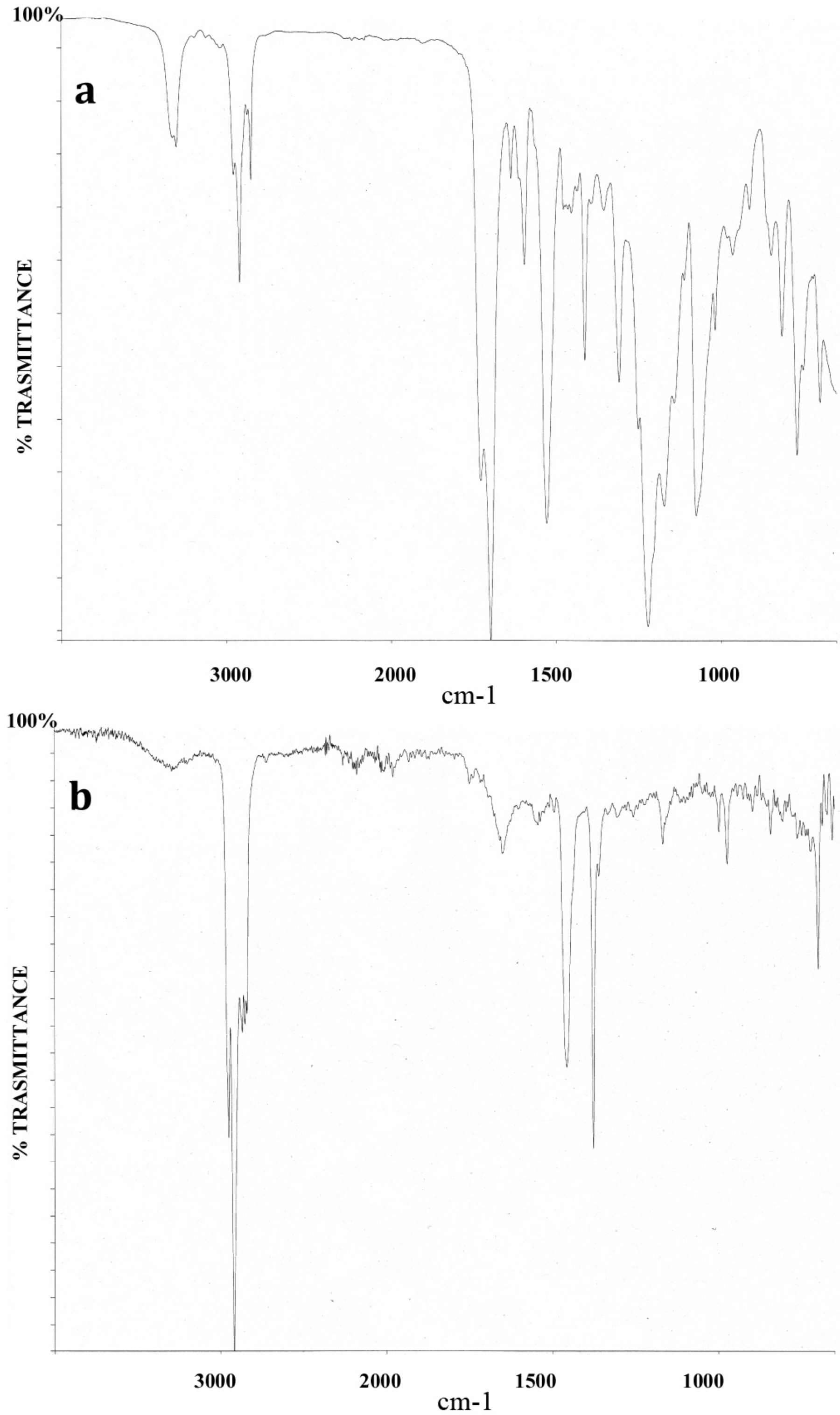

Figure 3.10: FITR analysis of the material used for Boot-1 (a) and for Boot-2 (b)

The hardness of the plastic of the different parts of the ski boots have been analysed using a Shore D durometer proving that cuff and shell of the same ski boot have the same hardnesse. This is a further confirmation that each boot is produced using the same material. In particular Boot-1 presents a hardness of 56 shore D and Boot-2 51 shore D.

The thermal properties of the materials have been investigated by differential scanning calorimetry (DSC) in order to define the effect of different pigments on the thermal transitions and crystallinity. In fact it has been proved that the use of different pigments and master-batches, usually utilized to colour a plastic material, can have a significant influence on the crystallization behaviour and therefore on the visco-elastic properties [15]. The DSC curve of the black part of Boot-2 is reported in Figure 3.11. Furthermore, Table 3.1 shows the thermal characteristics of the white and black parts of Boot-2, in terms of melting and crystallization temperatures and the enthalpy changes associated with these transitions.

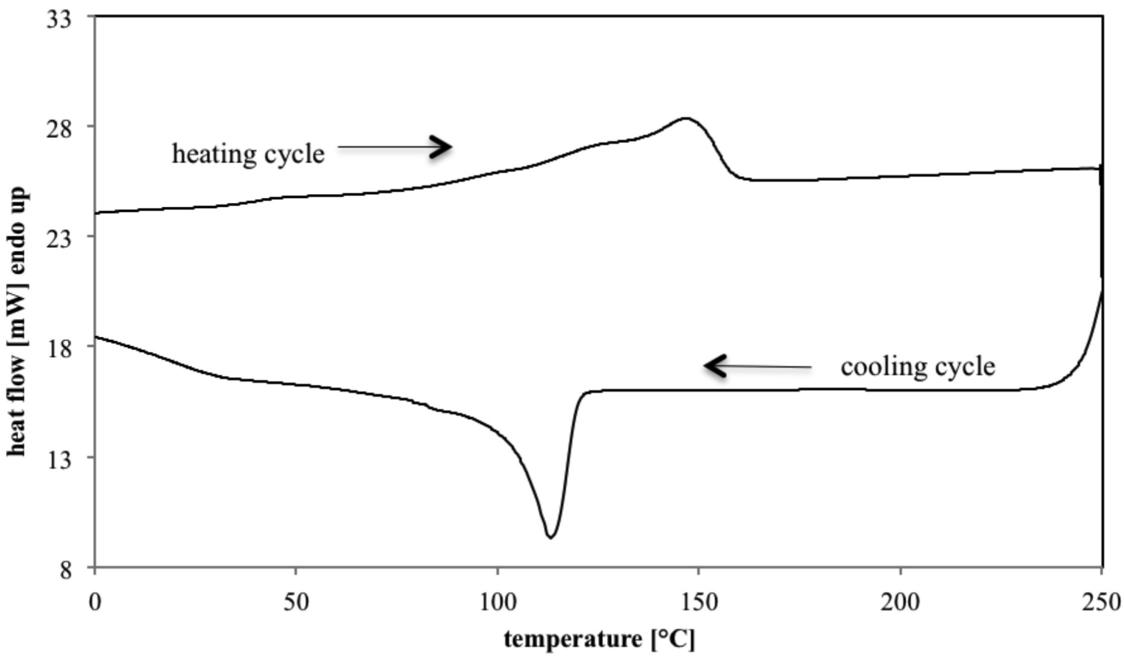

Figure 3.11: DSC curve for black part of Boot-2 showing the melting and crystallization peaks

The results of DSC analysis show there is no significant difference in the transition temperatures and enthalpies between the two materials in different colours. Thus it is possible to conclude that, in this case, different colour master-batches do not influence the melting and crystallization temperatures and the crystallinity. Similar results have been obtained for Boot-1, indicating that also in that case the master-batch used for the coloration has no effect on the thermal properties of the material.

	Heating cycle		Cooling cycle	
	Melting Temperature [$^{\circ}C$]	**Δ H** [J/g]	**Crystallization temperature** [$^{\circ}C$]	**Δ H** [J/g]
Black part	146.6	45.9	113.1	-51.3
White part	145.9	46.0	112.7	-46.4

Table 3.1: Thermal properties of parts with different colours of Boot-2

DSC analysis has also been used to find out if the injection moulding process performed to prepare the samples for DMTA analysis has an effect on the crystallinity of the material. Indeed, it is reported in the literature [16] that the moulding conditions can have an effect on crystallinity and therefore on the mechanical properties of semi-crystalline polymeric materials. In fact in some cases the thermal cycles can induce the formations of secondary phases in the material. To test this effect DSC analysis has been performed on samples taken directly from the ski boots, and comparing them with samples obtained from the lab-scale injection moulding. The results of the DSC analysis in Table 3.2 show that crystallization, melting temperatures and degree of crystallinity do not change after the injection moulding process necessary to prepare the samples for DMTA analysis. For this reason, it can be assumed that the results of DMTA analysis on the samples moulded in the laboratory are representative of the material of the boots and thus can be correlated with the results obtained from the flexural and rebound test benches.

	Heating cycle		Cooling cycle	
	Melting Temperature [$^{\circ}C$]	**Δ H** [J/g]	**Crystallization temperature** [$^{\circ}C$]	**Δ H** [J/g]
Boot-1	181.5	42.6	125.9	-41.7
Boot-1 after moulding	182.4	42.0	127.2	-38.9
Boot-2	146.6	45.9	113.1	-51.2
Boot-2 after moulding	145.3	43.9	112.3	-52.3

Table 3.2: Effect of the laboratory moulding process on the thermal properties for Boot-1 and Boot-2

Dynamical Mechanical Thermal Analysis (DMTA)

Dynamical mechanical thermal analysis measurements were performed on samples obtained directly from the two ski boots, in particular temperature scans have been performed, in the temperature range between $-30°C$ and $+50°C$. The results of the variation of the elastic modulus and damping with temperature are reported respectively in Figure 3.12 and Figure 3.13. Moreover the values of the elastic modulus and tan δ at the temperatures of $-12°C$, $-2°C$ and $+12°C$ are reported in Table 3.3, these three temperatures have been selected as being representative of the different conditions encountered during real skiing.

The tan δ peaks, reported in Figure 3.13, give and indication of the position of the glass transition temperature (Tg). Using the position of the tan δ peak to determine the glass transition temperature is an alternative method to the one based on the baseline variation measure by DSC. The value of Tg is an important descriptor of the polymer thermo-mechanical response [17, 18, 19].

The data in Table 3.3 and Figure 3.12 show a more consistent increase in stiffness for the polyurethane used for Boot-1 compared to the polyolefin used for Boot-2. In fact the elastic modulus of the PU has a 73% variation from $-12°C$ to $+12°C$, whereas the PO only 59% in the same temperature range.

Moreover, from the analysis of the curves in Figure 3.13 it emerges that between $-30°C$ and $+13°C$ the PO used for Boot-2 has a more viscous behaviour with respect to the TPU used for Boot-1. This is linked to the higher value of tan δ for Boot-2. On the other hand for temperatures higher than $+13°C$ there is an inversion in the behaviour, with Boot-1 being the more viscous.

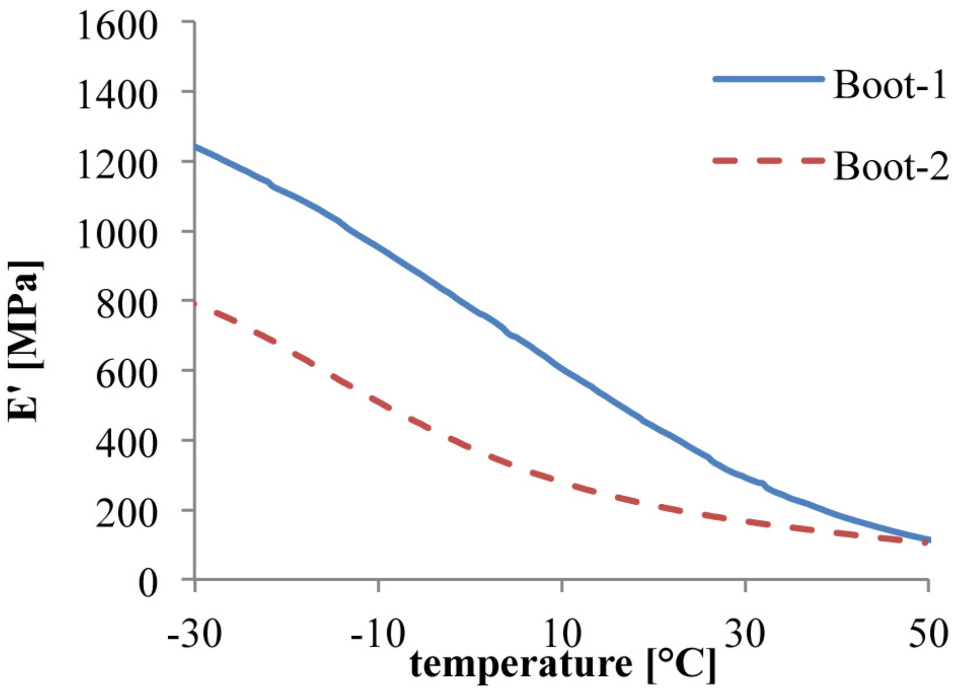

Figure 3.12: Variation of the elastic modulus with temperature for Boot-1 and Boot-2 in the temperature range between $-30°C$ and $+50°C$

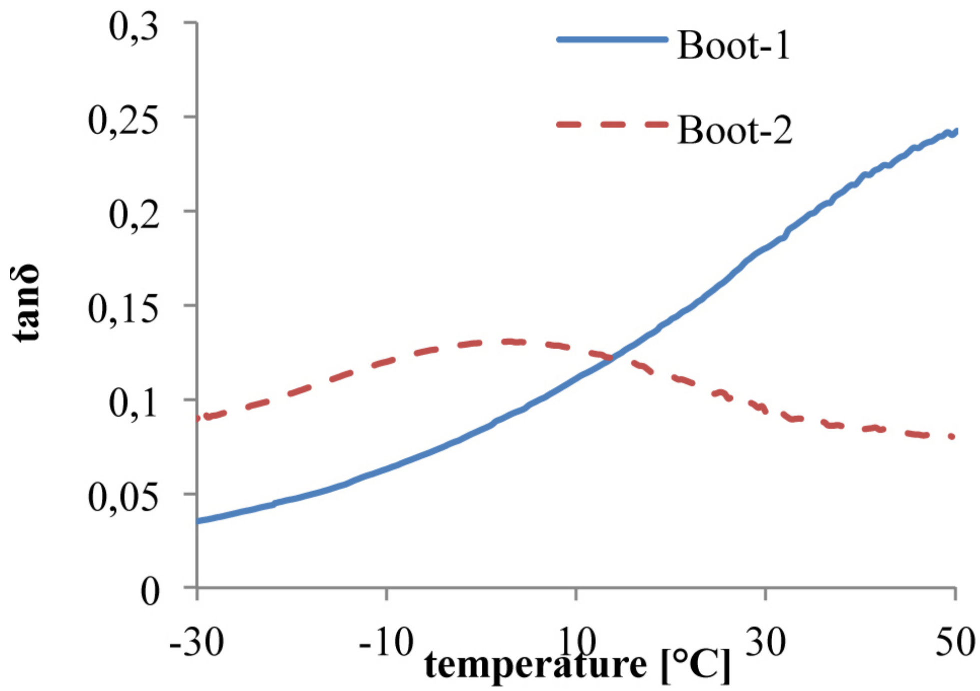

Figure 3.13: Variation of the damping with temperature for Boot-1 and Boot-2 in the temperature range between $-30°C$ and $+50°C$

	Elastic modulus $[MPa]$			tan δ		
	$-12°C$	$-2°C$	$+12°C$	$-12°C$	$-2°C$	$+12°C$
Boot-1	986	816	571	0.0595	0.0794	0.1167
Boot-2	547	403	343	0.1169	0.1289	0.1239

Table 3.3: Elastic modulus and damping of the materials used for Boot-1 and Boot-2 at $-12°C$, $-2°C$ and $+12°C$

Finally, the influence of the colour master-batches on the visco-elastic properties was investigated as well. Figure 3.14 and 3.15 show the elastic modulus and tan δ curves of the parts with different colours taken from Boot-2. It is clear that there is a limited influence of the master-batches on the visco-elastic properties of the material, in fact the curves are overlapping. A similar behaviour was observed for the material used for Boot-1 and thus the curves are not reported in this work.

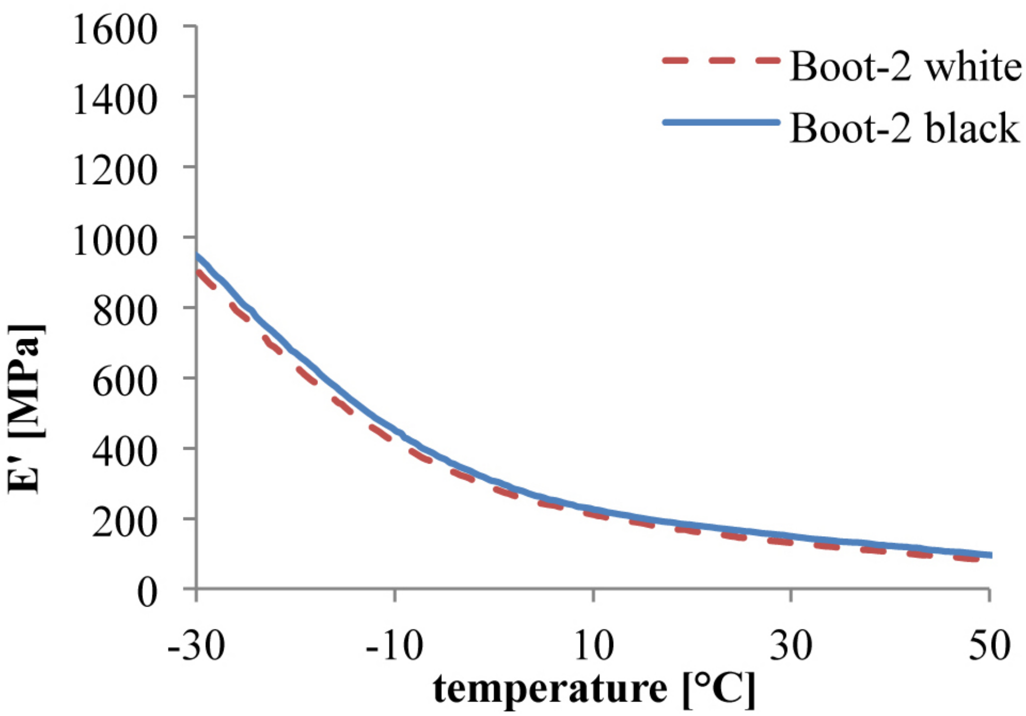

Figure 3.14: Elastic modulus of the white and black parts of Boot-2 in the temperature range between $-30°C$ and $+50°C$

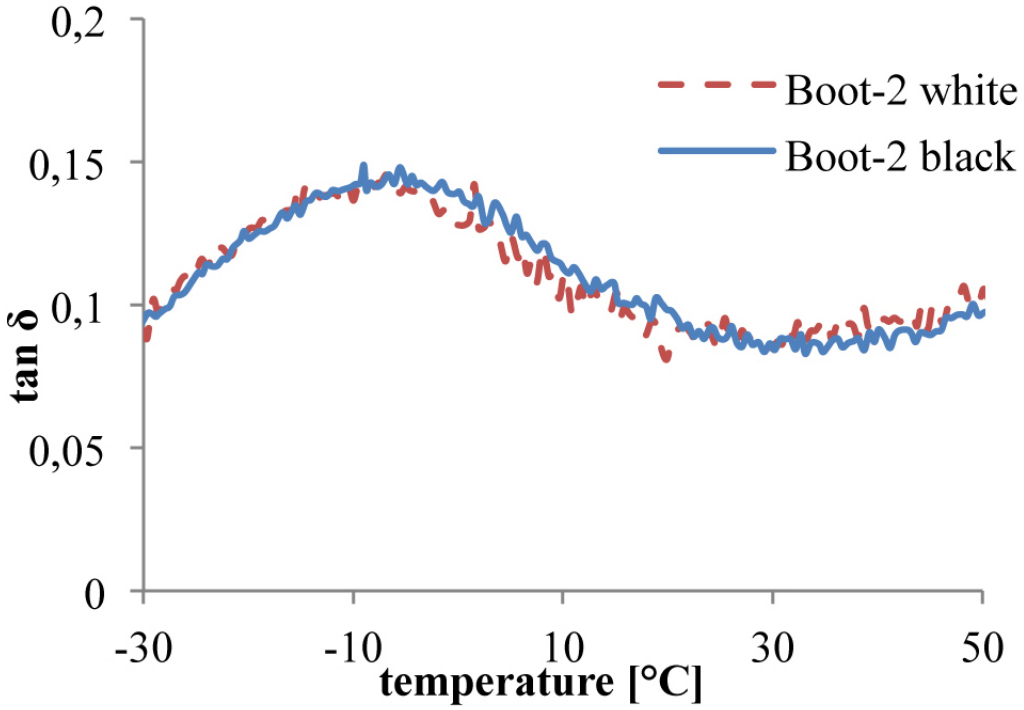

Figure 3.15: Damping of the white and black parts of Boot-2 in the temperature range between $-30°C$ and $+50°C$

Ski Boot Flexural and Rebound Tests

To investigate the influence of the temperature on the flexural behaviour of the ski boots and thus find a correlation with the behaviour of the materials, all the flexural tests have been performed at three temperatures: $-12°C$ (Figure 3.16), $-2°C$ (Figure 3.17) and $+12°C$) (Figure 3.18). These three temperatures have been selected as being representative of the different conditions encountered during real skiing. Before running the tests the ski boots were left for two hours at the selected temperature, in order to allow a stabilization of the temperature throughout the whole sample. From the curves in Figure 3.16, Figure 3.17 and Figure 3.18 emerges clearly that when the temperature is lowered the bending moment increases due to an increase of the stiffness of the material at lower temperatures. This effect has been demonstrated by the DMTA analysis of the variation of the elastic modulus with temperature in the previous section. The bending moments for both boots at all the temperatures investigated at the maximum forward flexion of $+17°$ from the neutral position during forward bending are reported in Table 3.4. It should be noted that for this test setup, the bending moment measured at $+17°$ coincides with the maximum value of the flexion moment (peak bending moment), but for materials with more rounded hysteresis curve these two values are not coincident. Moreover, the values for the eFI [4] extrapolated from the curves in Figure 3.16, 3.17, 3.18 are reported also in Table 3.4. The eFI is the bending moment corresponding to a flexion angle of +10° from the neutral position during forward bending.

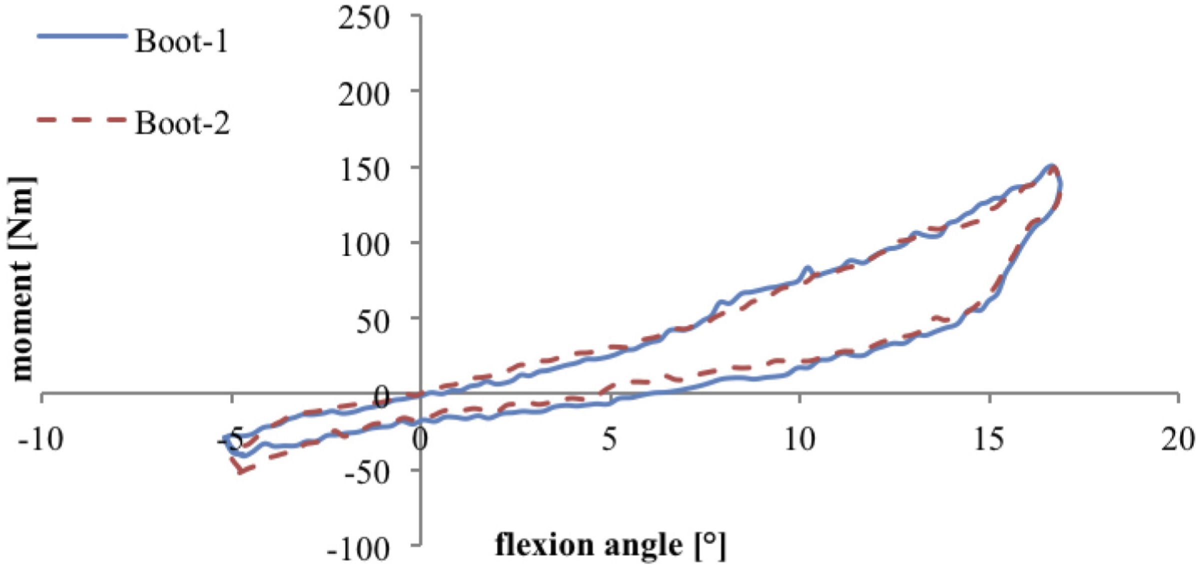

Figure 3.16: Bending moments for Boot-1 and Boot-2 as a function of prosthesis flexion angle at $+12°C$

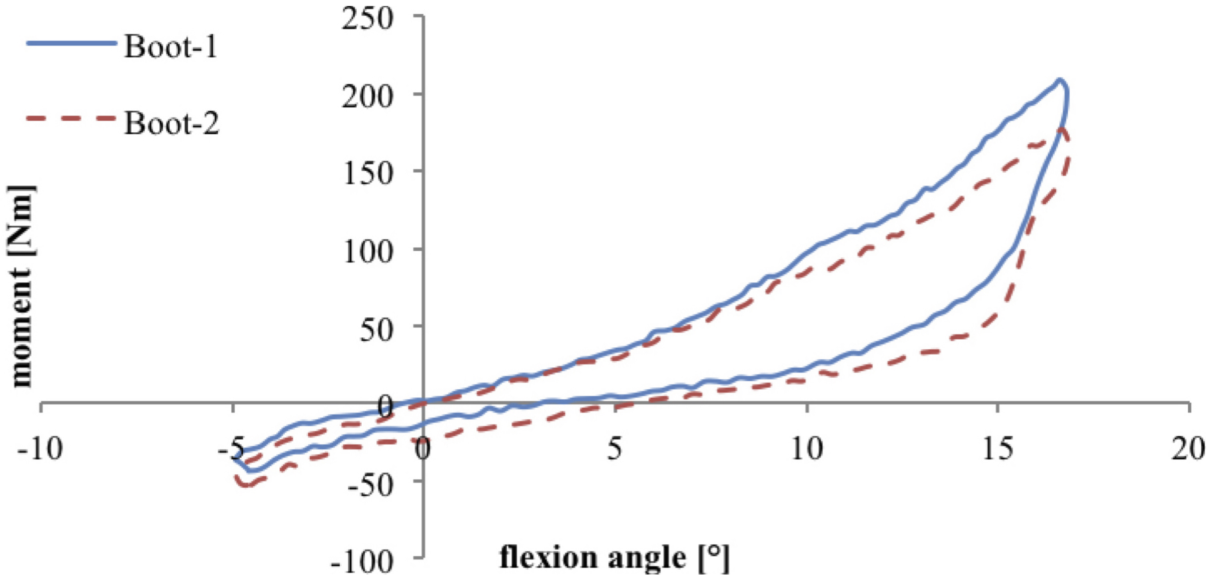

Figure 3.17: Bending moments for Boot-1 and Boot-2 as a function of prosthesis flexion angle at $-2°C$

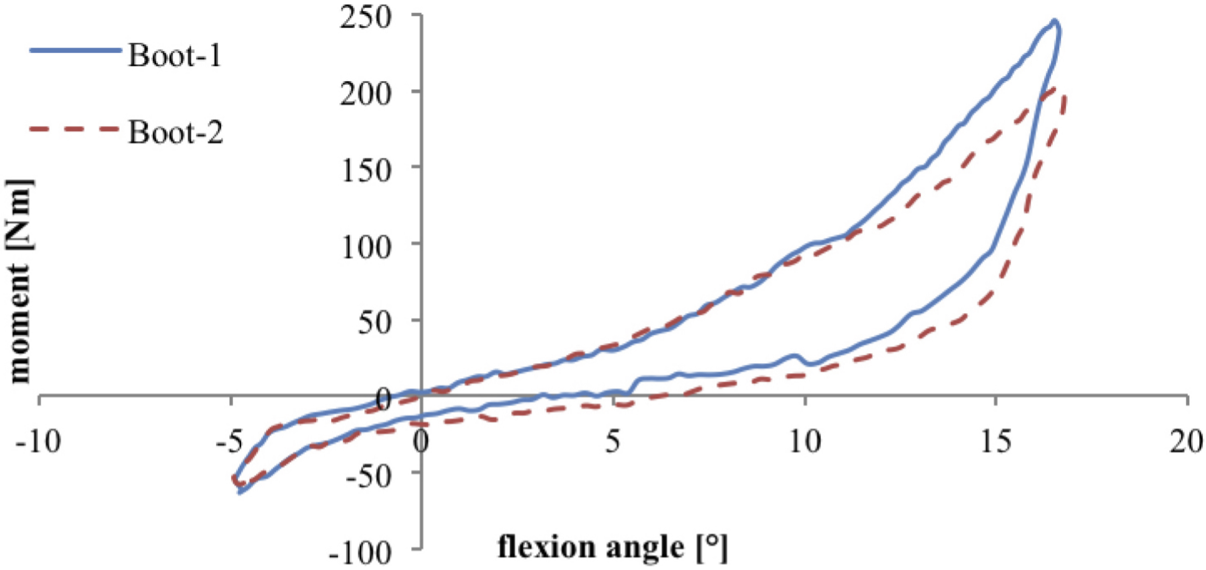

Figure 3.18: Bending moments for Boot-1 and Boot-2 as a function of prosthesis flexion angle at $-12°C$

	Bending moment $[Nm]$ **at** $+17°$			**eFi** $[Nm]$ **at** $+10°$ [4]		
	$-12°C$	$-2°C$	$+12°C$	$-12°C$	$-2°C$	$+12°C$
Boot-1	246	208	150	99	99	84
Boot-2	203	176	149	93	88	75

Table 3.4: Bending moment at the maximum forward flexion and eFI

The results in Table 3.4 show that at $+12°C$ the peak bending moment ($+17°$ in forward flexion) has a similar value both for Boot-1 and Boot-2. Furthermore a more consistent increase in bending moment is observed for Boot-1. In particular, Boot-1 presents a 64% increase when the temperature is lowered from $+12°C$ to $-12°C$, opposed to the 36% increase of Boot-2. The values for the eFI are smaller compared to the values reported by Petrone et al [4] that were comprised between 175 and 121 Nm for ski boots with NFI between 150 and 70. This discrepancy can be caused a series of experimental parameters such as the different test set-up used, which includes different prosthetic leg and different test bench, the different design and construction of the ski boots tested and the different force used to close the buckles. This fact also clearly points out that a standardized method, which takes into account all the parameters mentioned above (shape of the prosthesis, buckle closure, temperature, humidity, angular velocity etc), must be developed and used for the measure of the eFI.

Finally to complete the characterization of the temperature variation on the mechanical behaviour of ski boots, the rebound speed has been measured at the same three temperatures of $-12°C$, $-2°C$ and $+12°C$ starting from a forward flexion angle of $+17°$ from the neutral position. The results are shown in Figure 3.19. Boot-1 shows a pronounced increase in the rebound speed as the temperature decreases explained by the less viscous behaviour of the polyurethane at lower temperatures. On the other hand Boot-2 has a more constant trend, increasing just between $-2°C$ and $-12°C$. Overall, Boot-1 has a faster rebound compared to Boot-2 at all temperatures. The difference in rebound speed has a decrease for temperatures above $+5°C$, reaching a minimum at $+12°C$.

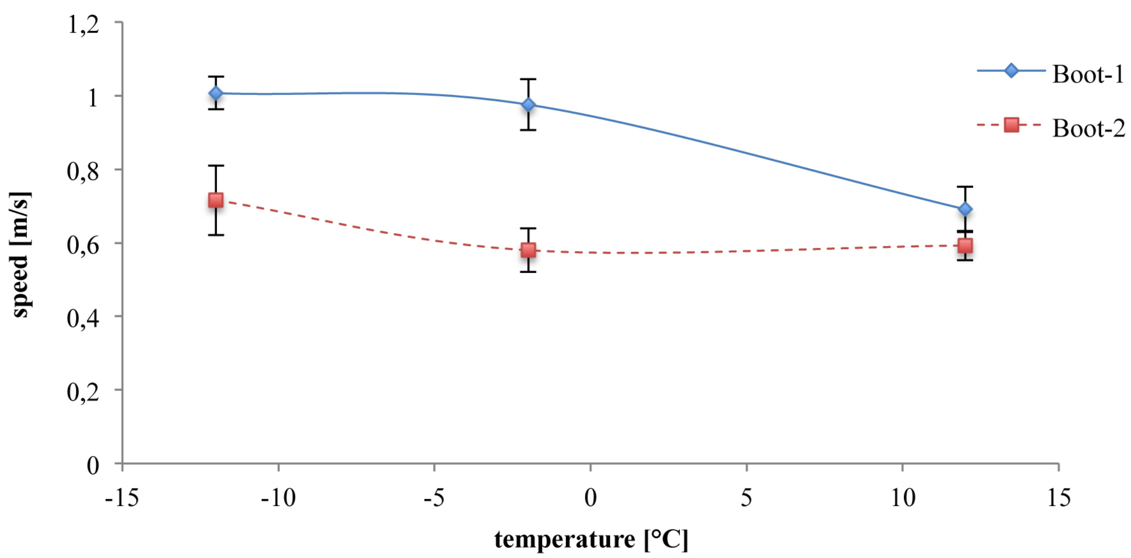

Figure 3.19: Average rebound speed at different temperatures

3.3.2 Influence of Design

Chemical composition (FT-IR) and Hardness testing

The chemical composition of the different parts of the three ski ski boots (two overlap and one 3-pieces) used in this study has been analysed by FT-IR. The resulting FT-IR spectra were compared to a database of known polymeric materials pointing out that for all the models shell and cuff are made in polyurethane (TPU) based on methylene diphenyl diisocyanate (MDI) and polyether soft blocks. Furthermore the shore D hardness of the materials was measured and the elastic modulus was taken from the data sheet of the materials used.

The results show that the TPU used for the 3-pieces boot has a shore D hardness of 64 and an elastic modulus of 250 MPa. Moreover, this design has two interchangeable 2 tongues made of polyamide 12 (PA). On the other hand the overlap Dalbello Scorpion 130 (overlap hard plastic) has a shore D hardness of 60 and an elastic modulus of 200 MPa. The other ovelap boot, Dalbello Scorpion 110 (overlap soft plastic) has a shore D hardness of 57 and an elastic modulus of 170 MPa. For this design there is no interchangable tongue. All the results are summarized in Table 3.5.

	Overlap design			3-pieces design		
Part	**Material**	**Elastic modulus** $[MPa]$	**Hardness** $[ShoreD]$	**Material**	**Elastic modulus** $[MPa]$	**Hardness** $[ShoreD]$
Cuff and Shell	TPU	170/200	57/60	TPU	250	64
Tongue	na	na	na	PA	250/450	52/64

Table 3.5: Chemical composition, elastic modulus and hardness of different parts of ski boots.

Ski Boot Flexural and Rebound Tests

The flexural behaviour has been tested on the overlap and 3-pieces boots at $+20°C$ in an angular range between 0° and +12° from the neutral position. The flexion was only tested in forward direction since the forward flexion is more important during the skiing action and is more influenced by design with respect to the backward flexion. Figure 3.20 shows the results obtained for the flexural behaviour, clearly indicating a more linear response of the 3-piece ski boot, opposed to a faster increase of the moment at higher flexion angles for the overlap ski boot.

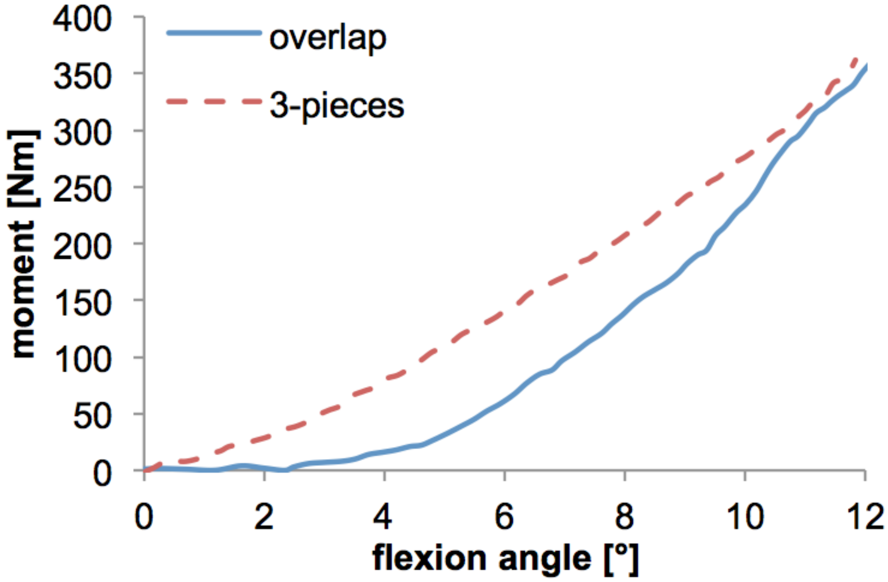

Figure 3.20: Comparison of the flexural behaviour of 3-pieces and overlap ski boots

This difference in flexural behaviour can be ascribed to the different design and construction. In fact in the 3-pieces ski boot the tongue acts as a spring, opposing to the forward flexion since the first degrees and resulting in a linear response as the flexion angle increase. On the other hand in the overlap boot the first degrees of flexion are free since the cuff can rotate around the hinge points. Once the lower front part of the cuff touches the shell the flexion moment increases rapidly, as more force is needed to deform the shell of the boot. This deformation increases with the flexion angle and causes a variation of the internal volume of the boot.

Furthermore the rebound speeds for the two designs were tested on a purpose built test bench for three forward bending angles: $+5°$, $+10°$ and $+15°$ from the neutral position. The test temperature was kept constant at $+20°C$. The tests have been repeated for 10 times and the results averaged. The rebound speed has been calculated from the rebound time and total displacement of the cuff, both measured using a draw wire sensor, as explained in the previous section. The results in Figure 3.21 show a faster rebound speed for the overlap ski boot as the forward flexion angle increases. In this case, too, the different behaviour can be ascribed to the design. In fact, in the overlap ski boot, if flexion exceeds $+5°$ from the neutral position, the shell is compressed and deformed storing elastic energy then released during the unloading cycle. The same effect has been seen for the flexural behaviour and in this case it results in a faster rebound. In Table 3.6 are summarized all the rebound speeds measured for the two overlap boots produced using materials with different hardness and elastic modulus and the for 3-pieces boot with the two different tongues and also with the insert.

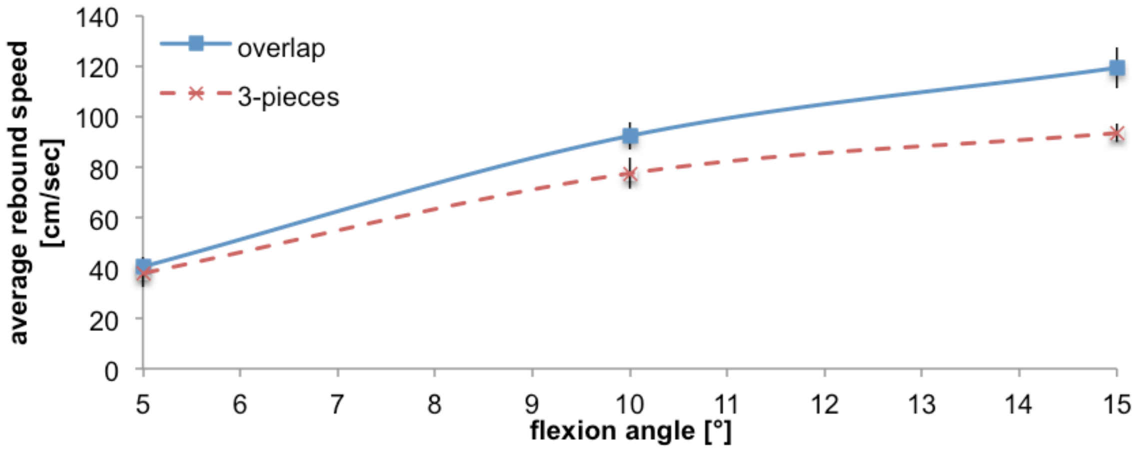

Figure 3.21: Rebound speed at different fexion angles for overlap and 3-pieces ski boots at $+20°C$

Design	**Material**	**Elastic Modulus body** $[MPa]$	**Elastic Modulus tongue** $[MPa]$	**Average rebound speed** $[cm/s]$
overlap	TPU-1	200	na	97.0 ± 10.02
overlap	TPU-2	170	na	92.43 ± 5.61
3-pieces	Toungue 1	250	450	81.20 ± 11.30
3-pieces	Toungue 2	250	250	70.89 ± 6.59
3-pieces	Tongue 1 + insert	250	450	173.18 ± 9.11

Table 3.6: Influence of material, tongue and insert on rebound speed of 3-pieces and overlap boots; tested at $+20°C$ with a forward flexion of $+10°$

One of the benefits of the 3-pieces design is the possibility to change the flexural stiffness of the boot in a simple and quick way. This can be done by replacing the tongue with another made of a softer or stiffer material, or by using some insert in the upper rear part of the cuff. These inserts block the forward flexion of the cuff, increasing greatly the flexion moment. To investigate the effect of different tongues and inserts on 3-pieces design stiffness, flexural tests have been performed at a temperature of $-2°C$ using two tongues:

- soft tongue: polyamide with E' of 250 MPa and shoreD hardness of 52
- hard tongue: polyamide with E' of 450 MPa and shoreD hardness of 64

The results show that the use of materials with different elastic modulus (E') for the production of the tongue influence the flexural response of the boot as described in Figure 3.22. The different tongue causes a 32% increase in the peak bending moment at +12°.

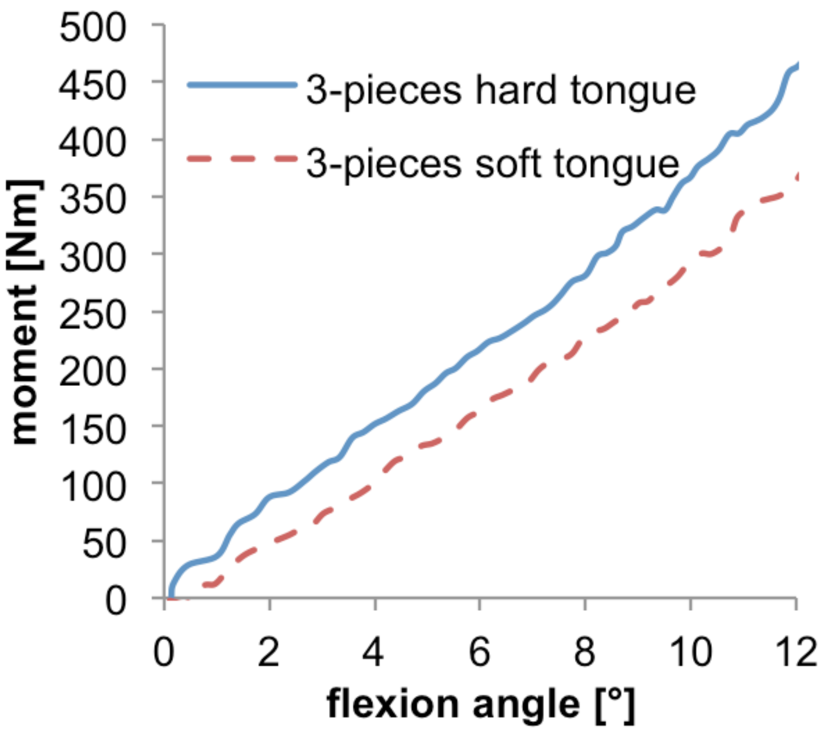

Figure 3.22: Flexural behaviour for 3-pieces boot with different tongues at $-2°C$

A further possibility to modify the flex is the use of inserts placed in the upper rear part of the cuff, as described in Figure 3.4. These inserts limit the cuff rotation resulting in an increase in flexural stiffness as described in Figure 3.23. In this case the variation in the peak bending moment at +12° is 13%.

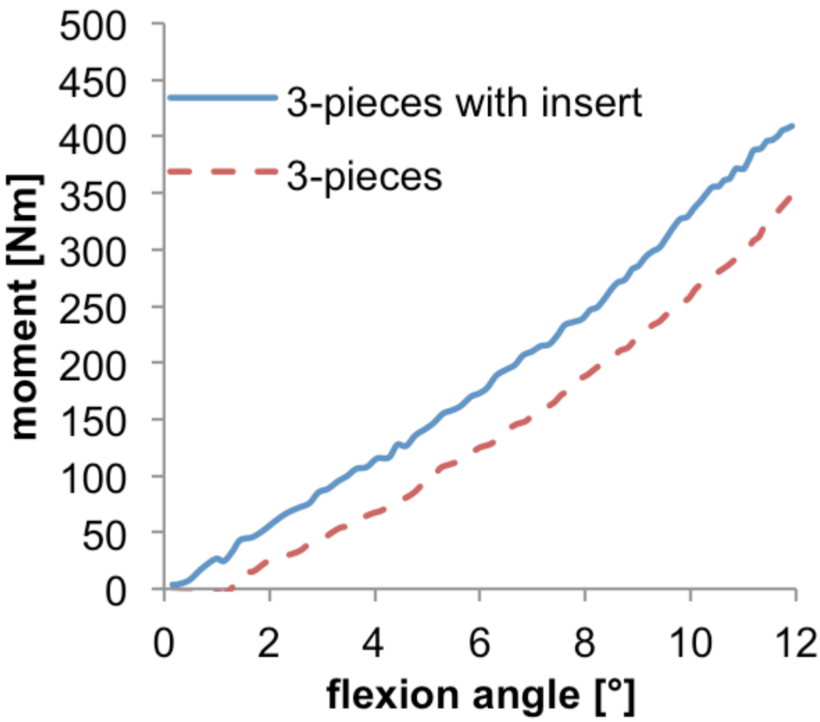

Figure 3.23: Flexural behaviour for 3-pieces boot with insert and soft tongue at $-2°C$

The stiffness of the overlap ski boot can not be modified as in the case of 3-pieces design. In fact the only structural part comprising an overlap ski boot are shell and cuff and thus can not be modified of interchanged easily. The only possibility to change the flexural behaviour is changing base material. Two boots with different materials have been tested to assess the effect of the stiffness of the plastic used on the flexural behaviour:

- Scorpion 110: TPU with E' of 170 MPa and shoreD hardness of 57
- Scorpion 130: TPU with E' of 200 MPa and shoreD hardness of 60

The results in Figure 3.24 show that the stiffness of the plastic used to produce the ski-boot has a direct influence on the flexural behaviour without changing the shape of the flexion curve. In particular in this case the harder material causes an increase of 29% in the peak bending moment at $+12°$. This effect has been already proved in the previous section of this chapter.

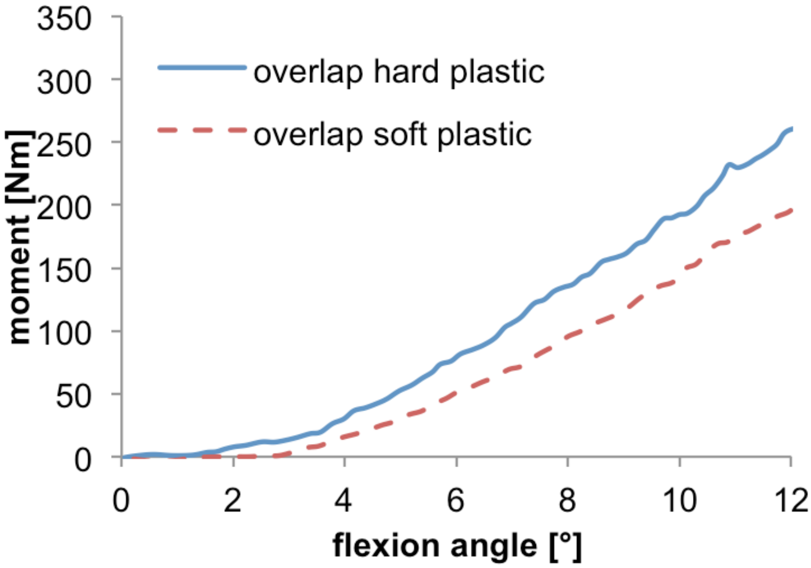

Figure 3.24: Flexural behaviour for overlap boot in two different materials at $-2°C$

Finally the effect of temperature on flexural stiffness has been investigated also for the two different designs, to get a confirmation of the results obtained in the previous section. The tests conducted at different temperatures show that the flex of the overlap boot, Figure 3.25 is more sensible to temperature, having a 52% stiffness increase, compared to the 38% increase of the 3-pieces boot, Figure 3.26.

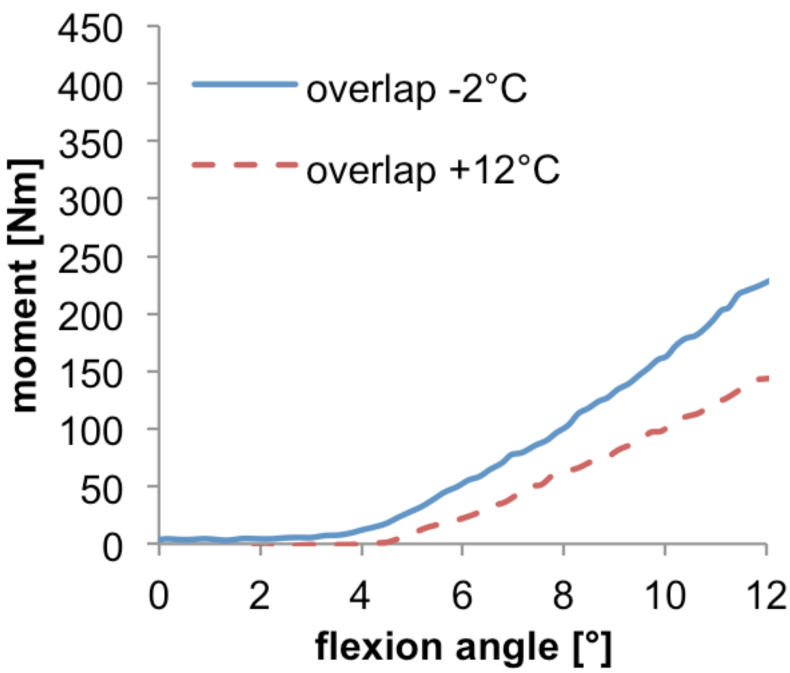

Figure 3.25: Influence of temperature on flexural stiffness for overlap boot

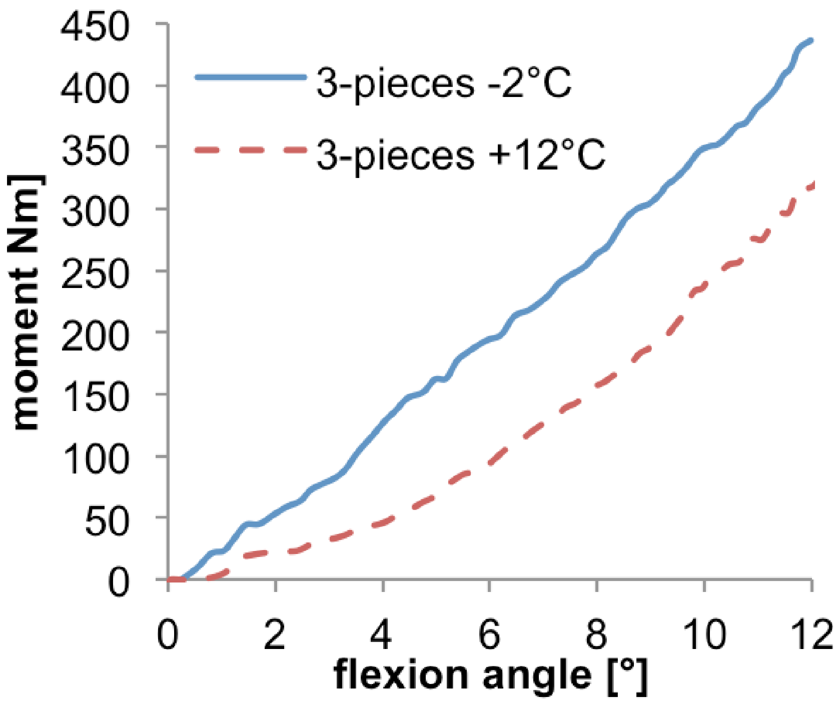

Figure 3.26: Influence of temperature on flexural stiffness for 3-pieces boot

3.4 Discussion

This work studies the effect of the visco-elastic properties of thermoplastic polymers, measured by DMTA analysis, on the mechanical properties of the finished products. Moreover the influence of the design and construction on the flexural and rebound properties is analysed.

The DSC analysis of the crystallinity and transition temperatures and enthalpy (melting and crystallization) show that both the master-batch used to give colour and the moulding process have a negligible influence on the final thermal properties of the polymeric materials analysed in the present study. Therefore, the assumption that the materials used in the ski boot production are comparable with the samples produced in the lab-size injection moulding apparatus from pieces cut directly from boots and then analysed by DMTA analysis is justified. For this reason, it is possible to search for a general correlation between the results of DMTA analysis and the flexural and rebound behaviours of ski boots.

From the comparison of the flexion curves obtained in this study with the results reported in the literature [4] it is clear that several parameters affect the measurement of the flex index. In fact significant differences have been observed with the value of eFI previously reported [4]. As previously reported [4], the buckle closure, angular velocity, shape of the prosthesis and type of ski boot design have a significant effect on the flexural moments. For this reason, a standardized method that takes into account the parameters mentioned above, is necessary in order to have a reproducible measure of the eFI. Nevertheless, the main focus of the present work is the study of the effect of materials on the flex and rebound performances and thus several variables (buckle closure, liner, angular velocity) have been kept constant in order allow a comparison of the results of the different experiments.

The analysis of the flexural curve of the boots shows that the first part of the flexion does not require a consistent amount of moment, due to the fact that in the overlap design the cuff is free to rotate around the pivot points until the front part touches the shell. Around $+5°$ of forward bending the cuff engages the shell causing a change of the slope of the bending moment curve. Increasing the boot flexion angle causes a combined sliding of the cuff on the shell and a simultaneous deformation of the shell. From $+10°$ on the cuff is completely locked with the shell and any further flexion just deforms the shell, resulting in a second slope change in the bending moment-flexion angle curve. This effect is more pronounced at lower temperatures since the materials become harder and more difficult to deform. The deformation of the shell increases with the flexion angle and causes a variation of the internal volume of the boot. Moreover elastic energy is stored in this deformation, which is the released during the rebound phase of the flexion.

All the data obtained by DMTA analysis have been compared with the performance of ski boots measured with the flexural and rebound test benches. In particular, DMTA analysis indicates that polyolefine has a lower elastic modulus throughout the temperature range analysed with respect to polyurethane. This behaviour is in agreement with the lower flexural stiffness observed with the flexural test bench for Boot-2 (made of PO) with respect to Boot-1 (made of TPU). Moreover, the increase in stiffness at lower temperatures is different for both boots. In particular, Boot-1 (made of TPU) has a more consistent stiffening with respect to Boot-2 (made of PO). This difference is confirmed and reflected by the different variation of the elastic modulus of the materials measured by DMTA analysis.

DMTA analysis is also able to predict the rebound speed, a correlation between the damping and the rebound speed has been found. Indeed, DMTA analysis show that polyolefin provides more damping below $+13°C$ with respect to polyurethane, due to the higher tan δ value. This is in agreement with the slower rebound speed of the ski boot made of polyolefine (Boot-2) compared to the one made of polyurethane (Boot-1).

Furthermore, polyolefine presents a constant tan δ between $-2°C$ and $+12°C$ which is also reflected by the same trend of the rebound speed. Moreover, a less consistent increase in rebound speed is observed between $+12°C$ and $-12°C$ for Boot-2 (made of PO) with respect to Boot-1 (made of TPU) in agreement with the smaller increase in tan δ for polyolefine in the same temperature range.

On the basis of these results, DMTA analysis can be used to predict the behaviour of a ski boot from a flexural and rebound point of view. This can help during the choice of the correct plastic for a ski boot since it is much easier to mould a test specimen for DMTA analysis with respect to mould and assemble an entire ski boot. The optimal type of material can also be chosen accordingly to the type of skiing discipline (racing, freestyle, recreational, moguls etc) and of skier (weight, physical characteristics, skiing technique etc). For example, a boot with high rebound speed is more appropriate for slalom racing skiing, where the speed and frequency of the flexion is very high. On the other hand, for freestyle disciplines a material with high damping helps to absorb the shock caused by landings from jumps. Therefore, for slalom skiing a material with lower tan δ should be selected while for freestyle a boot made of a material with higher tan δ should be preferred. For these reasons it can be concluded that DMTA analysis is able to explain the reason why slalom racing ski boots are made of polyurethane (low tan δ) and ski boots for intermediate and beginners (that need more comfort and damping) are made generally in polyolefine (higher tan δ). Nevertheless, it has to be considered that also other properties must be taken into account in the choice of the proper material. In particular polyurethane and polyolefine also differ in density, abrasion resistance [17] and costs and also for these reasons polyolefines (that are less expensive and with lower density with respect to polyurethanes) are generally used in low performance and low cost boots.

Besides the influence of the visco-elastic and chemical properties of the materials used for the production of ski boots, another important parameter that influences the flexural and rebound behaviour is the design and construction on the ski boot. The analysis of the two more common designs, overlap and 3-pieces showed that the flexural behaviour is significantly different. In particular the 3-pieces designed boots have a more linear increase in the stiffness compared to the overlap boots. This difference can be ascribed to the fact that the forward flex of the overlap boot is controlled by the bending of the upper-back part of the shell and by compression of the lower front part of the cuff on the shell, between the second and third buckle. However, the compression of the shell on the cuff only occurs in the second part of the flexion since at the beginning the cuff is not touching the shell. For this reason, the second part of the flexion curve becomes steeper with respect to the first part where only the bending of the upper-back part of the shell is opposing the forward flexion. Since the compression of the shell is blocked by the presence of the foot inside the boot, the boot increases its stiffness rapidly after the cuff starts compressing the shell. On the contrary, for the 3-piece boot flexion is only governed by the bending of the tongue, acting as a spring and therefore a more linear increase of the flex is observed. Such a difference in the flexion curve permits a fast power transmission from the skier to the ski edge for the overlap design in the second part of the flexion. That is why this design is used for World Cup racing ski boots. On the other hand, the linear increase of the stiffness makes the 3-pieces boot more efficient in adsorbing the roughness of the surface when skiing off-piste or in moguls. Moreover, the possibility to start absorbing energy from the beginning of the flexion permits to absorb the shocks in jump landing, thus explaining its widespread use in freestyle and off-piste disciplines. Another advantage of the 3-pieces design is the possibility to modify the flexural stiffness by changing the tongue or placing inserts in the top rear part of the boot. In the case of the overlap boot the only possibility to modify the flex is by using different materials for the production of the shell and cuff. Finally, even the rebound behaviour is influenced by the construction of the ski boot. In fact in the overlap ski boot during the deformation of the shell for high bending angles elastic energy is stored, this energy is then released during the rebound resulting in a faster speed compared to the 3-pieces design.

3.5 Conclusions

The effect of the visco-elastic properties of the materials on the flexural and rebound behaviour of the boot has been analysed, highlighting the relevance of DMTA analysis in a knowledge based design process. Indeed, this analysis allows the selection of the right materials for a desired flexural and rebound behaviour without the need to mould and assemble an entire ski boot to be then analysed using flexural and rebound tests.

Furthermore it has been showed that different designs of ski boot give rise to different mechanical behaviours, both in term of flexural stiffness and elastic rebound. Proving that besides the material choice also the design selected for a specific ski boot plays an important role in the properties of the final product.

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4 Effect of material properties and surface roughness on grip performances of ski boot soles

The thermoplastic materials employed for the construction of ski boots soles used for alpine skiing have been characterized in terms of chemical composition, hardness, crystallinity, surface roughness and coefficient of friction (COF). The results obtained a relation between material hardness and grip has been found, in particular softer materials provide more grip with respect to harder materials. On the contrary, the surface roughness has a negative effect on friction since the materials with the highest Sa (arithmetic mean high) have the lower coefficient of friction, because of the decrease in contact area. The measure of grip on inclined wet surfaces show again a relation between hardness and grip, the softer materials having the best performances. The performance ranking of the different materials has been the same for the COF and for the slip angle tests, indicating that COF can be used as a parameter for the choice of the optimal material to be used for the soles of ski boots. The comparison of different sole treads indicates that the best results in terms of anti-slip behaviour are obtained with the soles that present the wider contact area with the ground.

4.1 Introduction

Slips and falls are very common when walking with ski boots and they are often the cause of serious injuries in both outdoor environment, such as ski slopes and resort walking areas, and indoor conditions, such as huts or rental shops. For this reason, understanding the factors influencing the friction coefficient of the materials used for the production of soles on wet floors and icy surfaces is of crucial importance [1].

In the case of alpine ski boots the shell is a single piece and thus the soles are generally made of the same hard materials used for the main body of the boot, i.e. polyolefines or polyurethane based thermoplastic polymers with a hardness from 50 to 65 Shore D [2, 3, 4]. Furthermore the tread of the soles is not extended, resulting in a low friction with the ground [5]. The use of the same base materials and limited tread is justified by the reduction of the costs and complexity of the moulds used for the production of ski boots and the need to fulfil certain requirements for the interaction between the sole and the binding set by specific ISO norms. On the other hand, for ski-touring and freeride boots the soles are made of thermoplastic elastomers or vulcanized natural or synthetic rubber, with the purpose of providing good grip when hiking and climbing. The drawback of the use of a soft rubber material is the lack in power transfer between the skier and the ski since the sole tends to bend when a load is applied, leading to a less precise control of the skis. In recent years some producers have provided the possibility to change the heel and the toe parts of the sole in order to have boots that can have the properties desired for the type of application needed. The soles of this type are generally attached to the shell using metal screws.

There are two ISO standards for the design of ski boot soles [2], which define the area of the ski boot in contact with the binding. This is due to the fact that the efficient behaviour of the binding in releasing the boot during a fall is significantly influenced by the geometry and rigidity of the ski boot part in contact with the binding. Therefore, in order to ensure the proper binding release function, alpine ski boots must be realized observing limits and prescriptions in terms of dimensions and design of the boot interface.

The two ISO norms are:

- ISO 5355 (Alpine ski boots Requirements and test methods [6]) that refers to ski boots for alpine skiing
- ISO 9523 (Touring ski boots for adults Interface with touring ski bindings - Requirements and test methods [7]) that refers to ski boots for ski-mountaineering

In terms of materials used, both standards require that the hardness of the material at the toe and heel binding interface (Figure 4.1) must be not less than 50 ShoreD, measured at a temperature of $+23°C$ in accordance with ISO 868.

The ISO 5355 norm specifies that the coefficient of dynamic friction at the toe and heel binding interfaces between the boot material and a low friction element of PTFE must be

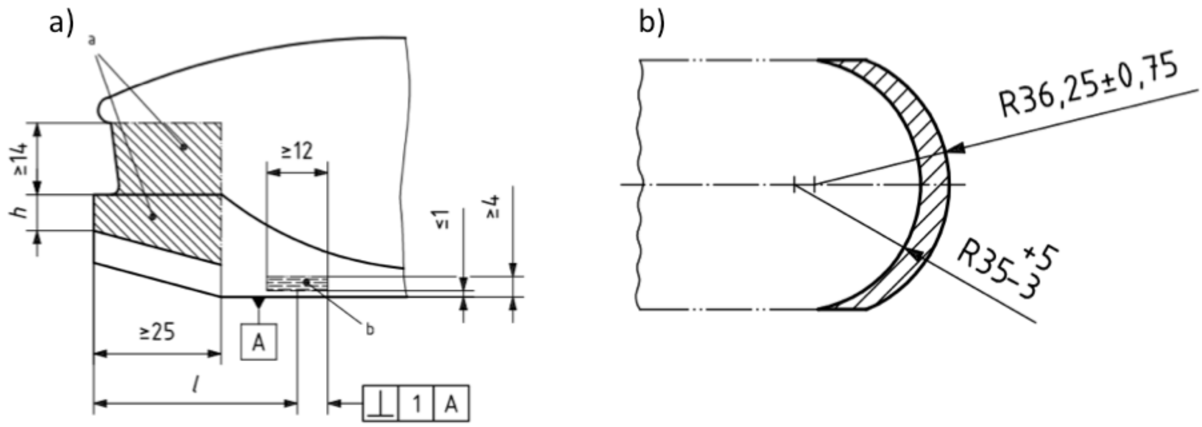

Figure 4.1: Front (a) and rear (b) part of the ski boot in contact with the binding for ISO 5355

less than 0.1. When materials different from TPU are used in the heel part of the boot, there must be at least one longitudinal low friction area to act as a bearing surface for the ski-brake.

The ISO 9523 norm requires a minimum percentage of the area in contact with the bearing surface of the binding of 25% in the toe and of 40% in the heel [6] but no restriction in the characteristics of the material for the sole are necessary. Other requirements requested by the ISO standards are the difference in sole length of two ski-boots in a pair (2 mm maximum) and perpendicularity of the sidewalls and toe (1 mm for ISO 5355 and 2 mm for ISO 9593). The mounting point for positioning the binding on the ski must be indicated by a line on each side of the lower surface of the boot; the line must be clearly visible and permanent, not less than 10 mm in length. Ski-boots producers are pushing for the development of new norms that take into account different types of bindings, such as, for example, the binding system for ski-mountaineering developed by Dynafit. Since the amount of ski-mountaineering boots is less than 5% of the overall ski boots market [2, 3] it is clear that the interest of ski boot manufacturers and of the scientific community is mainly focused toward the study of soles for alpine skiing.

In recent years significant work has been performed in order to understand and model the friction behaviour of elastomers on different surfaces and gain a better physical understanding of the dynamic frictional contact of tyres with road tracks during breaking and cornering, mainly due to the interest of the automotive industry on this topic. For example, Heinrich et al [8] have investigated the role of rubber friction in tire traction, focusing on the load and velocity dependence of the friction coefficient. The results showed that due to the presence of a load dependence of the local rubber-road friction coefficient the tread contact patch is globally never entirely in a fully sliding situation.

Attention has also been given to the study of materials used for the sole of shoes, because of the importance of the understanding of the friction of shoes on floor coverings in connection with the occurrence of slips and falls. Important factors influencing measurement uncertainty in pedestrian slip resistance metrology comprise the surface conditions of the sole materials and floor covering in contact, the ambient conditions as well as measurement conditions related to the devices, test parameters, procedures and operators [9]. In particular, Derler et al [10] have studied the influence of abrasion and temperature on grip, combining friction measurements (performed using a portable tribometer) with hardness measurements. The factors that influence the results of friction measurements were investigated for two elastomer materials and leather. From the results it was possible to conclude that mechanical abrasion of the sole material caused significant linear trends on series of successive friction measurements. Furthermore for all the material combinations investigated the mean coefficients of friction increased with temperature, due to the gradual softening of shoe sole materials, resulting in a more effective draping about floor surfaces asperities in combination with an increased contact area and higher friction forces. Li et al [11] have found a correlation between the tread pattern and the coefficient of friction on different wet and water-detergent covered floors. In particular it has been demonstrated that tread groove depth is a significant factor influencing the coefficient of friction (COF), with an averaged COF gain per tread groove depth increase in millimetres, on either wet of water-detergent-covered floor, ranging from 0.018 to 0.108, depending on the tread groove width, floor and contaminant. Furthermore, they have demonstrated that the tread groove depth design was not significant in the conditions studied.

Some authors have focused their attention on soles friction on ice [5, 12, 13, 14, 15]. Among these, Gronqvist et al [5] have tested 49 types of winter footwear on dry and wet ice using a prototype apparatus simulating actual foot slippage at surface temperatures of $-10°C$ and $0°C$, determining the most important parameters for each condition. Their evaluation demonstrated that the properties of the ice surface, in particular temperature, structure and hardness, influence greatly the coefficient of kinetic friction. For instance 90% of the tested footwear was classified as very slippery on wet ice and 60% as slippery on dry ice. Furthermore only five were slip-resistant on dry ice and only one on wet ice. None were slip-resistant both on dry and wet ice. On dry ice material type, hardness and cleat design were the most important factors. In particular soft thermoplastic rubber with a cleated area as large as possible is recommended in these conditions. The hardening of the material when keeping the footwear at $-10°C$ reduced the coefficient of dynamic friction by 7% on average. On the other hand, on wet ice material type and hardness alone effects are negligible, only the tread design has an influence on the friction properties. In fact sharp cleats combined with very hard heel materials gave the highest friction readings due to scratch formation. Finally it was proved that strewing sand on ice improved the slip resistance to a safe level, paticularly on wet ice. The high slipperiness of melted or wet ice was confirmed by Gao et al [16], who have measured the effect of sole abrasive wear on the coefficient of friction on dry ice, melting ice and lubricated steel plate, for 9 types of footwear. The results proved that artificially abrasive wear of soles improves slip resistance on hard ice, but not on melting ice.

The sole of a ski boot is a very unique system that must have a stiff behaviour in order to efficiently transmit the impulse from the ski boot to the ski, but must also have a good grip on icy and wet surfaces. Generally, stiffer materials have lower friction characteristics and less grip on hard and wet surfaces compared to soft materials [16]. However, as previously stated, the material that compose the sole should also satisfy mechanical characteristics reported in ISO standards in order to permit an efficient and safe release of the ski boot from the binding during a fall. It has also to be considered that the chemical composition of the material can have an effect on the friction on wet and icy surfaces. Moreover, the chemical composition and the hardness have an effect on the scratch resistance that affect the surface roughness during use [17]. For all these reasons, it is clear the need of a study that takes into account the different parameters (hardness, chemical composition and roughness) of the materials used for ski boot soles in order to detect the parameters that can permit to obtain the best balance in terms of energy transfer and of grip on wet and icy surfaces. Therefore, the aim of this work is to evaluate the friction performance of different materials for ski boots soles on wet floors and icy conditions, correlating the performances with the chemical composition and with the surface hardness and roughness of the material.

4.2 Materials and Methods

4.2.1 Materials

An alpine ski boot, model Aerro, in size 26.5 Mondopoint produced by Calzaturificio Dalbello was used in all the tests, Figure 4.2. This model has the possibility to change the soles that are attached to the lower shell by means of screws: 4 for the heel and 4 for the toe.

Figure 4.2: Ski boot used for the testing

Two different soles designs have been used:

- Design 1: bi-injected, Figure 4.3 (a)
- Design 2: mono-injected, Figure 4.3 (b)

A total of six different soles have been tested: soles 1 and 2 with design 1; soles 3, 4, 5 and 6 with design 2. Moreover the material for soles 1, 2, 3 and 4 has been provided by a plastic manufacturer (A), while for soles 5 and 6 has been provided by a different manufacturer (B). Table 4.1 summarized everything. All the soles have been prepared by injection moulding with the same moulding conditions that are industrially used by the ski boot manufacturer (Calzaturificio Dalbello) to produce commercial soles. Finally all the sole are conform to ISO 5355 norm for alpine ski boots.

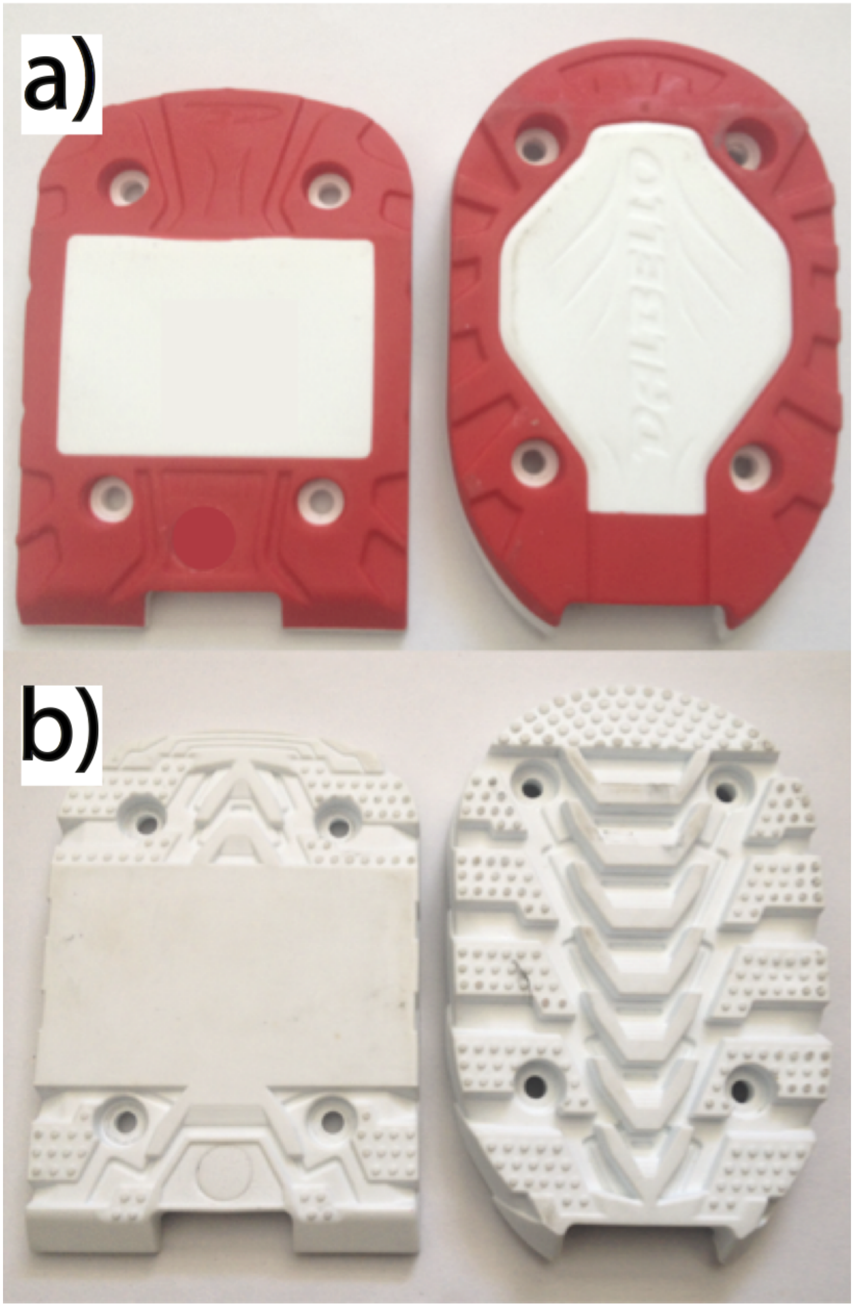

Figure 4.3: Soles used for the testing: a) Design 1 and b) Design 2

Sample	Design	Plastic Manufacturer
Sole 1	1	A
Sole 2	1	A
Sole 3	2	A
Sole 4	2	A
Sole 5	2	B
Sole 6	2	B

Table 4.1: Design and plastic manufacturer of the soles tested

4.2.2 Methods

Fourier Transform Infrared Spectroscopy (FT-IR), Hardness testing and Differential Scanning Calorimetry (DSC)

The chemical composition was determined via Fourier transform infrared spectroscopy (FT-IR) (2.2.2) using a Perkin Elmer Spectrum One spectrometer equipped with an attenuated total reflectance (ATR) detector.

The Shore D hardness of the materials was measured according to ISO 878 at $+23°C$ and at $-10°C$ in order to evaluate the temperature dependence of hardness (2.2.2).

Calorimetric measurements have been carried out using a Perkin Elmer DSC7 instrument calibrated with high purity standards (3.2.2). Weighted samples of approximately 10 mg were encapsulated in aluminium pans. Temperature scans were performed with a heating and cooling rate of $20°C$/min from $0°C$ to $+250°C$ (heating scan) and from $+250°C$ to $0°C$ (cooling scan).

Contact Area

The contact area between the boot sole and the ground has been measured with an image analysis technique, usually applied in biological sciences. In order to have a good image of the boot sole all the tests have been performed on a Plexiglas platform (108x108 cm; thickness 10 mm), Figure 4.4. For the image acquisition a Casio Exilim EX-FH25 digital camera has been used, able to take photographs with a resolution of 3648x2736 pixels. The image analysis and processing has been done through an open source software, ImageJ, developed by the National Institutes of Health. Through its threshold colour plugin, the software is able to select and isolate specific colours or grey-scale tones and measure the area of the user-defined selections. The key point is obtaining a good contrast between the areas in contact with the Plexiglas surface and those not in contact. For this purpose a solution of water and black wall paint has been prepared, with a concentration of 1.3 g/L. A total of 5 measurements for each sole has been preformed and the finale area determined as the average.

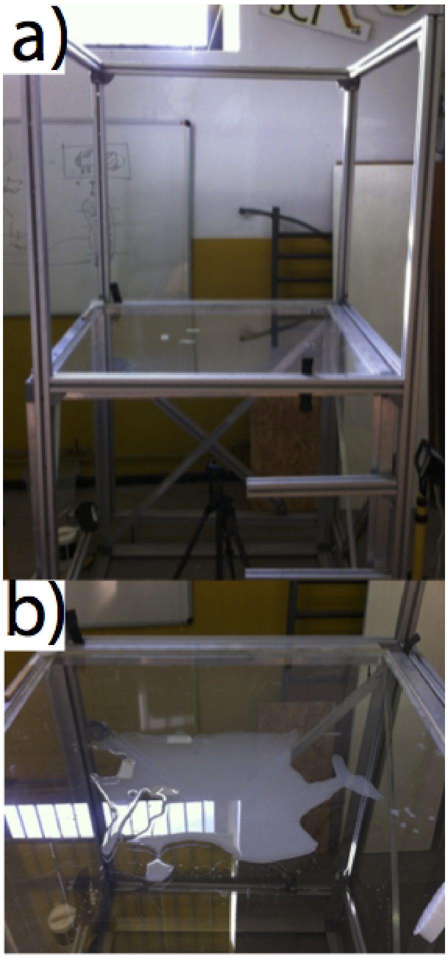

Figure 4.4: Testing platform (a) and contrast liquid (b)

Coefficient of Dynamic Friction

The coefficient of dynamic friction was obtained in accordance with the British Ceramic Research Association (B.C.R.A.) method. This method, developed by the British Ceramic Research Association Ltd., was created to measure the resistance of ceramic tiles to slipperiness and is based on a patented device. This device belongs to the category of the "drag-sled meters", it travels across the flooring under its own power at a constant speed with a sample of standardized dimensions dragging on the flooring. The machine records the amount of friction created by the sample on a selected surface and calculates an average coefficient of dynamic friction as it travels a predetermined path length. A surface in order to be classified as anti-slip has to have a coefficient of dynamic friction bigger than 0.40 (Italy, D.M. 236) both for the slipping elements made of leather on dry surfaces and for slipping elements made of hard rubber on wet surfaces. The main advantages of this technique are the ease of use and capability to run many tests in a short time in different conditions. Furthermore there is little influence of the operator on the results of the test since is a completely automated machine.

For this work, each sole has been tested six times in each condition and the mean value as well as the standard deviations have been calculated. Tests have been performed using a Scivolosimetro SM, slip resistance tester, produced and sold by Gabbrielli (Italy). The instrument is a vehicle with 4 wheels composed by an aluminium chassis and a steel epoxi painted cover. A gear motor propelled by a battery Li-ION moves two wheels at 17 mm/s. The COF measure is acquired during the movement of the instrument by a slider, where the sample tested is mounted, in contact with testing surface. The vibration of the slider is transmitted to an LVDT sensor. The LVDT sensor converts the mechanical signal in a proportional electronic signal. The signal processed by an A/D microprocessor shows the medium coefficient of friction COF [18].

The coefficient of dynamic friction has been measured over three different surfaces:

- Porcelain stoneware
- Glass
- Ice

These surfaces were considered as the most representative for the ski boot field of use. Porcelain stoneware (Figure 4.5a) and glass (Figure 4.5b), have been tested in the laboratory ($+20°C$, 60% RH) while the test on ice has been performed on a indoor ice skating field ($-10°C$, 70% RH) (Figure 4.5c). The porcelain tiles have been used to simulate a ceramic flooring of alpine huts while glass was used in order to determine an alternative surface to mimic the behaviour of iced surfaces.

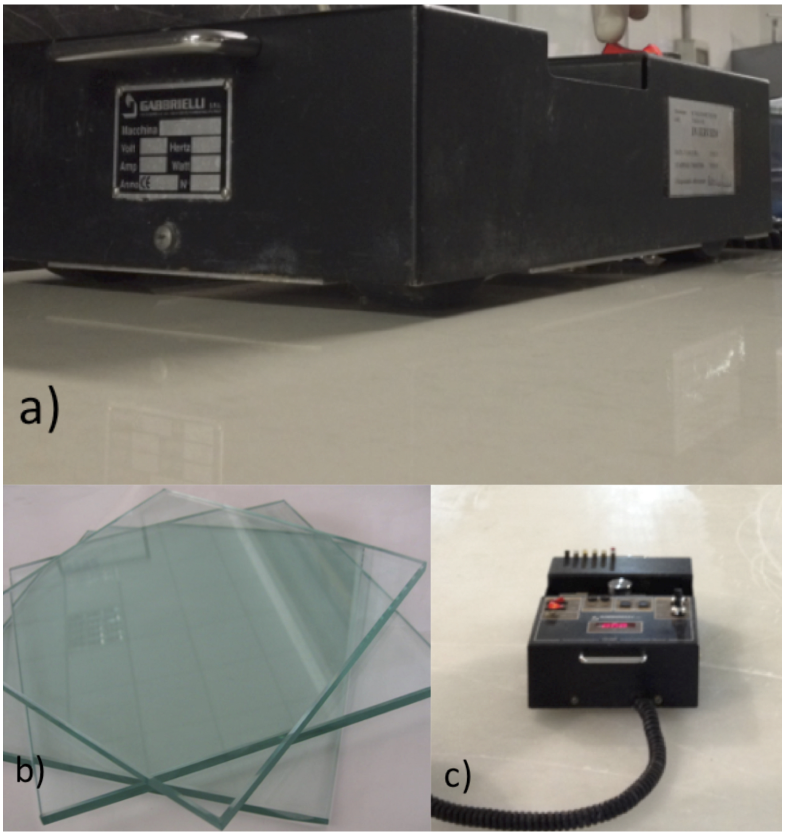

Figure 4.5: Porcelain stoneware (a), glass (b) and ice (c)

Ramp Test

The grip of sole on wet surfaces have been measured using the procedure for testing the slipperiness of different surfaces (DIN 51130-R ramp test). The tests have been performed on a ramp, in wet condition, using porcelain stoneware as surface. In this method, a tester walks on a ramp forward and backward while the ramp angle is steadily increased until the subject begins to slip, Figure 4.6 [19]. The angle at which the person slips is recorded and averaged over a total of five tests for each sole. A total of three testes has been used to confirm the consistency of the results.

Figure 4.6: Ramp test setup from [19]

Surface Analysis

The samples surface texture characteristics have been evaluated using a 3D optical surface metrology system Leica DCM 3D (Leica Microsystems), equipped with a confocal objective 20x. The areal surface roughness parameter Sa (the arithmetic average height of the surface) has been measured according to ISO 25168. The areas acquired have also been processed through binarization, setting a threshold value of 12 mm for the distinction of the grains.

4.3 Results

In this section the results obtained during the study are presented. Starting from the chemical characterization of the materials used for the different soles by means of FT-IR, DSC and hardness testing. Moreover the COF has been measured on three different surfaces, i.e. wet porcelain stoneware, wet glass and ice. The results were correlated with the chemical properties and the surface morphology, measured through a profilometric investigation. Finally ramp testing on wet porcelain stoneware has showed which sole provided the best grip performance while walking with the ski boots.

4.3.1 Chemical composition (FT-IR), Hardness testing and Differential Scanning Calorimetry (DSC)

The chemical composition of all six soles has been detected by FT-IR analysis (Figure 4.7). The resulting FT-IR spectra were compared to a database of known polymeric materials resulting that Boot-1 was composed of a polyether based polyurethane (obtained using MDI as isocyanate precursor) and Boot-2 was composed of a polyolefin blend containing SBR rubber. The characteristic absorptions peaks of the PU are observed at 3306 cm^{-1} (N-H stretching frequency), 2925 - 2852 cm^{-1} (-CH2- and -CH3 stretching frequencies), 1731 cm^{-1} (carbonyl urethane stretching), 1526 cm^{-1} (CHN vibration), 1223 cm^{-1} (coupled C-N and C-O stretching), and 1079 cm^{-1} (C-O stretching) [2]. The polyurethanes that compose the soles are based on methylene diphenyl diisocyanate (MDI) due to the presence in FT-IR spectra of a peak at 1596 cm^{-1} [2]. All the materials tested present the same FT-IR pattern and therefore a similar chemical composition, for this reason on the spectra of s ole 1 is reported in this work.

It is well known [20] that the length of copolymers blocks and molecular weight in polyurethane can have a significant effect on the thermal and mechanical properties of

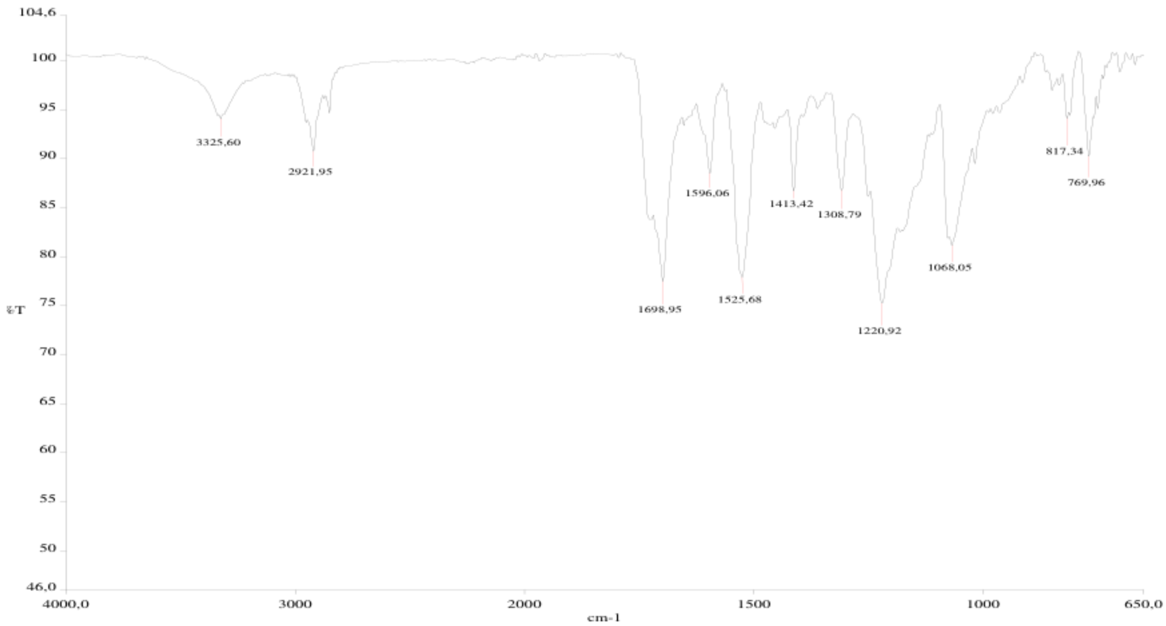

Figure 4.7: FT-IR spectra of Sole 1

the materials. In particular, the copolymers block composition has an effect on the crystalline structure that is responsible for the overall thermo-mechanical characteristics of the material [20]. For this reason, we have measured the melting temperature and crystallinity of all samples by DSC. In Figure 4.8 are reported the results for sole 1 and sole 5; sole 2, 3 and 4 have similar DSC spectra and sole 1 and sole 6 is similar to sole 5. The materials are all semi-crystalline with a larger melting peak at around $+180/+210°C$ and a smaller melting transition around $+50/+100°C$. Melting temperatures (T_m) and heat of fusion (ΔH_m) of the main melting peak are reported in Table 4.2. The results show that the materials used for soles 1, 2, 3, 4 and soles 5, 6 differs in the type of crystallinity and melting temperatures.

Furthermore the hardness has been measured at two different temperatures: $+23°C$ and $-10°C$, and the results are reported in Table 4.3.

The results in Table 4.3 show that there is a relation between the temperature dependence of hardness and the hardness measured at $+23°C$ since the softer materials at $+23°C$ (those used for soles 4 and 5) are more dependent on temperature with respect to the stiffer ones.

Finally the FT-IR, DSC and hardness results show that the materials used for soles 2 and 3 are identical. The two soles differ only for the type of design. Moreover the analysis confirmed that the two parts with different colours present on both soles 1 and 2 are made of the same material and thus the same material properties on the entire sole.

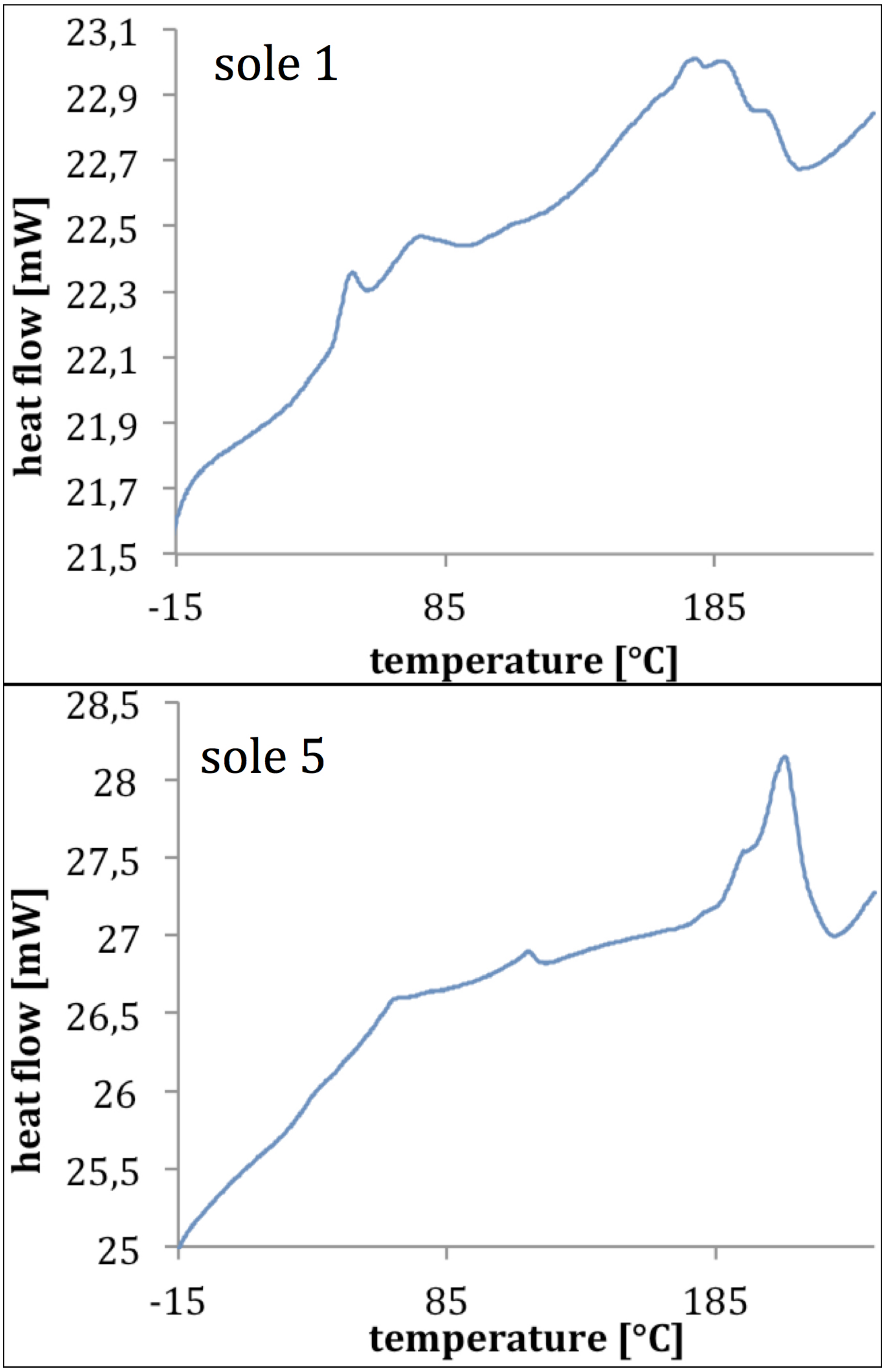

Figure 4.8: DSC heating curve of the materials of sole 1 and sole 5

Sample	**Melting Temperature** [$°C$]	**Δ H** [J/g]
Sole 1	178	11.1
Sole 2	173	7.8
Sole 3	173	7.8
Sole 4	176	6.0
Sole 5	209	4.8
Sole 6	210	6.6

Table 4.2: Melting temperature and heath of fusion for all soles tested

Sample	**Hardness** [$ShoreD$] ($+23°C$)	**Hardness** [$ShoreD$] ($-10°C$)	**Temperature dependence** % (from $+23°C$ to $-10°C$)
Sole 1	68	73	+6.7%
Sole 2	51	54	+6.3%
Sole 3	51	54	+6.3%
Sole 4	42	47	+15.7%
Sole 5	40	45	+12.1%
Sole 6	49	51	+5.5%

Table 4.3: Hardness measured at $+23°C$ and $-10°C$

4.3.2 Contact Area

The contact area between the boot sole and the ground has been measured with an image analysis technique using a contrast liquid, in a static situation. In Figure 4.9 is reported an image of the sole obtained with the contrast liquid as well as the surface in contact after the image analysis process. Furthermore in Table 4.4 the contact areas measured for the six soles are reported. As expected sole 1 and 2 have the same contact area since the have the same design, same can be said for sole 3, 4, 5 and 6.

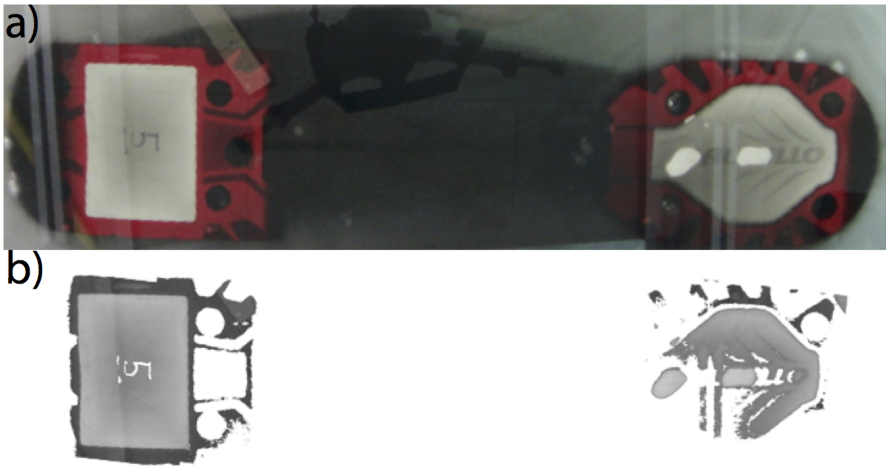

Figure 4.9: Image of the sole 1: a) sole with contrast liquid b) surface in contact

Sample	**Contact Area** $[cm^2]$
Sole 1	46.1
Sole 2	46.2
Sole 3	39.7
Sole 4	39.8
Sole 5	39.6
Sole 6	39.7

Table 4.4: Contact area of the sole with the ground for the six samples

4.3.3 Coefficient of Dynamic Friction

The coefficient of dynamic friction (COF) has been measured for all the six soles investigated in this work, using the B.C.R.A. method on wet porcelain stoneware and on wet glass at $+20°C$ and the results are reported in Table 4.5 and 4.6. As explained previously the COF is automatically measured by a robot that drags a sample of the material tested on a certain flooring. Moreover, measurements of the COF have been performed on ice at $-10°C$. From the values obtained and reported in Table 4.7 it clearly emerges that in this case the values are significantly lower than those measured at $+20°C$ on porcelain stoneware and glass.

The results obtained show significant differences among soles made of different materials and designs. In particular a higher COF have been observed on wet glass with respect to wet porcelain stoneware and ice for all samples. Furthermore sole 4 and sole 5 present the highest COF among the samples tested on all the surfaces. Even if on ice the difference is less pronounced.

Sample	**COF**	**Std. dev.**
Sole 1	0.36	0.01
Sole 2	0.45	0.01
Sole 3	0.45	0.01
Sole 4	0.70	0.04
Sole 5	0.58	0.03
Sole 6	0.49	0.01

Table 4.5: Coefficient of dynamic friction (COF) and standard deviation on wet porcelain stoneware

Sample	**COF**	**Std. dev.**
Sole 1	0.54	0.01
Sole 2	0.58	0.02
Sole 3	0.58	0.02
Sole 4	0.71	0.01
Sole 5	0.67	0.01
Sole 6	0.54	0.01

Table 4.6: Coefficient of dynamic friction (COF) and standard deviation on wet glass

Sample	**COF**	**Std. dev.**
Sole 1	0.12	0.01
Sole 2	0.13	0.01
Sole 3	0.13	0.01
Sole 4	0.15	0.01
Sole 5	0.14	0.01
Sole 6	0.12	0.01

Table 4.7: Coefficient of dynamic friction (COF) and standard deviation on ice

4.3.4 Ramp Test

The slip behaviour has been tested by 3 testers wearing the ski boots equipped with the six soles considered in this work. The tests have been performed at $+20°C$ on wet porcelain stoneware and the angle ats at which the tester slip are reported in Table 4.8.

The results in Table 4.8 show the same trend for each sole for the 3 testers, proving that there is limited influence of the tester and its walking dynamics on the results. In general the slipping happened during the backward movement or during the inversion between forward and backward.

Overall sole 2 and sole 4 are those with more grip since the slip angle observed in those cases was higher.

Sample	**Tester 1** Slip angle [°]	**Tester 2** Slip angle [°]	**Tester 3** Slip angle [°]	**Average** Slip angle [°]
Sole 1	13.0	13.7	13.2	13.3
Sole 2	16.4	16.4	16.2	16.3
Sole 3	14.5	14.9	14.9	14.8
Sole 4	15.5	16.3	15.7	15.8
Sole 5	13.8	14.6	14.0	14.1
Sole 6	12.5	13.0	13.1	12.9

Table 4.8: Results of the testing on ramp test in wet condition (according to DIN 51130-R)

4.3.5 Surface Analysis

The surface texture of the soles have been evaluated using an optical profilometer. Images of the surfaces are reported in Figure 4.10, 4.11, 4.12, 4.13 and 4.14.

Soles 1, 2, 3 and 4 present a morphology of the surface texture very similar to each other. In fact not only the value of the heights of the peaks and the depth of the valleys is almost coincident, but also the distributions of the peaks and of the empty spaces within the area analysed are comparable (Fig. 4.12 and 4.13). The value of Sa for these soles is around 2 μm. In Table 4.9 all the arithmetic mean heights are reported.

The surface texture morphology of sole 5 and 6 is different from the one of sole 1, 2, 3 and 4. In fact the materials used for sole 5 and 6 (plastic manufacturer B) have higher Sa with respect to the soles made of the materials from the other plastic manufacturer (plastic manufacturer A). The better anti-slip behaviour of sole 4 compared to the others could be associated to the greater number of contact points towards the surface trampled.

Sample	**Sa** $[\mu m]$
Sole 1	2.63
Sole 2	2.49
Sole 3	2.73
Sole 4	2.37
Sole 5	3.52
Sole 6	11.23

Table 4.9: Sa (arithmetic mean height) of the materials used for the soles

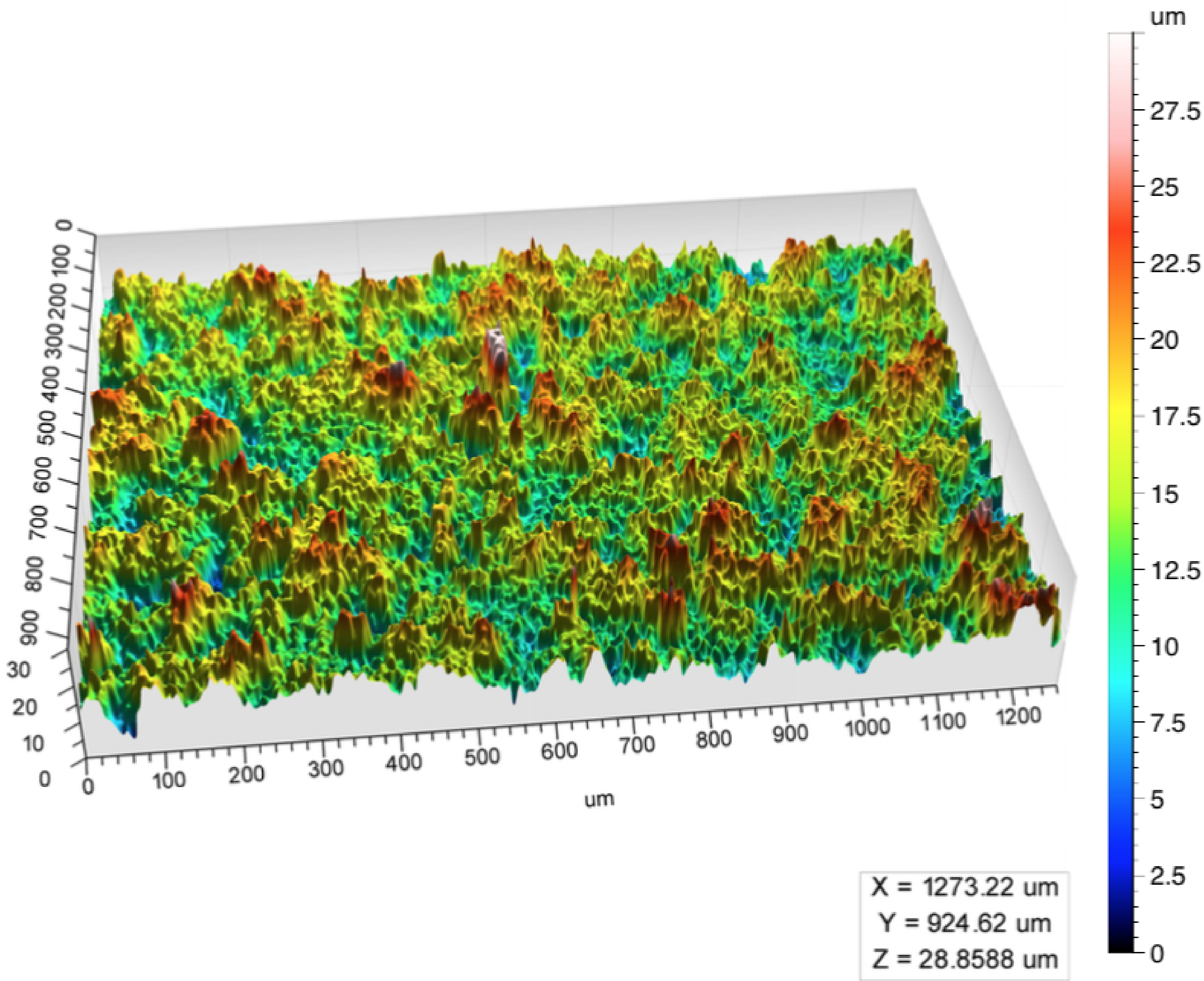

Figure 4.10: 3D image, a colour scale in μm, of an area acquired on the material used for sole 1

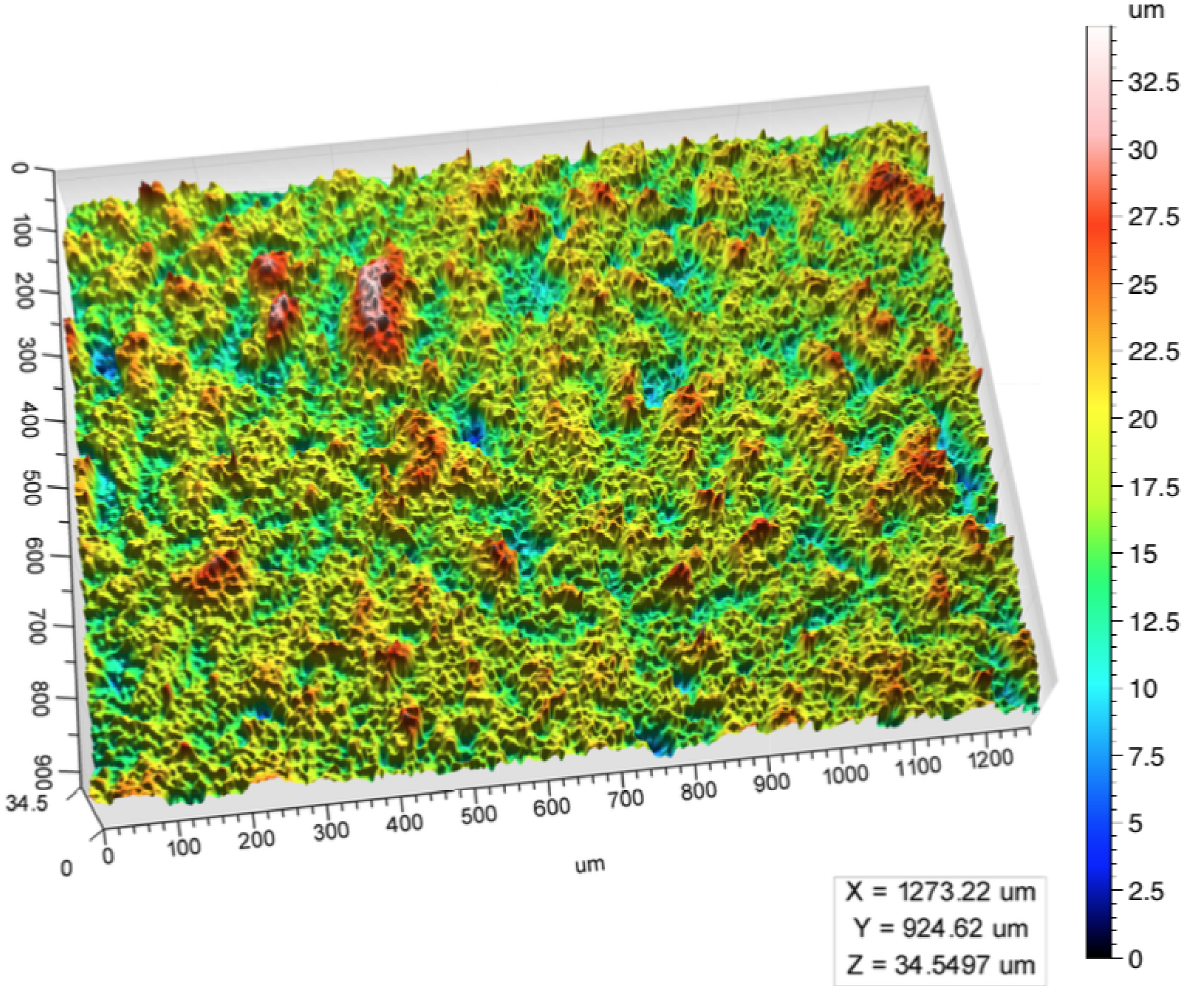

Figure 4.11: 3D image, a colour scale in μm, of an area acquired on the material used for sole 2

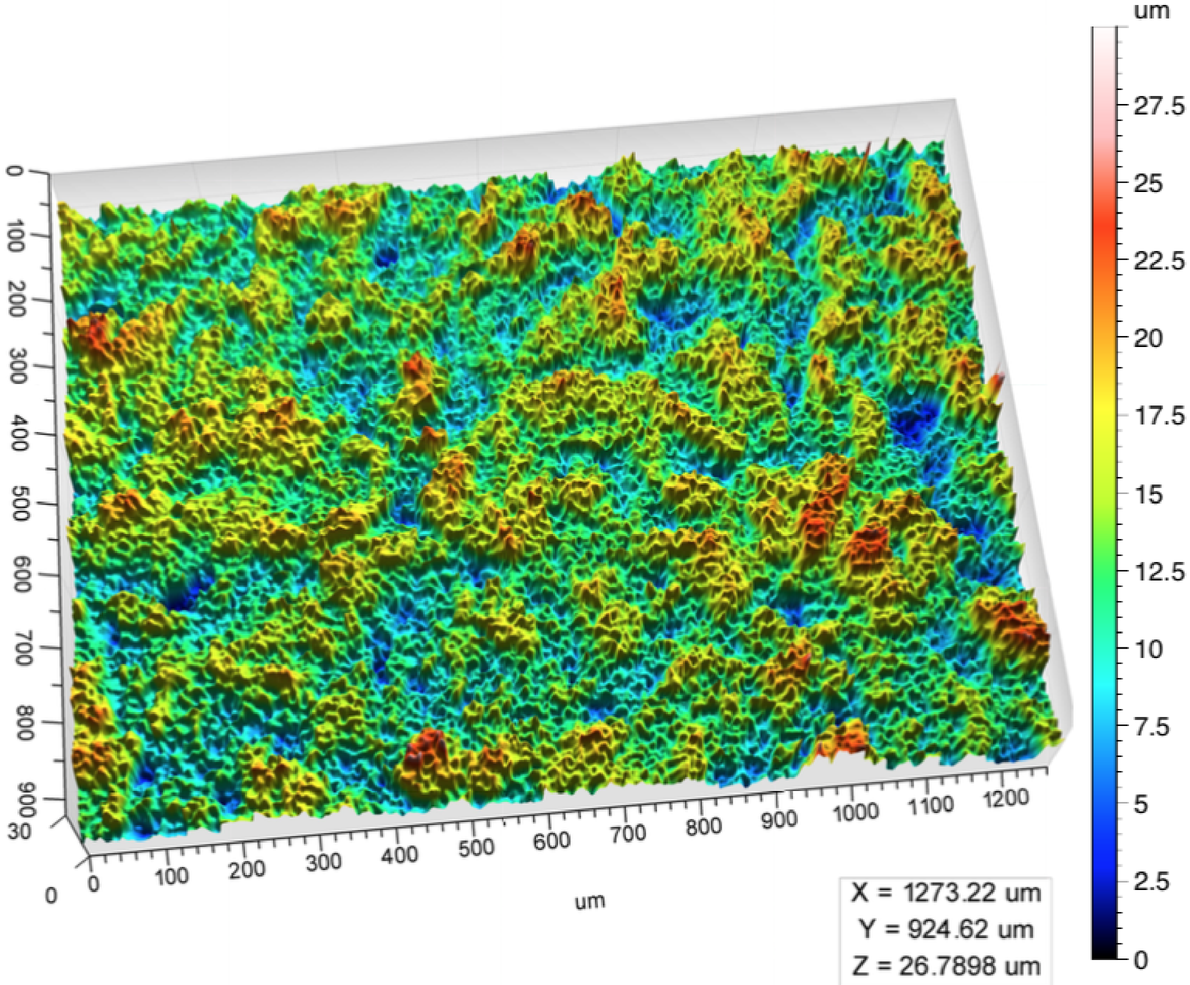

Figure 4.12: 3D image, a colour scale in μm, of an area acquired on the material used for sole 3

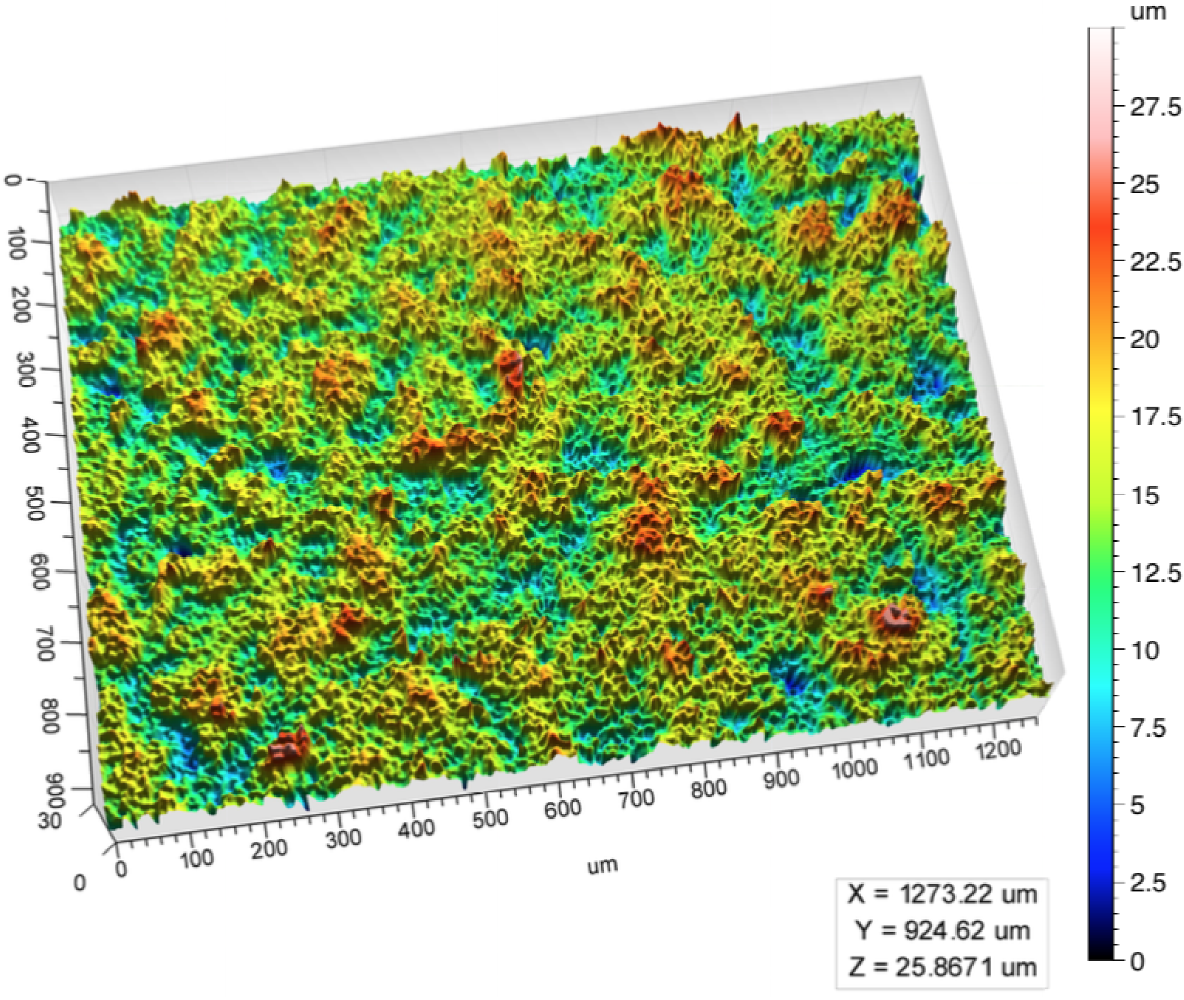

Figure 4.13: 3D image, a colour scale in μm, of an area acquired on the material used for sole 4

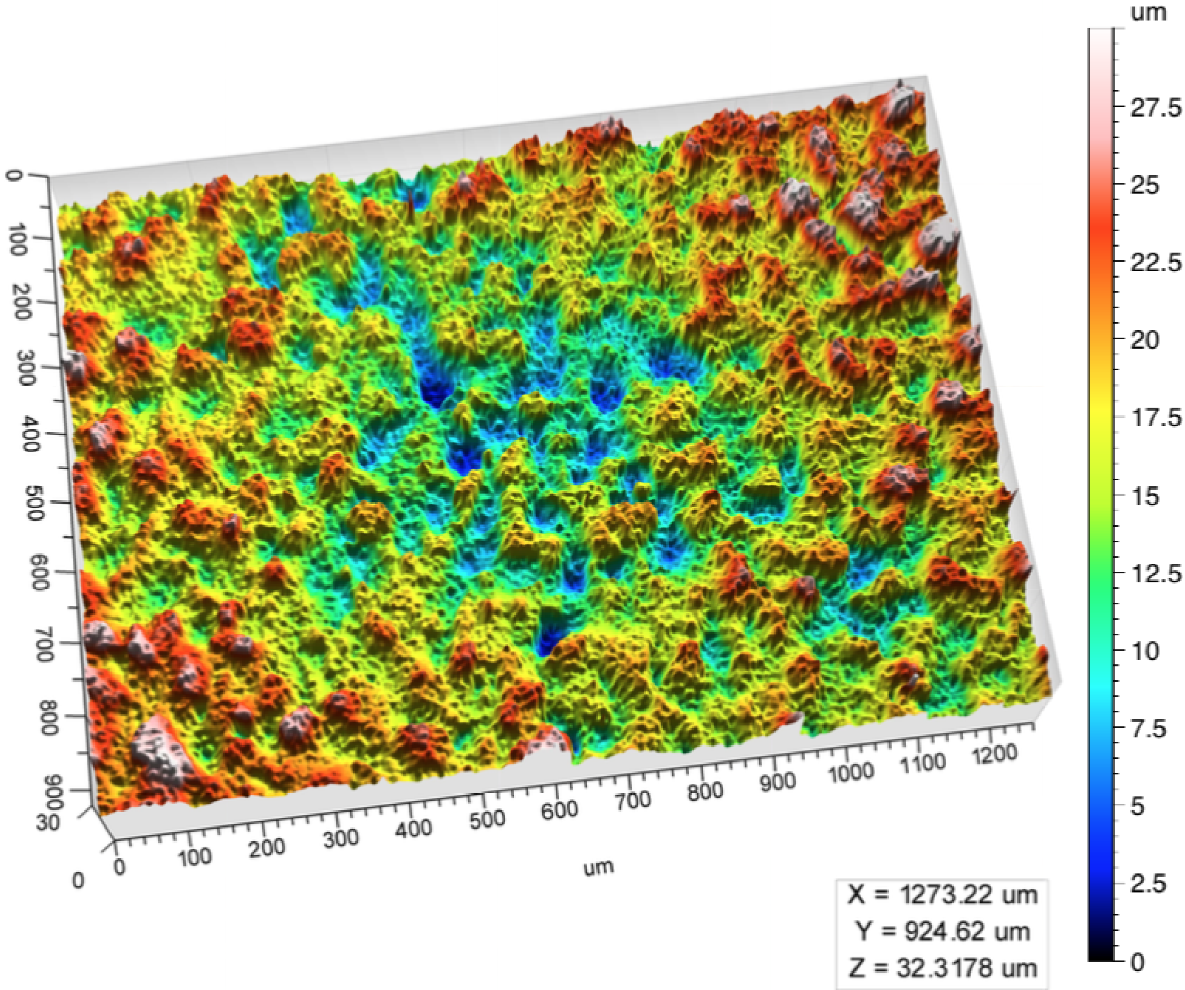

Figure 4.14: 3D image, a colour scale in μm, of an area acquired on the material used for sole 5

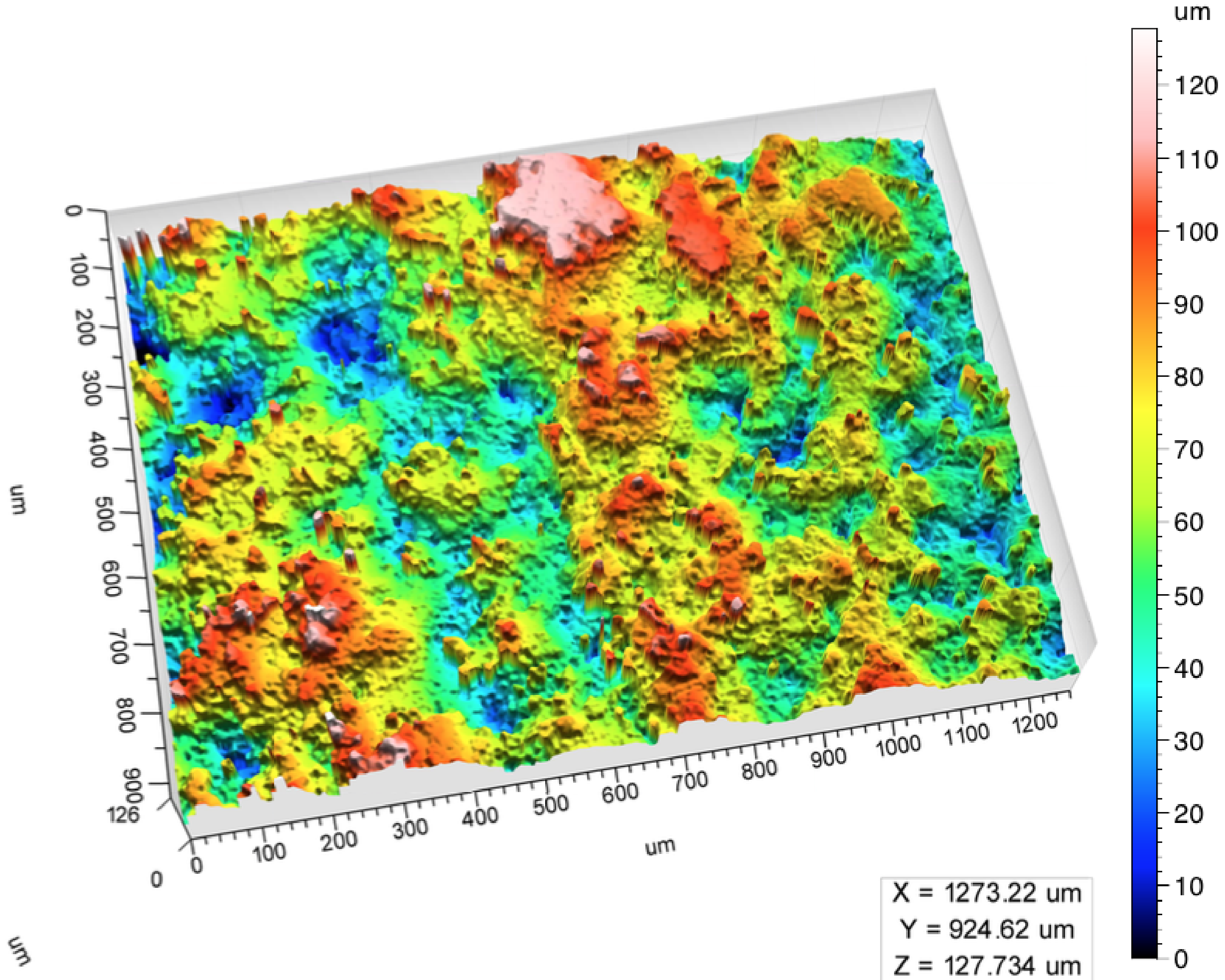

Figure 4.15: 3D image, a colour scale in μm, of an area acquired on the material used for sole 6

The higher COF of the material used for Sole 4 with respect to the other materials can be ascribed to the greater number of contact points with the surface. As can be seen from the comparison of binary images of areas acquired on soles 3 and 4 (Fig. 4.16 and 4.17) and the relative diagram of the equivalent diameters of the grains identified, the surface of the sole 4 has a greater number of grains (probable contact point), which occupy a smaller area and which have an equivalent diameter with better distribution. This hypothesis is also supported by the value of area roughness parameter Ssk (skewness) negative of sole 4 (Ssk = -0029), while for the other soles is positive.

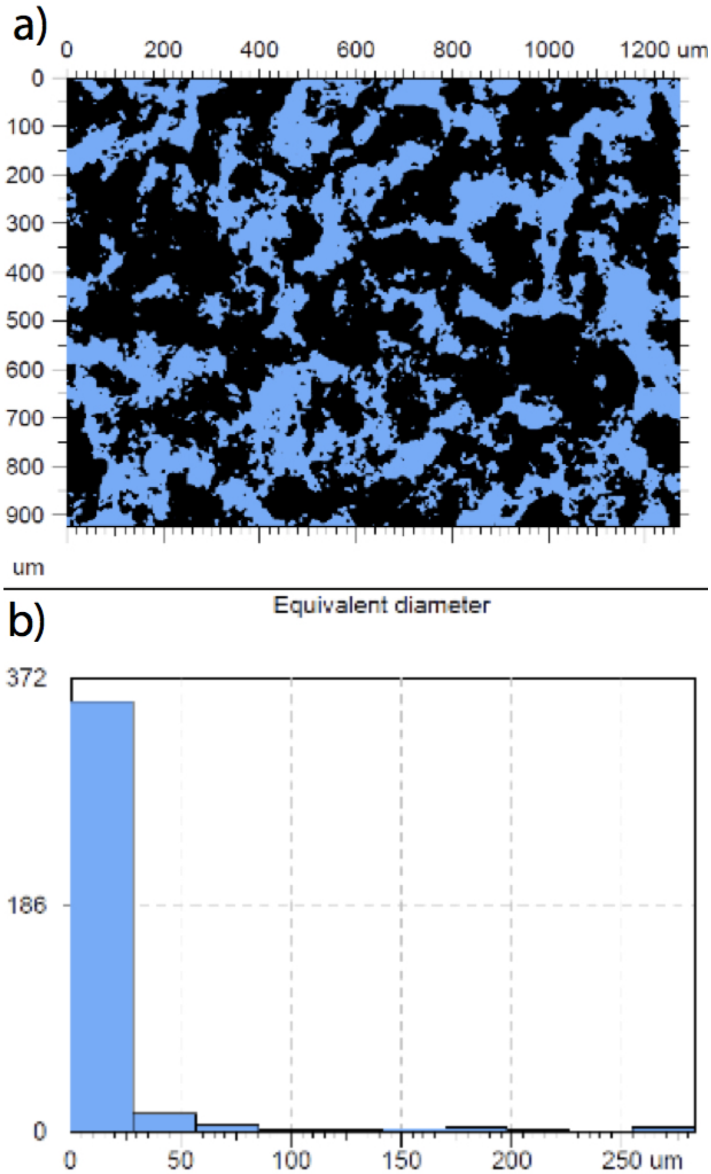

Figure 4.16: Binary image (a) and diagram of the equivalent diameter (b) of an area of sole 3

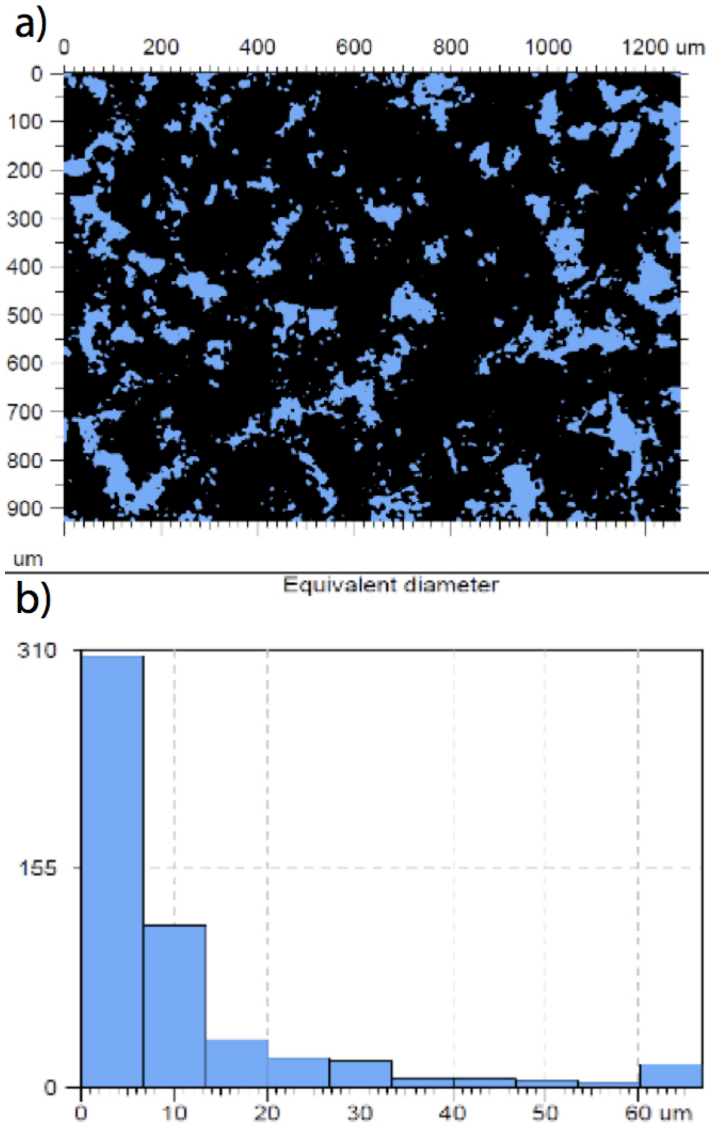

Figure 4.17: Binary image (a) and diagram of the equivalent diameter (b) of an area of sole 4

4.4 Discussion

The measure of COF on wet porcelain stoneware shows that the surface hardness has an effect on friction since softer materials present higher coefficient of dynamic friction. In fact sole 4 and 5 have the higher COF, being the two softest. The same trend is observed also on wet glass and ice. In particular, comparing materials of sole 3 and 4, since both have a similar chemical composition (plastic manufacturer A), melting temperature and design (design 2) it is clear the effect of hardness on friction. Same can be said for the soles produced using the plastic manufacturer B, sole 5 and 6, in fact also in this case the softer material (sole 5) presents a higher friction.

A comparison of the materials made by different plastic manufacturers shows that the best material is the one used for sole 4 that has a sensibly higher coefficient of dynamic friction on wet porcelain stoneware with respect to the material used for sole 5. This result is surprising as sole 4 is harder than sole 5: 40 shoreD for sole 5 compared to 42 shoreD for sole 4. The difference can be related to the different crystalline structure, in fact melting temperature and crystallinity are not comparable, furthermore there is also a difference in roughness of the surface (Sa is lower for sole 4). Similar trends have been observed for glass with a clear effect of surface hardness on friction even if there is less difference between the friction of the harder and of the softer materials with respect to that observed on porcelain stoneware. Finally the tests conducted on ice show small variations between the materials tested, since all the materials have very low friction on ice. This can be due to the lower temperature at which the tests have been performed on ice ($-10°C$) with respect to the other tests ($+20°C$). At lower temperature the materials increases their stiffness but the increase is more consistent (Table 4.3) for the materials that are softer at $+23°C$ (sole 4 and 5) and therefore less differences are observed in hardness at $-10°C$ with respect to hardness at $+23°C$.

Coming to the comparison of surface hardness and roughness it appears clearly that the harder materials are also rougher. In fact, staying within the same plastic manufactures, sole 1 (68 shoreD) is rougher than sole 4 (42 shoreD) and sole 6 (49 shoreD) is rougher than sole 5 (40 shoreD). Moreover, the comparison between friction and roughness indicates that rougher materials have also a lower coefficient of dynamic friction and therefore offer less grip compared with materials with low roughness. This behaviour can be also connected to the fact that rougher materials are also harder, and therefore provide less friction. Furthermore a rougher material with high hardness is less deformable and thus has a reduced contact area with the ground at the microscopic scale, resulting in a lower friction.

The results of the slip behavior on ramp test on wet porcelain stoneware highlight a clear effect of the design of the sole. In particular, comparing sole 2 and 3, which are made of the same material, having same hardness, crystallinity and chemical composition, the design of sole 2 (design 1 in Figure 4.3 a) provides more grip compared to the design of sole 3 (design 2 in Figure 4.3 b). From a simple visual inspection and confirmed by the contact area measurements it is clear that the design used for sole 2 has more contact point with the surface compared to the design of sole 3, with a difference of 14 %. This indicates that on wet porcelain stoneware the grip behaviour is governed by the contact of the material with the floor surface. This is also in agreement with the results of surface roughness that show a higher coefficient of dynamic friction for the less rough materials.

The comparison of the grip performance of soles with the same design and type of material show a clear effect of material hardness on grip performances. In particular, given the same design, softer materials have more grip compared to hard materials, i.e. sole 1 compared to sole 2, sole 4 compared to sole 3 and sole 5 compared to sole 6. These results are in agreement with the measurements of the coefficient od dynamic friction that indicate that soft materials have more friction compared to hard materials.

Finally the measurement of the coefficient of dynamic friction permits to explain the lower grip of sole 5 compared to sole 4 with similar hardness. Indeed, sole 4 has a higher COF compared to sole 5 on wet porcelain tile.

4.5 Conclusions

The analysis of the friction behaviour of ski boots soles for alpine skiing show that the coefficient of friction of the materials used for the production of boot soles depends on the hardness and on the crystalline structure of the materials. The materials with lower hardness also present the best grip properties.

The thermoplastic polyurethanes used for the soles have more grip on glass compared to porcelain stoneware surfaces. The grip on ice is significantly lower also due to the lower temperature that increases the stiffness of the material. Therefore, materials that increase less their hardness at low temperature should be preferred.

The surface roughness seems to have a negative effect on the friction, more rough materials being those with less grip.

The measure of grip on inclined wet surfaces shows again a relation between hardness and grip, the softer materials having the best performances. The ranking of the different materials and design is the same for the coefficient of dynamic friction and for the slip angle indicating that COF can be used as a parameter for the choice of the best material to be used for the soles of ski boots.

The comparison of two soles with different designs indicates that the best results in terms of friction are obtained with a surface that have a wider contact area with the floor. This is in agreement with the results of the surface roughness that indicates that more rough materials have also less grip.

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5 Conclusions

This thesis was focused on the study of the basic chemical and physical properties of the materials used for the production of snow sports equipment and on finding a correlation between these properties and the mechanical behaviour and performance of the final products. Three product categories have been investigated: personal protection, ski boots and soles.

In the first chapter the impact behaviour and thermo-mechanical properties of the materials used for back protectors have been characterized and from the results emerged that the newly introduced polymeric foams present low density and a shear-sensitive behaviour. In fact the visco-elastic properties, both elastic modulus and damping, depend on the frequency of the applied stress. This will result in a back protector with high ergonomic comfort, allowing freedom of movements during skiing, as well as protecting the body in the event of a fall or collision. Furthermore these materials improve the multi-impact behaviour but are more sensible to temperature changes. In particular their stiffness increases at low temperature due to the reduced polymeric motion.

The second chapter investigates the effect of the visco-elastic properties of the materials on the flexural and rebound behaviour of the ski boots. DMTA analysis on polymeric samples has been combined with flexural and rebound test bench testing on the ski boots. The results highlighted the relevance of DMTA analysis in a knowledge based design process, in fact using this approach it is possible to select the right materials for a desired flexural and rebound behaviour without the need to mould and assemble an entire ski boot. Moreover it has been showed that different designs of ski boot give rise to different mechanical behaviours, both in term of flexural stiffness and elastic rebound. Proving that besides the material choice also the design selected for a specific ski boot plays an important role in the properties of the final product.

Finally in the third chapter the effect of material properties and surface roughness on grip performances of ski boots soles has been studied, combining contact area and coefficient of dynamic friction (COF) measurements, ramp testing and surface analysis. The results showed that the coefficient of friction of the materials used for the production of boot soles depends on the hardness and on the crystalline structure of the materials. In particular the materials with lower hardness also present the best grip properties. Furthermore, thanks to a profilometric investigation of the surfaces emerged that surface roughness seems to have a negative effect on the friction, rougher materials being those with less grip. The comparison of two soles with different designs indicates that the best results in terms of friction are obtained with a surface that has a wider contact area with the floor. This is in agreement with the results of the surface roughness that indicates that more rough materials have also less grip. Finally the ramp testing confirmed again a relation between hardness and grip, the softer materials having the best performances. The ranking of the different materials and design is the same for the coefficient of dynamic friction and for the slip angle indicating that COF can be used as a parameter for the choice of the best material to be used for the soles of ski boots.

It is notable that all the research performed in this thesis can be used as a protocol during the design and development process to reduce costs and time as well as improve performance. In fact the knowledge of the influence of the materials on the final products can lead to the development of specific and tailor made solutions for a certain application.

List of Figures

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6 List of Publications

6.1 Publications in international journals

- **Effect of the visco-elastic properties of thermoplastic polymers on the flexural and rebound behaviours of ski boots for alpine skiing.** M. Nicotra, M. Moncalero and M. Colonna. *Journal of Sports Engineering and Technology*, published online on 23rd December 2014. DOI: 10.1177/1754337114564481.

- **Thermo-mechanical and impact properties of polymeric foams used for snow sports protective equipment.** M. Nicotra, M. Moncalero, M. Messori, E. Fabbri, M. Fiorini and M. Colonna. *Procedia Engineering*, **72**, 678 (2014). DOI: 10.1016/j.proeng.2014.06.115, 72, 678-683.

- **Thermal behaviour of ski-boot liners: effect of materials on thermal comfort in real and simuated skiing conditions.** M. Colonna, M. Moncalero, M. Nicotra, A. Pezzoli, E. Fabbri, L. Bortolan, B. Pellegrini and F. Schena. *Procedia Engineering*, **72**, 368 (2014). DOI: 10.1016/j.proeng.2014.06.066.

- **Materials, Designs and standards used in ski-boots for alpine skiing.** M. Colonna, M. Nicotra and M. Moncalero. *Sports*, **1**, 78 (2013). DOI: 10.3390/sports1040078

6.2 Books and book chapters

- **Effect of ski-boot design on flexural and rebound performances.** M. Colonna, M. Nicotra, M. Moncalero and M. Fiorini. In *Science and Skiing VI*, Meyer and Meyer Sport (UK) Ltd., pp. 119-128 (2015). ISBN: 978-1-78255-066-2.

- **Ski boots for Alpine Skiing: Designs, Materials and Testing Procedures.** M. Colonna, M. Nicotra and M. Moncalero. *Lambert Academic Publishing*, United States, pp.72 (2014). ISBN-13: 978-3-659-63676-9.

6.3 Conferences

- **Effect of frequency on damping and visco-elastic properties of materials for ski-boots.** M. Nicotra, M. Moncalero, M. Fiorini and M. Colonna. *Book of abstracts International Congress on Science and Skiing 2013.*
- **Effect of ski-boot design on flexural and rebound performances.** M. Colonna, M. Nicotra, M. Moncalero and M. Fiorini. *Book of abstracts International Congress on Science and Skiing 2013.*
- **Pilot study for the evaluation of thermal properties and moisture management on ski boots.** M. Moncalero, M. Colonna, A. Pezzoli and M. Nicotra. *Proceedings icSPORTS 2013*
- **Viscoelastic properties of thermoplastic materials used for ski boots.** M. Colonna, M. Moncalero and M. Nicotra. *Book of abstracts The Engineering of Sport 9, ISEA 2012.*

7 Experiences abroad and Collaborations

7.1 Experiences abroad

Research activity in the research centre of Marker Germany GmbH in Penzberg, Germany, from 01.05.2013 to 01.11.2013, focused on the development and testing of back protectors for skiing.

7.2 Collaborations

Throughout the PhD program several collaborations have been carried out:

- Research centre of Calzaturificio Dalbello for the work on the ski boots.
- Research centre of Vibram spa for the work on the ski boot soles.
- Dipartimento di Ingegneria "Enzo Ferrari", Università di Modena, in particular Prof. Massimo Messori and Dr. Elena Fabbri for the impact testing on the materials for the back protectors.
- Centro Ceramico Bologna, in particular Dr. Barbara Mazzanti and Dr. Pietro Bruzzi for the testing of the grip of the ski boot soles.

7.3 Tutoring

- Tutor at the *ISEA Winter School in Sports Engineering 2014.*
- Tutor at the *ISEA Winter School in Sports Engineering 2013.*

7.4 Awards

- FIS Young Investigator Award of the 6^{th} International Congress on Science and Skiing, St. Christoph am Arlberg, Austria, December 2013.
- ISPO 2014 gold award for the MAP technology developed during the period in Marker Germany GmbH.

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