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TITOLO TESI

HIGH PERFORMANCE POLYMERIC MATERIALS FOR SPORT EQUIPMENT, FUNCTIONAL CLOTHING AND FOOTWEAR: INTERACTIONS OF MATERIALS, HUMAN BODY AND ENVIRONMENT IN TERMS OF MECHANICAL, THERMAL AND ERGONOMIC PROPERTIES.

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Abstract

The study of the influence on mechanical, thermal and ergonomic properties of advanced polymeric materials used to produce outdoors gear and footwear has been the topic of the present PhD thesis. The study has addressed several aspects of ergonomics, safety and mechanical properties of sport equipment. The following topics are reported in the thesis:

- The evaluation of thermo-physiological comfort of soft-shell back protectors, investigating how design and materials can affect moisture management and heat loss. Heat retention has been identified using infrared thermography and testers have answered a questionnaire to take into account their subjective thermo-physiological sensations.
- The effect of liners used in ski boots. Three different ski boot liners have been tested to evaluate the insulating behaviour and the moisture management capability of the materials used. Tests have been conducted in climatic chamber and then repeated in real skiing conditions. Scanning Electron Microscopy has been used to evaluate the effect of cells morphology on thermal insulation.
- The effect of different materials used for the production of thermo-formable ski boots have been analysed in order to determine their performance in the process used to adapt the shape of ski boots to the skier's foot morphology. The effect of foot compression on the thermal comfort has also been evaluated.
- The effect of glass fibre/rubber composites on the grip on icy surfaces. The study has been conducted analysing the friction of a ski boot sole containing an insert made of composite material and comparing the results with those obtained using rubber and a thermoplastic elastomer. Scanning Electron Microscopy has been used to perform the morphological analysis of the composite.
- Thermal comfort of trekking shoes has been evaluated in climatic chamber using wireless temperature and relative humidity sensors embedded in the midsole. Additional evaluation of heat retention through the sole and the upper has been performed using thermal imaging.

Contents

Ai miei sacrifici,
Alla mia mamma,
Alla mia famiglia e a chi mi vuole bene.

1 Introduction

People live interacting with each other and with the environment. Every object we use and every environment in where we live interacts with our own body, no matter if we are walking outdoor, training indoor, watching a movie or simply sleeping. This is the reason why we dress up in winter and we choose comfortable shoes when doing sport. We make choices to be in a comfortable condition to perform activities or to accomplish a task in the best way. Beside of being a necessary condition for our health, comfort is a fascinating condition because a person is in comfort with the environment when experiencing a sense of neutrality.

The interactions that takes place between human body and environment, involve materials as a third crucial element. In fact, this work is specifically focused on how high performance polymeric materials used for outdoor gear and footwear can perform in obtaining the best results in terms of mechanical properties, thermal and ergonomic comfort.

In the outdoor industry, the only way to design products, which can accomplish these tasks, is to consider all the multiple interaction between these three elements:

- MATERIALS (e.g. Apparel, Equipment, Footwear)
- HUMAN BODY (e.g. Thermal comfort, Ergonomic Comfort)
- ENVIRONMENT (e.g. Temperature, Relative Humidity, Wind)

Nowadays, the research for innovative high performance materials in the field of functional garments and footwear is a constant rush. At the time, European outdoor business is weighed in 4.8 billion Euros for wholesale and 10.2 billion Euros for retail. Moreover is a growing market with 1,2% value and 1,4% volume increase [1].

Footwear led the growth, up 2.8% in value and 4% in volume, while apparel, the largest market, is effectively flat with less than 0.5% growth [1].

Market request is one of the main reasons why the outdoor industry is making huge technological improvements in terms of product performance, but there is a gap, that this work is willing to fill, which is called *Comfort*.

Most of the outdoors sport activities, and in particular winter sports, are strongly influenced by the variation of meteorological parameters. It follows that the evaluation of bio climatological conditions has a fundamental importance not only for a proper planning of training programs and the nutritional plan, but also for a better evaluation of the race strategy [2]. Despite these observations, the influence of meteorological and environmental conditions is often disregarded in the outdoors sport performance assessment [3].

Based on Lobozewicz [4], Kay et al. [5] and Pezzoli et al. [6] studies, a qualitative-quantitative assessment of the influence of environmental variables on sport performance can be performed using the Haddon matrix [7].

William Haddon Jr. developed his conceptual model, the Haddon matrix, in 1980. Since that time, the matrix has been used as a tool to assist in developing ideas for preventing injuries of many types.

The application of the Haddon matrix in the field of the sports activities allows determining the factors that mostly affect the performance, such as:

- Personal factors (psychophysical preparation)
- Vector or Agent Factors (materials and opponent)
- Physical and environmental factors (meteorological and environmental analysis)
- Socio-environmental factors (of internal and external social environment)

Referring to environmental parameters and thus thermal comfort [8,9], it is well know that wellness and environmental quality can be divided in different classes of environmental quality, although highly correlated, namely:

- Thermo hygrometric wellness: state of thermal neutrality, in which the subject does not feel either hot or cold.
- Respiratory/smell wellness: state of satisfaction of an individual in relation to the air he is breathing.
- Visual wellness: the state in which the individual can play the different tasks he has to perform in the best way
- Acoustic wellness: psychophysical condition when an individual, in the presence of a sound pressure field, is said to be in a state of well being considering the work he is doing.

In addition to this, wellness is general and not unique: in fact, many factors interfere with each another and sensory perception overlaps, resulting in a synergic effect generating the feeling of wellbeing.

On the contrary, dissatisfaction can be caused by:

- Discomfort from the heat or the cold perceived by human body
- Not desired cooling or heating of a particular part of the body
- Vertical temperature difference between head and ankle is too high
- Asymmetry of the radial temperature is too high
- Metabolic energy is too high
- Inappropriate clothing

A second more comprehensive definition [9], defines thermal wellness as the condition of comfort, in which the environmental parameters, acting with the human body's reactions, eliminate the sensations of heat or cold perceived by the subject (thermal neutrality). Obviously, this must be done without massive intervention of the body's thermal control system, as its extreme actions are a source of discomfort.
It follows that the main variables that affect the thermal comfort can be listed as follows:

- Average radial temperature
- Air moisture
- Average relative speed
- Physical activity
- Thermal resistance of the apparel worn

To characterize the thermal resistance of clothing, three variables are commonly used in literature: total insulation ($R_{T)}$), intrinsic insulation ($R_{cl)}$) and effective insulation ($R_{cle)}$). It is widely used to measure these resistance (I) in *clo,* inconsistent units linked to the corresponding International System units by the relation:

$$1 \text{ clo} = 0{,}155 \text{ m}^2 \text{ KW}^{-1}$$

Total insulation, R_t (m^2 KW^{-1}), is defined as:

$$R_T = A_b (t_{sk} * t_0) / H$$

Where A_b is the surface area of the naked human body (m^2), t_{sk} is the average temperature of the skin surface of the human body (°C), t_0 is the operating temperature of the environment in which the subject is located (°C) and H is thermal power (W).

The intrinsic insulation, R_{cl}, is defined as:

$$R_{cl} = A_b (t_{sk} – t_{cl}) / H$$

Where t_{cl} represents the average temperature of the surface of the human body with clothes (°C).

Finally, the effective isolation, R_{cle} (m^2KW^{-1}), is defined by the relation:

$$R_{cle} = R_T - R_A$$

Where R_A is the unit superficial thermal resistance subject-environment.

It is well known how garments, in sport activities and with stressful weather conditions, can affect sport performances. But is also true that apparel and footwear can affect comfort in everyday use, especially considering the latest weather and climate alteration that the world is experiencing.

The chance to study directly on the athlete the benefits of a particular piece of equipment represents a new frontier in applied sport research on sports. Winter sports, trekking and mountaineering are performed in some of the coldest and harshest external conditions of all sports and the effect of the external environment in terms of cold is therefore significant for all the aspect of performance, safety and comfort.

Nowadays, sport equipment like footwear, protection gear and apparel plays a key role in the outdoors market, representing a huge variety of product in which polymeric materials are used on a large scale. Moreover they act as the functional interface between human body and environment, protecting from cold or impacts or transmitting our force from the feet to the ground.

It follows that the need of selecting the best material and design to accomplish one of the above-mentioned tasks has become of crucial importance in product management and research. At the same time, the whole retail chain has also become very demanding on the subject of performance and comfort. Nevertheless, outdoors activities require the highest safety standards especially when performed in the harshest environmental conditions, when frostbite, injuries or pain may occur.

For all these reasons, a specific work has been done in order to develop and manufacture high performance products, which can allow users to obtain the best mechanical properties while achieving thermal and ergonomic comfort.

This work, in the precise attempt to unite the mechanical, thermal and ergonomic contribution, has been gathered in the following chapters.

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2 Aim of the Thesis

The aim of this work is to understand the effect of how different materials performs in terms of thermal and ergonomic comfort. The choice of the appropriate material for the design of functional clothing, sport equipment and footwear is of fundamental importance in order to achieve mechanical performances, ergonomic comfort and a proper thermal insulation. The effect on user's safety, thermal comfort of different materials used for commercial products and prototypes has been analysed.

A multi purpose flowchart sets the standards for an updated design approach for outdoors products that can take into account some underestimate parameters such as the relevant and multiple interactions between materials, human body and environment:

1) PERFORMANCE AND COMFORT DRIVEN DESIGN

- Chemical and mechanical properties research and testing

2) PRODUCT TESTING

- Mechanical testing
- Thermal Comfort Evaluation
- Ergonomic Comfort Evaluation
- Evaluation of the Comfort Subjective Perception

3) PERFORMANCE AND COMFORT ASSESMENT

4) SAFETY ASSESMENT

The third chapter of this work is about the evaluation of thermo-physiological comfort of back protectors, investigating how design, materials and technical details can affect moisture management and heat loss. Several parameters have been taken into account during the climatic chamber tests, such as hearth rate, average skin temperature, sweat production and microclimate temperature and humidity. On the other hand, heat losses have been identified using infrared thermography and testers have answered a questionnaire to take into account their subjective sensation due to their thermo-physiological comfort or discomfort sensations. High-end innovative back protectors made of pseudo-dilatant material have been tested, this materials has a soft response for low speed forces applied to its surface while gets firm and offers a hard response in case of high speed impact.
Compared to hard shell protection, those characteristics have allowed producer to create a new generation of back protectors with improved ergonomic comfort and unparalleled thermal comfort due to the chance of create holes patterns on the foam pad.

In the fourth chapter the effect of liners used in ski boot has been investigated. Three different ski boot liners, made of different materials, have been tested to evaluate their insulating behaviour and their moisture management capability. Tests have been conducted in climatic chamber and than repeated in real skiing conditions. Scanning Electron Microscopy has been used to evaluate the contribution of cells morphology in the achievement of thermal insulation. Infrared thermography has been used to define the most sensitive district of the human foot, thus helping in advanced liner’s design.

The fifth chapter is about ski boots shells for alpine skis from both the ergonomic and thermal point on view. Different materials used for the production of thermo-formable ski boots have been analysed in order to determine their performance in the thermo-formation process used to modify the shape of ski boots and therefore improve their comfort. Chemical composition and thermo-mechanical properties have been analysed.
On the other hand, the effect of foot compression on the thermal comfort of ski boots has been evaluated comparing the temperature in the toe area of two ski boots with a 10% difference in internal volume, during simulated skiing in a climatic chamber at -10 °C for 60 minutes.

The sixth chapter discusses the use of ski boot soles based on a glass fibre/rubber composite with improved grip on icy surfaces. A study on the effect of glass fibre/rubber composites on the grip on icy surfaces has been conducted in order to develop new materials for ski boot soles with increased grip in winter environments. The study has been conducted analysing the friction of a ski boot sole containing an insert made of composite material and comparing the results with those obtained using rubber and a thermoplastic elastomer. Scanning Electron Microscopy has been used to perform the morphological analysis of the composite. The measure of the contact angle has been used to evaluate material's water repellence. Moreover, the effect of material elastic properties and surface roughness on grip performances of ski boot soles has been investigated. A set of thermoplastic materials used in soles for alpine skiing boots have been characterized in terms of chemical composition, cristallinity, hard-ness, surface roughness, and grip. The friction experiments have been made on different substrates reproducing real environmental conditions.

The topic of the seventh chapter is the evaluation of thermal comfort of trekking shoes in climatic chamber using wireless temperature and relative humidity sensors embedded in the midsole and coupled with the evaluation of the heat dispersion through the sole and the upper lining with thermal imaging and sensors. Hiking boots have been subjected to human testing to evaluate the thermo-physiological comfort. Volunteers have made a reproducible physical activity on a treadmill, in controlled environmental conditions (-10 °C; 60% RH). Physiological parameters have been acquired using wireless sensors. The acquired data have been statistically processed and analysed to evaluate the thermal insulation of the boots.

Additional evaluation of heat dispersion through the sole and the upper has been performed using thermal imaging and sensors.

3 Protective equipment for snow sports: thermal and ergonomic comfort

The following chapter is about protectors for winter sports. Especially during freeride and freestyle skiing and snowboarding, speed could be very high and rocks, trees and other natural elements represent an increased risk when falls occurs. For these reasons the use of proper protections is widely used in such activities and since the number of users is rapidly increasing, companies started to put a lot of attention on this product range.

Back protector is usually made by a pad, which size is almost the size of the back and it is possible to wear it through the use of a vest or suspenders.

Pad material can strongly influence the impact properties as well as the overall comfort sensation. In fact, thick pads made of a rigid plastic shell do not promote any ventilation and moisture wicking effect and their rigid behaviour can restrict the movement of the body. Materials also influence the weight and the heat retention of back protectors, thus offering variable comfort.

In this chapter a new generation of soft-shell back protectors for winter sports, made of soft foamed pad, has been tested in climatic chamber under controlled environmental conditions during intermittent physical activity to evaluate the influence of materials and design in achieving the best thermal and ergonomic comfort.

3.1 Introduction

Outdoors clothing has experienced huge functional improvements since the 70's; outdoor apparel has become lighter, warmer, waterproof, breathable and often fancier. Accessories for outdoors activities have to follow the same criteria to satisfy user's needs and body protectors are not an exception. Winter sports are generally high-energy outdoor activities and therefore involve inherent risks, resulting in numerous falls and collisions with an average of approximately 1.5/1000 traumatic injuries skier/day [1].

In recent years, outdoors companies have pushed their research to set new performance standards for protection gear (e.g. winter sports): nowadays, a new generation of back protectors made of foam is able to offer improved comfort from both the ergonomic and thermal point of view.

A full range of soft-shell back protectors for winter sports have been tested to evaluate which design combination (pad material, vest material, dimensions) is able to offer the best properties in terms of thermal and ergonomic comfort.

Back protectors have the critical task of shielding the spinal cord to prevent damages that can cause severe injuries (e.g. paralysis), this make the topic very relevant in the active sports market. In the last years this product faced significant changes in terms of design and material used, passing from hard shell (hard thermoplastic outer shell, coupled with a inner padded insert) to soft shell pad made of polymeric foams and inserted in a functional body vest. In older products, the shock absorbing action was delivered by the transmission of the forces over a wide area while soft polymeric foams have pseudo-dilatant nature [2], acting like a hard material under high-speed force application and staying soft under low-speed forces. This behaviour allows producer to reduce the protector's thickness and to create perforated structure patters instead of having a hard and continuous surface, improving both the ergonomic and thermal comfort.

Final products result in a high level of protection in case of crash as well as a good flexibility and comfort [3].

Since back protector stays between clothing layers, representing an additional layer, thermal properties as thermal insulation and water vapour resistance become key parameters such as mechanical ones like hardness, density and shock absorbing capability in winter sports design.

Moreover, recent studies have demonstrated how apparel can influence comfort and performance, especially in severe environmental conditions such as extremely cold or extremely hot [4,5,6]

The alternating phases of alpine skiing, characterized by downhill and chairlift sections, along with the need of protection from cold environment, contribute to multiply the variables that can affect thermo-physiological comfort. In the ideal condition body temperature should stay as constant as possible and next to skin moisture should be quickly removed to avoid condensation.

Climatic chamber simulation allows performing thermal comfort evaluation [7,8,9,10,11,12,13] recent studies tried to quantify the thermal physiological comfort on manikin [7].

The aim of this study was to investigate thermo-physiological comfort of soft-shell back protectors identifying design features able to enhance heat loss and moisture management.

This work is performed human testers, such as recently others have done on ski boots liners in both real and simulated environmental conditions [14], showing strong correlation between the results obtained from the outdoors and indoors tests.

The aim of the present study is to investigate the back protectors performances in terms of temperature control and moisture management in order to fully understand and identify the parameters that affects thermal comfort during winter sport activities.

3.2 Materials and Methods

3.2.1 Materials

As shown in Fig. 3.1, three different models of commercial soft-shell back protectors have been analysed and tested. All back protectors (BP1, BP2, BP3) are made of polymeric foam different in thickness, shape, density and moulding pattern, and they differ in terms of materials and design of the vest with which they are coupled.

Fig. 3.1 Soft-shell back protectors

BP1 provides a proper fitting by using two shoulder straps and a large hip-belt. On the contrary, BP2 and BP3 use a slim fitted vest, where the foam pads are inserted in. BP2 uses an elastic band on the hip while BP3 has a hip-belt too and provides protection of the spinal cord up to the sacrum. The weight of the foam pad compared to the back protector weight is 60% BP1, 50% for BP2 and 47% for BP3.

Also the materials of which the vests are made play a key role in thermo-regulation. All the back protectors features are shown in Table 3.1.

BP2 has the lowest polymeric foam density and the lowest overall weight.

Protector	**Chemical composition**	**Shock absorber shell mass** (g)	**Density** (g/cm^3)	**Thickness** (mm)	**Hardness** (Shore A)	**Textile lining composition**	**Overall weight** (g)	**Vest**
BP1	PU and PDMS	459	0.38	13	14	100% Polyester	755	No
BP2	EVA and nitrile rubber	345	0.15	16	40	80% Polyamide 20% Elastane	685	Yes
BP3	EVA and nitrile rubber	455	0.30	20	25	45% Polyester 37.5% Polyamide 7.5% Elastane	970	Yes

Table 3.1 Characteristics of back protectors

3.2.2 Methods

Climatic Chamber

Tests have been performed in a climatic chamber (54 m^3 volume), under controlled environmental conditions. Average air temperature (T_a) was set to 12.83 ± 0.38 °C, relative humidity (RH) was 65.07± 1.12% and airflow in the room was set to 0.2 m s^{-1}.

Even if the room temperature could simulate some spring skiing conditions, is well know that winter sports took place generally in colder environments. This said, since back protectors are usually worn between clothes, the choice was made to evaluate back protectors thermal performance without any additional clothing layer over it.

Test Protocol

Five volunteers, three women and two men, have been involved in the tests. Average age was 33.0 ± 3.8 with an average weight of 57.38 ± 2.87 kg. The number of testers has been chosen according to the literature standards in the field of the evaluation of thermal comfort of sport equipment and functional clothing [15,16,17].

Test protocol follows the Code of Ethics of the World Medical Association (Declaration of Helsinki); testers have been informed about procedures and freely took part at the experiment. To avoid circadian cycles alterations, tests took place in different days but at the same hours; testers performed the same physical activity pattern with each back protector.

Identical clothing were worn for each tester, long-sleeved shirt and pant made of 100% polypropylene inner layer and 75% polyamide and 25% elastane outer fabric (Fig. 3.2).

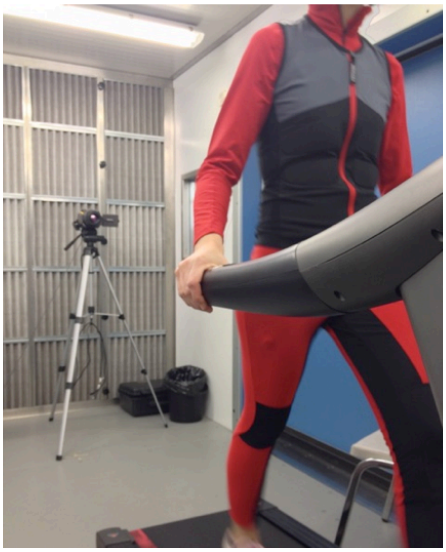

Fig. 3.2 Tester outfit

Test duration has been 1 hour, divided in three specific phases: 10’ acclimation, 20’ physical activity, and 30’ recovery/cooling. The 20’ physical activity pattern over the treadmill is shown in Fig. 3.3.

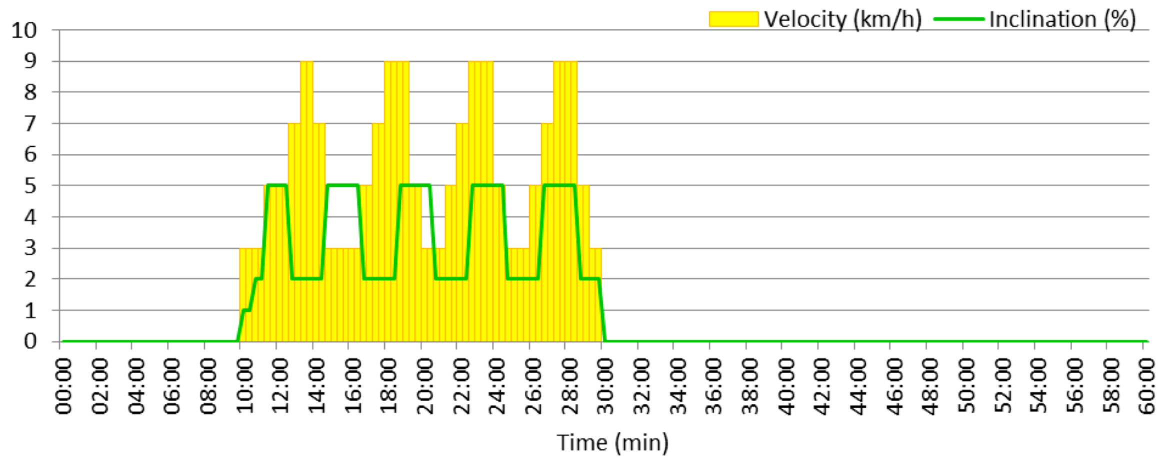

Fig. 3.3 Physical activity pattern, treadmill speed [Km/h] and platform inclination [%]

Acclimatization and recovery represent two key phases when performing this type of trials, no matter what is the simulated activity [17,18]. Even if short to avoid uncomfortable cold sensations, acclimation helps to provide uniform thermo-physiological conditions before each test; instead, the recovery phase contributes to highlight the thermal resistance of back protectors while the tester is resting and his body temperature is decreasing, even if the metabolic heat produced during the physical activity kept the subject comfortable until the finish of the test.

The evaluation of the amount of water vapour exchanged (sweat) between human body and environment has been estimated by weighting (precision of ±5 g) subjects before and after the test.

Wireless Temperature And Relative Humidity Sensors

Eleven Maxim-Dallas miniaturised temperature and relative humidity sensors (Fig. 3.4) were used for each tester; these passive data-logger have a resolution of 0.04% for relative humidity and 0,0625°C for temperature recording; they have been set with a sampling rate of 30 s.

Fig. 3.4 Maxim-Dallas miniaturised temperature and relative humidity sensors

According to the prescription of norm ISO 9886:2004 [19], eight sensors have been applied to the tester's skin by using small stripes of highly breathable medical tape in order to evaluate the Average Skin Temperature (T_{ASK}) through the following formula:

$$(T_{ASK}) = (0{,}19*T_{Thigh}) + (0{,}07*T_{Deltoid}) + (0{,}07*T_{Forehead}) + (0{,}07*T_{Elbow}) + (0{,}05*T_{Hand}) + (0{,}2*T_{Calf}) + (0{,}175*T_{Scapula}) + (0{,}175*T_{Chest})$$

In this multi-linear formula, each sensor's contribution is a function of the surface of a specific parts of the body surface compared to the overall skin surface. Sensors have been located as shown in Fig. 3.5.

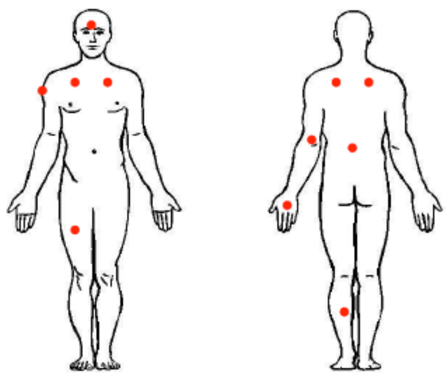

Fig. 3.5 Sensor positions

Fig. 3.6 Sensors applied to the tester's skin

Three sensors on the testers back as shown in Fig. 3.6 have specifically monitored microclimate skin temperature under back protectors.

A much more specific investigation has been performed by the evaluation of the Average Torso Skin Temperature (T_{TASK}), isolating the contribution of scapula and chest sensors using the following formula:

$$(T_{TASK}) = (0{,}25*T_{Right\ Scapula}) + (0{,}25*T_{Left\ Scapula}) + (0{,}25*T_{Right\ Chest}) + (0{,}25*T_{Left\ Chest})$$

This choice was based on the observation that the scapula and chest temperatures have the same weights in the average skin temperature of the norm ISO 9886:2004 [19], suggesting that scapula and chest contribute in the same extent to the average skin temperature.

Infrared Thermography

High resolution infrared thermo camera Thermo Tracer TH9100MW (NEC Avio Infrared Technologies Co., Ltd, Tokio, Japan), working in the wave length band 8–14 μm with a resolution of 0.02°C, has been used to record thermo graphic images of the volunteers' back during the climatic chamber test with resolution of 320 x 240 pixels. Images have been acquired during at the end of the acclimatization phase (t10'), at the end of the physical activity (t30'), 15 minutes after the end of the physical activity (t45') and 30 minutes after the end of the physical activity (t60').

Additional back protector inner face thermography (the face in contact with the body) were acquired immediately after taking the back-protector off at t60'.

Subjective Sensations

The evaluation of the subjective comfort sensations of each volunteer has been recorded using a purpose built questionnaire containing eight questions. The questionnaire has been filled four times for each test: after acclimatization (t10’), at the end of physical activity (t30’), after 15 minutes of recovery (t45’) and at the end of the test (t60’).

The questionnaire is shown in Tab. 3.2: Q1 and Q2 are focused on the volunteer's overall thermal sensation, Q3 and Q4 on the perceived skin sensation, while Q5 summaries the apparel thermal insulation assessment (Q5a), breathability (Q5b) and touch sensations (Q5c, Q5d). At the end of the test, volunteers were asked to give an overall score to the back protector overall comfort.

For each question, a numerical scale was associated to the answers, with the most uncomfortable sensation associated with the minimum level of the scale and the most comfortable sensation with the maximum (e.g. Score 1 was given to answer "Dripping sweat", score 2 to the answer "Wet", score 3 to the answer "Slightly wet", score 4 to the answer "Dry”). Scores have been multiplied by the frequency of that answer and a single numerical value has been assigned to each question. The score value of each question has been normalized to 10.

Q1	*Are you in a thermal comfort condition?*	Yes (2)	No (1)			
Q2	*If not, how the air temperature should be to be in comfort?*	Warmer (1)	The same (2)	Colder (1)		
Q3	*What is your skin temperature sensation?*	Very cold (1)	Cold (2)	Neutral (3)	Slightly hot (2)	Hot (1)
Q4	*What is your skin humidity sensation?*	Dripping sweat (1)	Wet (2)	Slightly wet (3)	Dry (4)	
Q5a	*How do you score your outfit?*	Light (1)	Right (2)	Heavy (1)		
Q5b		Non- Breathable (1)	Little breathable (2)	Breathable (3)		
Q5c		Cold (1)	Neutral (2)	Warm (1)		
Q5d		Wet (1)	Damp (2)	Dry (3)		

Table 3.2 Subjective sensations questionnaire

3.3 Results

3.3.1 Heart rate and sweat production

In Fig. 3.7 is reported a typical hearth rate output of one tester wearing back protectors, the four peaks represent the four repeated activity steps as defined in Fig. 3.3. Good repeatability demonstrates that volunteers have performed a similar effort while testing each back protector.

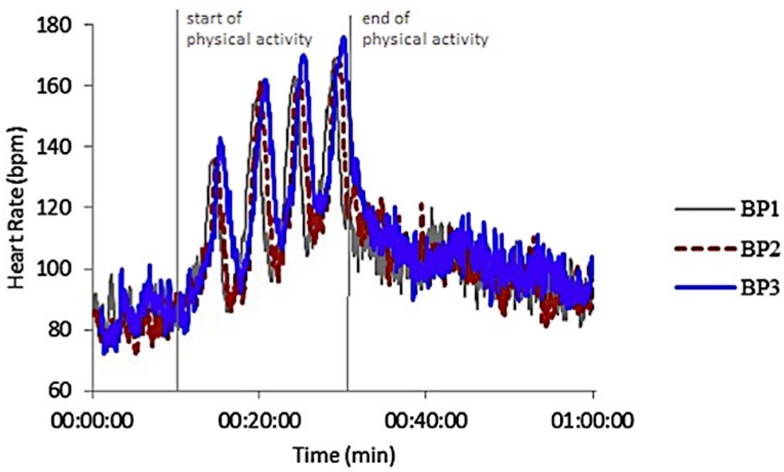

Fig. 3.7 Heart rate during the test (Volunteer: woman, 35 years old): from t=0 to t=10' acclimatization phase; from t=10' to t=30' training phase; t=30' to t=60' recovery phase.

Mean and maximum heart rates, have been averaged over the whole population, results are shown in Fig. 3.8. The use of ANOVA in Table 3.3, with confidence interval set to 95%, confirmed that the mean and maximum heart rate did not show significant differences.

Sweat evaporation shows great variations among participants as shown in Fig. 3.9.

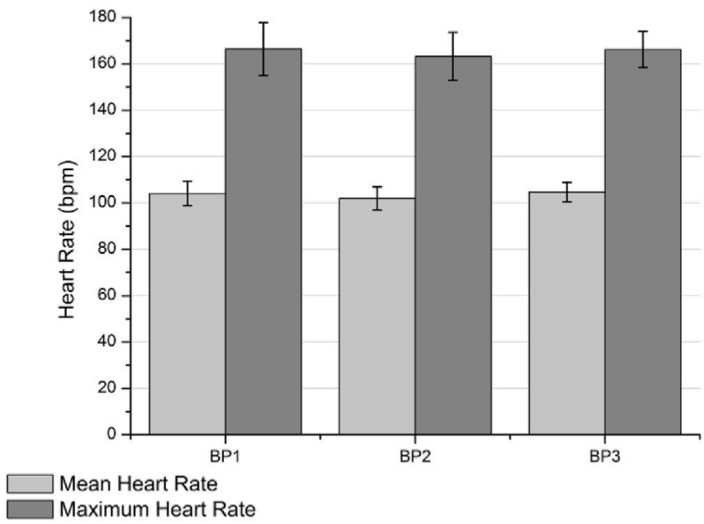

Fig. 3.8 Mean and Max heart rate for each back protector.

	P-VALUE		
	Mean HR	**Max HR**	**Sweat Production**
BP1-BP2	0.524	0.654	0.134
BP2-BP3	0.366	0.618	0.211
BP1-BP3	0.839	0.839	0.467

Table 3.3 P-values of the ANOVA for heart rate and sweat production

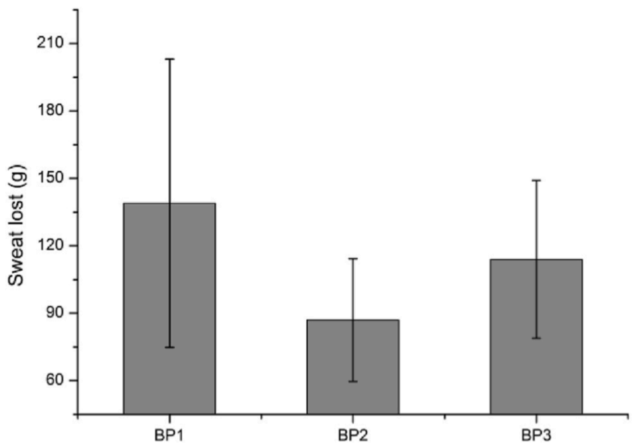

Fig. 3.9 Volunteers sweat loss [g]

Sweating is a process that begins first in specific parts of the body: at the onset, perspiration appears on the forehead initially, followed in order by the upper arms, hands, tights, feet, back and abdomen [20].

Sweat intensification occurs when the number of participating glands increases and when the output of each active gland increases too [20]. Moreover, the primary response to heating a local skin area, is the increasing of the individual glands output, rather than the stimulation of a larger number of glands to sweat [21].

Having said that, a strong local physiological response in terms of sweat output of the back sweating glands is expected wearing a back protector.

As will be proven further on, back protectors can cause a sudden increase of the microclimate temperature and humidity that can lead to saturation in the back region. For these reasons, specific care must be taken to back protector design, trying to maximize breathability to quickly evaporate abundant amount of sweat from the back area; achieving this task is possible creating a perforated pattern over the polymeric foam pad without compromising shock absorbing properties.

3.3.2 Skin temperature

Skin temperature (T_{ASK}) has been averaged over the five volunteers; results are shown in Fig. 3.10. A relevant skin temperature decrease occurred during the acclimatization phase when the absence of physical activity can't compensate the metabolic heat loss.

During the activity phase a wavy trend is shown in Fig. 3.10 due to intermittent physical effort. From 20' to 30', T_{ASK} has been low because the evaporative cooling effect.

After the end of the physical activity pattern, T_{ASK} has grown significantly due to less ventilation and less sweating and showed a constant trend during the recovery phase.

BP1 has a lower average temperature compared to BP2 and BP3, this is a consequence of the back protector design: the only one without a vest (Fig. 3.1), in fact, vest can be considered an additional layer that can influence chest temperature.

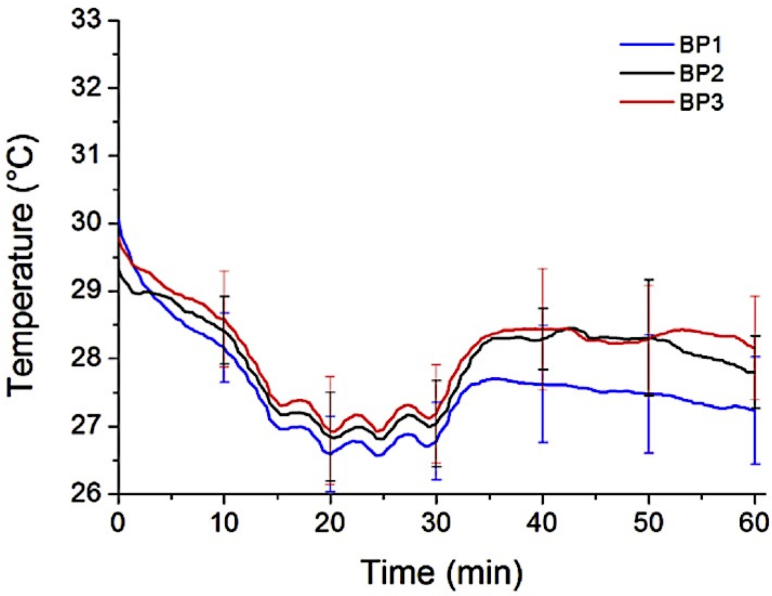

Fig. 3.10 Average Skin Temperature (T_{ASK})

Quantitative comparison between the back protectors has been performed using the ANOVA of the following parameters: average skin temperature at the end of the acclimatization phase ($T_{ASK\ 10}$), average skin temperature at the end of the physical activity ($T_{ASK\ 30}$), average skin temperature at the end of the recovery phase ($T_{ASK\ 60}$), average skin temperature averaged over the whole test duration (T_{ASK}). The same analysis was carried out for the average torso skin temperature (T_{TASK}) in the same test intervals. P-values of the ANOVA are shown in Table 3.4 for T_{ASK} and in Table 3.5 for T_{TASK}. P-values lower than 0.050 are in bold; the confidence interval of the differences has been set to 95% (Table 3.5).

	P-VALUE			
	$T_{ASK\ 10}$	**$T_{ASK\ 30}$**	**$T_{ASK\ 60}$**	**T_{ASK}**
BP1-BP2	0.452	0.520	0.224	0.265
BP2-BP3	0.667	0.741	0.406	0.152
BP1-BP3	0.309	0.355	0.096	0.198

Table 3.4 P-values of the ANOVA for average skin temperature (T_{ASK})

	P-VALUE			
	$T_{TASK\ 10}$	$T_{TASK\ 30}$	$T_{TASK\ 60}$	T_{TASK}
BP1-BP2	0.111	**0.039**	**0.039**	**0.022**
BP2-BP3	**0.050**	0.548	0.293	0.279
BP1-BP3	**0.001**	**0.018**	**0.018**	**0.006**

Table 3.5 P-values of the ANOVA for average torso skin temperature (T_{TASK})

The analysis on T_{ASK} when BP1, BP2 or BP3 is worn shows no significant difference. This makes sense because average skin temperature takes into account the contribution of eight skin districts, five of which were not covered by any of the back protector (Fig. 3.5).
Different comment has to be made for the average torso temperature (T_{TASK}) shown in Fig. 3.11, in this case BP1 is about 2°C lower than BP2 and BP3 in the recovery phase and this could represents a factor of discomfort.

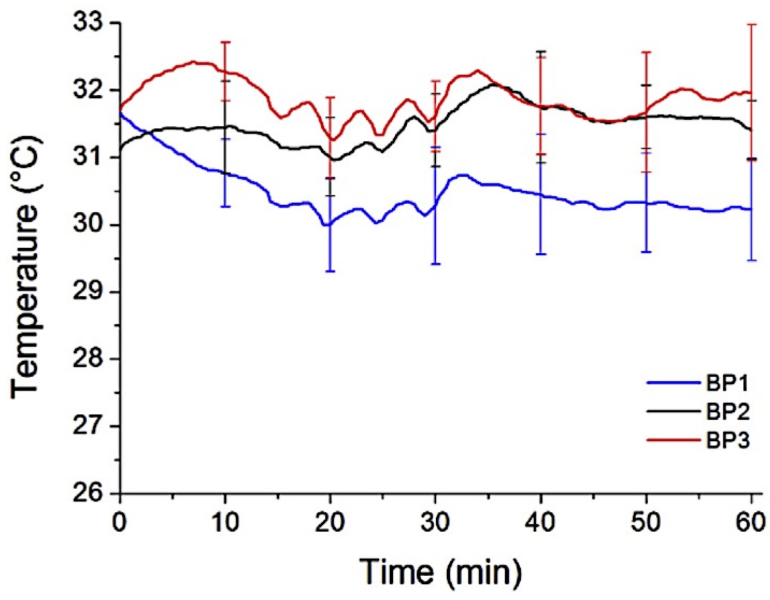

Fig. 3.11 Average Skin Temperature (T_{TASK})

Moreover, the acclimation phase shows a temperature decrease for BP1, while volunteers experienced a slightly temperature increase in this phase, suggesting a greater thermal insulation.
If average skin temperature T_{ASK} represents a tool to evaluate overall thermal loss considering the whole body, it is true that it might fail to identify major differences that involve the torso area.

Thus, average skin temperature gives an idea of overall thermal loss from the whole body but it might fail to identify differences between items of clothing covering the body only partially. The complete picture of temperatures recorded under the BP, have to take into account also the microclimate temperature discussed in the next section.

3.3.3 Microclimate properties

Microclimate properties such as temperature and relative humidity have been monitored during the test for each volunteer, averaged results are shown in Fig. 3.12. Microclimate, namely the thin air layer below the back protector, shows a different temperature trend compared to skin temperature. The wavy trend showed in Fig. 3.11 has been substituted in absence of the vasodilatation and evaporative cooling response. In fact, temperature is growing due to the thermal insulation provided by back protectors until the end of the physical activity while is decreasing in the end of the test, more steeply for BP2. This means that the shell offers high resistance to heat dissipation and heat loss by conduction is very low due to the pad's thickness and material. This implies that evaporative cooling and pumping effect represent the mean to heat dissipation in such system.

Due to a more perforated structure compared to others BPs, BP2 is more keen to vapour diffusion and ventilation through the shell and this results in a less steep temperature increase and quicker temperature decrease in the second half of the test. Confirmation comes from the fact that temperature growth has been steeper during the acclimatization phase than during the physical activity, when sweating and body movements were negligible and this minimize heat removal by forced convection through the shell and by sweat evaporation from the skin.

It comes of fundamental importance to create perforated structures to achieve maximum thermal comfort without compromising shock absorption.

Microclimate temperature increased quickly for al BPs (almost 4°C in less than 30'), while the decrease has been slower, despite the environmental temperature set at 12°C and no jacket has been worn over the back protectors.

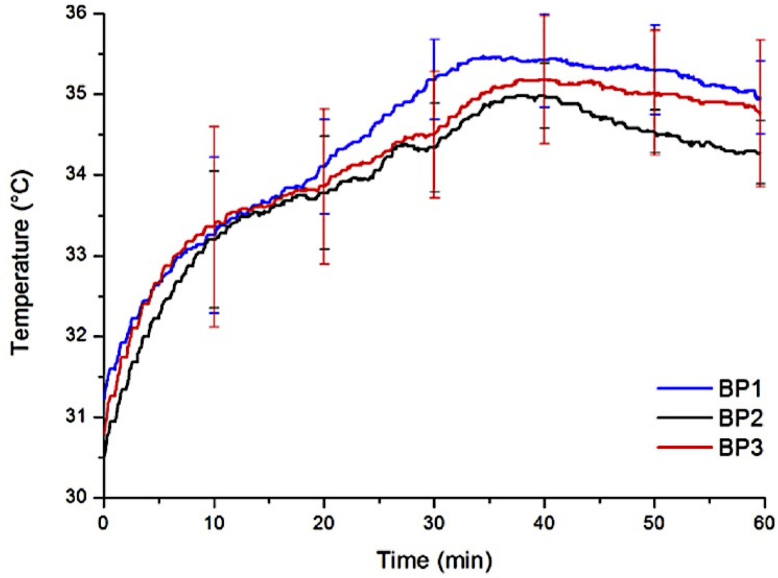

Fig. 3.12 Average microclimate temperature

The slower decrease in the recovery phase is due to the balance between heat generated and removed: when physical activity stops, metabolic heat production drops but evaporative cooling is still effective because plenty of sweat produced during the physical activity has still to be evaporated.

However, despite the holes in the structure, evaporative cooling could not be exploited to the maximum extent because forced ventilation was far less intense during the recovery since the subject has been without moving on the treadmill.

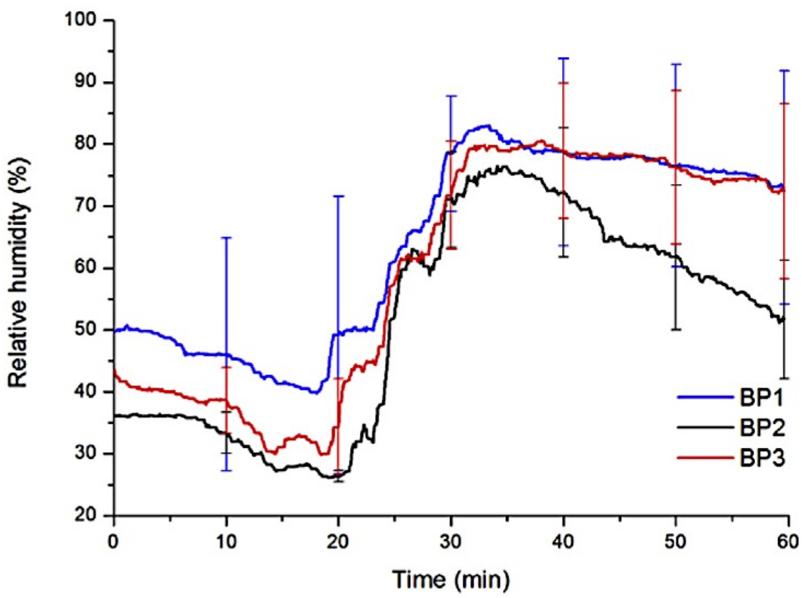

Fig. 3.13 Average microclimate relative humidity

What have been said about microclimate temperature is confirmed by the analysis of microclimate humidity shown in Fig. 3.13.

In the fist 20’, relative humidity decreases as a consequence of microclimate temperature increase. When sweating starts, usually between 20 and 24 min, relative humidity increases steeply up to 85%. Only BP2 has been able to perform a relative humidity decrease up to 60% due to its greater ventilation.

	P-VALUE			
	$T_{MC\,10}$	$T_{MC\,30}$	$T_{MC\,60}$	T_{MC}
BP1-BP2	0.203	**0.034**	**0.034**	0.198
BP2-BP3	0.932	0.718	0.309	0.562
BP1-BP3	0.292	0.140	0.671	0.655

Table 3.6 P-values of the ANOVA for microclimate temperature (T_{MC})

	P-VALUE			
	$RH_{MC\,10}$	$RH_{MC\,30}$	$RH_{MC\,60}$	RH_{MC}
BP1-BP2	0.397	0.208	**0.054**	0.137
BP2-BP3	0.861	0.893	**0.026**	0.152
BP1-BP3	0.408	0.277	0.957	0.600

Table 3.7 P-values of the ANOVA for microclimate relative humidity (RH_{MC})

P-values of the ANOVA analysis of the microclimate temperature and humidity are shown in Tab. 3.6 and 3.7: while no significant differences have been found for microclimate temperature, some differences can be highlighted for microclimate humidity, especially at the end of the test.

In fact, at the end of the acclimatization phase no significant difference could be detected among BPs but, when volunteers started sweating on the treadmill, the behaviour of BP2 became significantly different from the others, as shown in Fig. 3.13.

Microclimate analysis gets very important especially when microclimate environment is in direct contact with the body; in this case, heat transfer and sweat evaporation are regulated by the driving forces T_{ASK}, T_{TASK} and the two water vapour pressure contributions, skin and microclimate ones [22]

Besides temperature and vapour pressures driving forces, heat and mass flow are function of heat and mass exchange coefficients; these two coefficients are maximized in case of forced ventilation through the shell, it follows that the best design for back protectors should be based on maximizing ventilation through the shell to exploit forced convection and evaporative cooling to the greatest extent.

3.3.4 Infrared Thermography

Infrared thermography is a useful tool, which provides qualitative and quantitative data on heat removal mechanism from the body. As an example, which results have been found reproducible among testers, thermographs of one volunteer's back during the tests are shown in Fig. 3.14. In the last row, thermographs of the inner side of the BP just taken off by the tester are shown.

BP1 is characterized by sharp partitions of high temperature and low temperature areas, due to the shell variable thickness and big rectangular-shape holes located along the thinner channels. It follows that heat is transferred through the shell by conduction in the areas in contact with the body surface and by convection through the holes. Beside the lower part of the back, BP1 inner side thermo-image reveals a slightly uniform temperature, meaning that the back protector has been rather close fitted to the volunteer’s back.

In terms of shell design, BP2 has uniform thickness with evenly distributed holes on the whole surface with the exception of a cross formed on the upper-back, two vertical bands along the spinal column and two side bands. Due to the large numbers of holes, a less clear distinction of warmer and colder areas is visible in the thermographs. Nevertheless, the thermal images reveal that BP2 shell temperature was higher in the upper-back area than in the lower-back area during the whole test. This situation was attributed to the air gap formed on the lower back: while BP1 has a small shell completely adhering to the back, BP2 and BP3 have an elongated shape covering the back up to the sacrum.

BP2 inner side thermography shows a colder area in correspondence of the back concavity, which is a sign that BP2 was not completely adhering to the body in that area. BP3 is the thickest one and it is expected to be more thermally insulating. Indeed, thermographs show a colder outer side and a warmer inner side, confirming that BP3 has the highest conductive resistance.

The inner side temperature is homogeneous, confirming that BP3 shell structure was adhering to the back also in the area concavity area. In fact, the shell profile is arched and the shell width is reduced in correspondence to the back concavity to increase flexibility.

Summarizing, infrared thermography has shown that perforated structures are effective in conveying heat outside from the shell: areas without holes are colder on the exterior side with respect to the areas with holes, testifying delay in heat transfer. Smaller holes, closer one to each other, like in case of BP2, provide a more uniform heat exchange from the shell with respect to larger holes, like in case of BP1.

A proper distance between the shell and the body can provide the best heat exchange while Ventilation through the holes occurs in case of body movement even without a large air gap between the body and the shell, on the contrary, the air gap acts as an insulating air pocket. As already mentioned above, low conductivity is a limiting factor of BP thermo-physiological comfort. Thus, besides the shape of the shell and the position of the holes, foams with maximum shock absorption capabilities and greater thermal conductivity should be selected or developed to reduce shell thickness and increase heat flow by conduction.

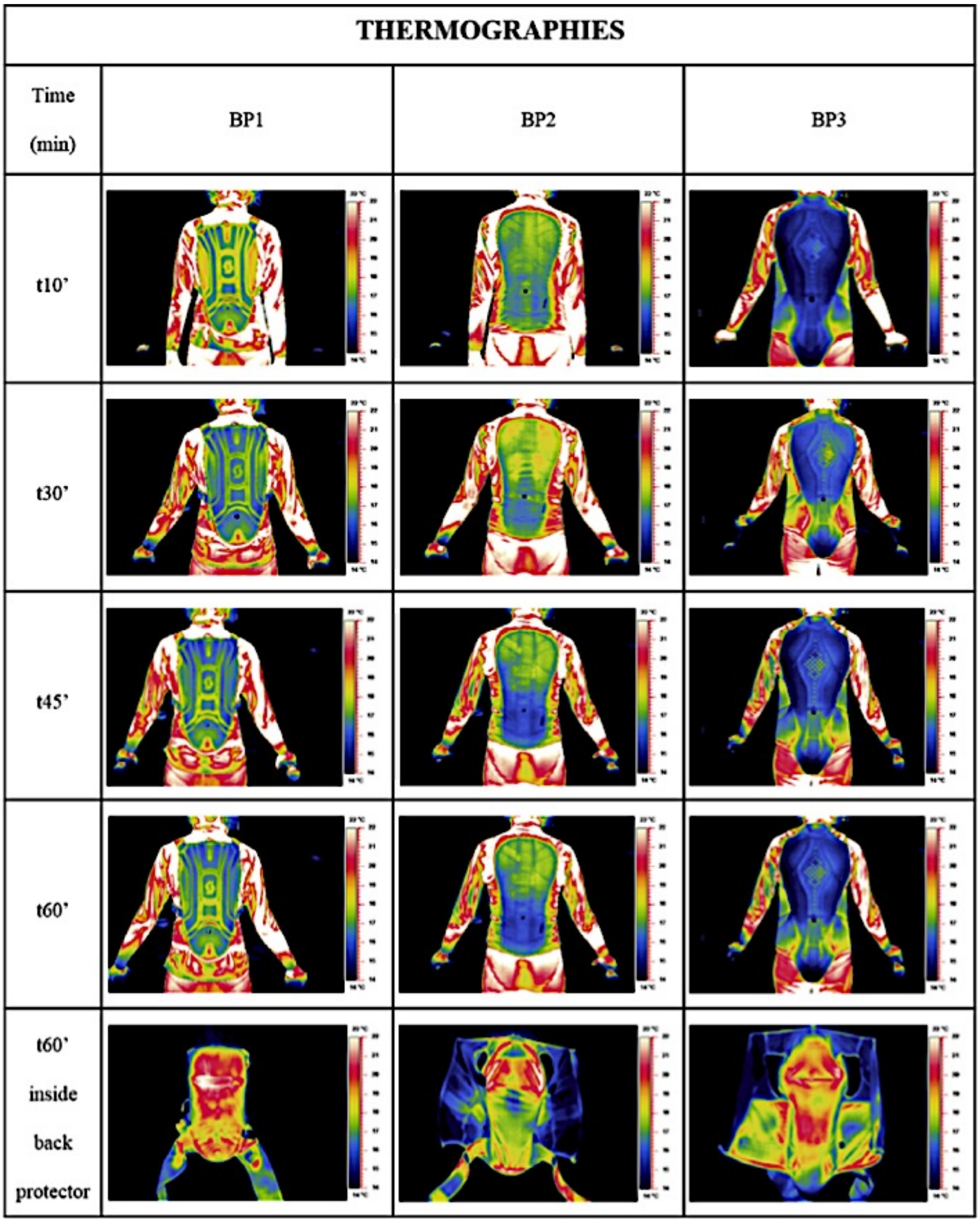

Fig. 3.14 Thermographs of a volunteer's back taken at different times during the test (temperature scale from 14°C to 21°C for all thermographs)

3.3.5 Questionnaire

The questionnaire was answered four times during the test and the score of each question has been averaged over the four questionnaires to have a single numerical value to quantify the BP appreciation during the whole test. This strategy can also evaluate consistency and reliability of the volunteer response. Results have been reported in the radar plot of Fig. 3.15: the higher is the score, the more positive is the sensorial feedback of the subject. BP2 seemed to be the most appreciated one, while BP1 has been the less appreciated in terms of Overall Score (Q8).

Fukazawa and Havenith [23], found that moisture on skin was more correlated to thermal discomfort than skin temperature. It was proved that un-evaporated sweat remaining on the skin surface was the major factor of discomfort [24].

The design of BP2, that guarantees a drier microclimate, seems to be the winning strategy to achieve better thermal comfort. In terms of thermal sensations (Q3 and Q5c), BP3 obtained the highest grades while BP1 obtained low scores. BP1 might have been penalized by the lack of the vest, as during cold exposure of the whole body, local warming of the chest and abdomen produced the strongest comfort feeling [25].

However, BP1 was appreciated for its lightness (Q5a) even though it was not the lightest, probably due to its structure without vest which permits free movements.

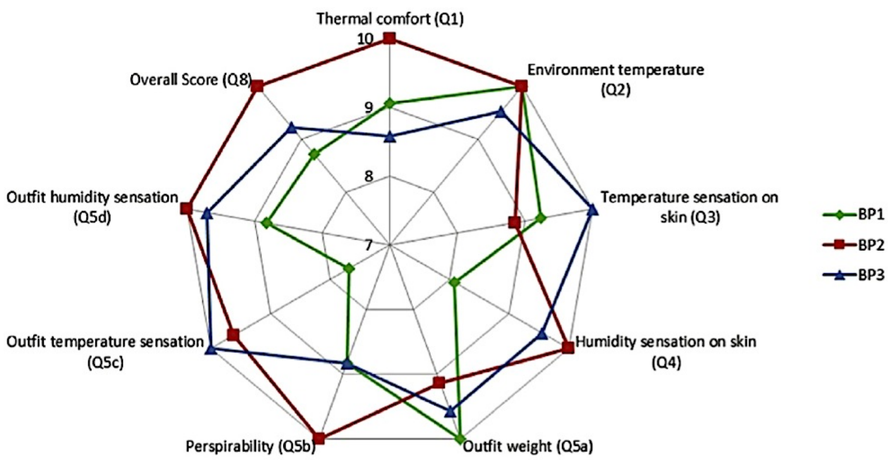

Fig. 3.15 Global Radar Plot of subjective appreciation of the back-protectors.

3.4 Conclusions

In-vivo trials have been performed to investigate how back protectors for winter sports perform in terms of moisture and heat management. Physiological parameters such as sweat production; skin temperature and microclimate temperature and humidity have been recorded to have an overall view of the volunteer thermal stress.

Information gathered from physiological parameters have been coupled with heat dissipation outputs obtained through infrared acquisitions and subjective sensations evaluation. The outfit configuration did not include a ski jacket covering the torso of the volunteer so the results do not mimic the real outfit of a skier but is able highlight the real behaviour of back protectors and their design’s features.

The analysis of the objective and subjective data has highlighted that back protectors offer different level of thermal comfort. All physiological parameters have been consistent and provided a general picture of the heat and mass transfer phenomena through the shell, with the following major findings:

- Thermal conductivity of all shells is poor and to improve thermal comfort, evaporative cooling and forced ventilation must be exploited to the maximum extent. The larger is the holes number in the BP shell structure; the greatest is the heat dissipation. This observation has been confirmed by infrared thermography and microclimate measurements.
- The average body and torso skin temperatures depends mainly on the vest, whose presence is appreciated by the wearers because of a better ergonomic fit and a more uniform thermal feeling.
- Moisture management was found to be the main factor determining back-protector appreciation. According to the questionnaire, the top-ranking back protector was the one giving the best sensations in terms of breathability and lower humidity sensation, while temperature sensation seemed to play a secondary role in thermal comfort feeling.

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4 Ski boots for alpine skiing: thermal and ergonomic comfort

This work embraces many fundamental aspects of ski boot's design to achieve the best performance in terms of mechanical properties, thermal and ergonomic comfort.

Ski boots represents the interface between our body and the skis so they have to provide the highest control and performance but at the same time they have provide comfort, causing no harm and they have to be safe in terms of injury and frostbite protection.

All these tasks must be accomplished by a severe material selection for each part that composes ski boots and precise design specifications have to be observed to guarantee the highest comfort and safety standards.

In this chapter all of these aspects will be treated considering the effect of:

- Liner shape and materials
- Shell shape and materials
- Effect of compression on feet

Tests took place in climatic chamber, simulating skiing conditions; moreover, a pilot study for the evaluation of thermal properties and moisture management of ski boots in outdoor conditions is presented.

4.1 Introduction

Thermal insulation is one of the most important factors for a safe experience on ski slopes. Since hands and feet have a large surface area compared to their volume and a small muscle mass, they both tend to be much more sensitive to cold exposure with respect to other parts of the human body [1]. It has also been reported that the feeling of cold discomfort into the feet will dominate even if clothes with proper insulation are used on the rest of the body [1]. The feet are comfortable when the skin temperature is about 33°C and the relative humidity next to the skin is about 60% [2].

The feeling of cold starts at temperatures around 25°C, while discomfort from cold is noted at temperatures below 20-21°C [1].

Thus said, the chance of evaluate the effect of a specific technical solution directly on athletes, represents a new frontier in product and materials development.

Alpine skiing is performed in some of the coldest and harshest outdoor conditions of all sports and the effect of the external environment in terms of comfort and safety is therefore significant; but with the right amount of insulation, it is possible to keep the feet into the range of comfort and to avoid frostbite [1].

The heat transfer from the feet to the liner, which interacts with the outer plastic shell and so with the external environment, characterizes the behavior of ski boots from a thermodynamic point of view. Inside the liner the heat transfer is ruled by the heat flow from the foot to the liner, by conduction and convection [3].

The insulation properties of footwear are directly proportional to the amount of air trapped inside the fabric and between the foot and the shoe indicating that convection has a negative effect on heat insulation of boots [1]. Another critical element among the characteristics of a boot is its ability to expel moisture from the inside to the outside. In recent studies [Hofer et al (2013) have] the temperature and humidity inside a ski-boot liner have been measured during simulated and real skiing actions, finding that the toe area is the most exposed to cooling effect. It has also been found that ambient temperature and moisture inside the ski boot strongly affect foot temperature and that high water socks and liner content reduces thermal insulation properties.

A pilot study, using wireless sensors, for the measure of temperature and humidity in outdoor conditions have been performed [4], concluding that different liners can achieve different thermal insulation behaviour.

For the first time in this application field, this work wants to correlate results with the composition of the liners. Moreover, a study of the temperature in the different points of the foot performed by thermo-graphic analysis has been performed, using wireless sensors and thermo-graphic images, correlating the results obtained with the chemical and physical characteristics of the liners.

4.2 Materials and Methods

4.2.1 Materials

Ski boot liners

Ski boot, model *Lupo*, from Calzaturificio Dalbello (size 28.5 Mondopoint), has been the model used in each test, while the inner liner has changed between three different commercial products, having the same construction and thickness but made of different materials as shown in Fig. 4.1.

The same type of socks have been worn form each tester for all the trials, Dalbello ID sock are made of a blend of 95% of polypropylene fibres and 5% Elastane.

Each volunteer used the clothes they usually wear in cold winter skiing conditions. The above-mentioned set-up has been kept the same in both indoor and outdoor tests.

Fig. 4.1 Ski Boot Liners, form left to right: Liner 1, Liner 2, Liner 3

Each liner differs from the others in terms of chemical composition of materials used to their construction:

- Liner 1: cross-linked ethylene vinyl acetate (EVA) with 14% of vinyl acetate
- Liner 2: sandwich made of a polyethylene (PE) based elastomer for the external part and EVA fort the internal part
- Liner 3: sandwich made of polyvinyl chloride (PVC) for the external part and EVA for the internal part

Liner 2 and 3 also have an extra insulation in the front part made of Thinsulate: a blend of non-woven fabrics made of PE (65%) and polyester (35%).

4.2.2 Methods

Fourier Transform Infrared Analysis (FTIR)

A common method to detect the chemical composition of polymers is based on infrared spectroscopy. In general, the test consists in scanning a sample with IR radiation and detecting the transmitted light obtain an IR spectrum. 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. FTIR outputs reports the IR light absorbance on the Y axis and the wave numbers (number of waves per unit distance) on the X axis.

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}.

Scanning Electron Microscopy (SEM)

The scanning electron microscope (SEM) provides high-resolution images of the surface of an object by scanning it with a concentrated beam of electrons. The electrons interact with the object’s surface, generating an output signal, which can give information about the sample surface morphology and chemical composition. SEM can be proficiently used to investigate samples over a wide range, from nanometer to micrometer scales length.

Cross-sections of the liner’s padding foams were obtained by fracturing samples by cryogenic cut (immersion in liquid nitrogen), using a JEOL JEM 2010 instrument.

Wireless Temperature And Relative Humidity Sensors

Maxim-Dallas miniaturised temperature and relative humidity sensors (Fig. 4.2) have been used for each tester to record temperature and relative humidity inside the liners; these passive data-logger have a resolution of 0.04% for relative humidity and 0,0625°C for temperature recording; they have been set with a sampling rate of 30 s, working with 12-Bit and with a sensor sampling rate of 30 seconds.

Fig. 4.2 Maxim-Dallas miniaturised temperature and relative humidity sensors

Due to very small dimensions, sensors did not interfere with the skiing action or caused uncomfortable pressures on skier's feet. Each boot has been equipped with one sensor placed on the inner sole as shown in Fig. 4.3. Each sensor has been placed in the toe area, considering this as the most critical part [5]. Proper slots have been obtained by removing small amounts of material from the insoles. These sensors have a most sensitive part, which has been oriented towards the foot.

Fig. 4.3 Sensor's position in the insole

Yo-Yo Squat Machine

Skiing activity has been simulated using a Yo-Yo Squat Machine (Fig. 4.4, Fig. 4.5). This machine is able to work both the upper and the lower part of the body and its inertial disc performs an eccentric work; it follows that volunteer needs force to extend the rope connected to the disc and must oppose resistance when the rope is released, it follows a continuous effort very similar to skiing activity.

Fig. 4.4 Yo-Yo Squat Machine

Fig. 4.5 One volunteer using the Yo-Yo machine inside the climatic chamber

Infrared Thermography

High resolution infrared thermo camera Thermo Tracer TH9100MW (NEC Avio Infrared Technologies Co., Ltd, Tokio, Japan), working in the wave length band 8–14 μm with a resolution of 0.02°C, has been used to record thermo graphic images of the volunteers' feet during the climatic chamber test with resolution of 320 x 240 pixels.

Climatic Chamber Test

In order to achieve maximum reproducibility, ski boots have been thermo-stated to 15°C before starting the indoor tests. Two testers performed both climatic chamber and outdoor tests:

- Tester 1 (T1), male, 43 years old, 85 kg, ski boot size 28,5 - expert skier.
- Tester 2 (T2), male, 36 years old, 75 kg, ski boot size 28,5 - expert skier.

Volunteers performed 60’ of simulated skiing, with a continuous alternation of 5 minutes of flywheel half squat (Yo-Yo Squat) and 5 minutes of rest, thus simulating classic alpine ski routine, in which downhill sections are alternate to chairlift sessions.

Environmental conditions inside the climatic chamber (Albafrigor S.r.l.) have been controlled and set to -10°C, with a relative humidity of 60%.

To represent the largest picture of thermal behaviour of the volunteer’s feet, thermography images have been recorded at the beginning (t0) and after 60’ (t60) for each session.

To describe the overall temperature of different regions of the foot, the contribution of each punctual measure as shown in Fig. 4.6, has been averaged using the following formulations:

$$T_T=(D1+D2+D3+L1+L2+L3+M2+S2+S2+S3)/10$$

$$T_I=(D4+D5+L4+L6+M2+M4+S4+S5)/8$$

$$T_H=(L5+M3+S6)/3$$

$$T_E=(D3+D5+L3+L4+L5+S3+S5)/7$$

$$T_M=(D1+D4+L1+M1+M2+M3+S1)/7$$

Where (T_T) represents the tiptoe region, (T_I) the instep , (T_H) the heel , (T_E) external and (T_M) the medial.

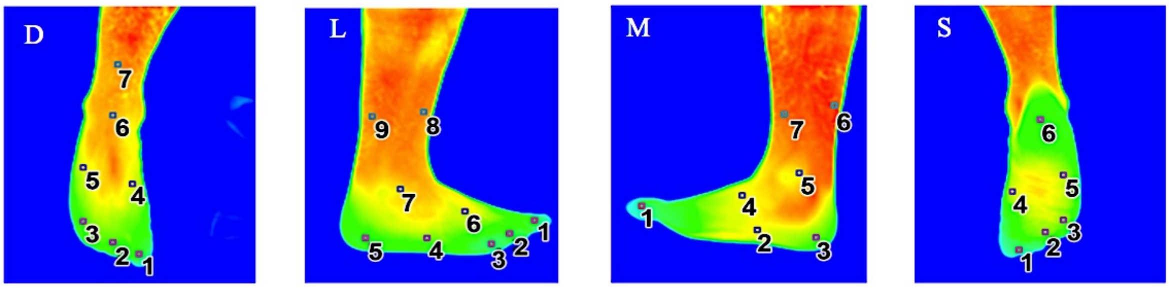


Fig. 4.6 Punctual temperature records for each foot region: Dorsal (D), lateral (L), medial (M) and sole (S)

All testers tested each liner two times. To avoid circadian cycles an alteration, no more than one test has been performed each day and test started always at the same time (10.00 a.m.).

On-field Outdoor Test

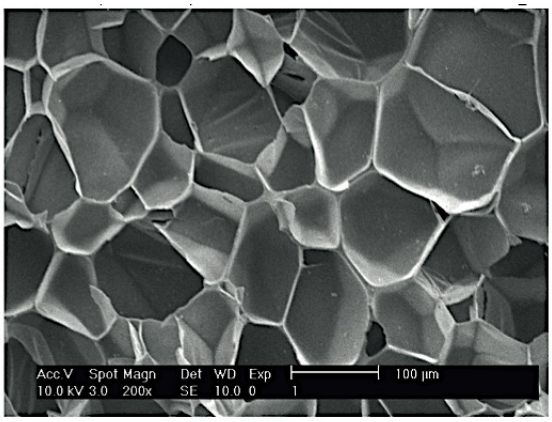
Outdoor tests have been carried out performing standard skiing sessions, trying to represent the standard alpine skiing recreational routine, made of intermittent activity due to the downhill and chairlift alternation. Two hours continuous recording for temperature and relative humidity has been performed using miniaturized data logger in the insoles as explained in chapter 4.2.1.

All tests have been performed in Val Senales (BZ, Italy), with top elevation of 3300 m and bottom elevation of 2000 m. To validate the results, during each session, measurements of the environmental parameters have been performed to take into account the weather contribution. A portable weather station (GEOS 11, Skywatch) has been used. An additional on-board sensor (Maxim-Dallas Hygrochron) has been used to measure air temperature and relative humidity for all the duration of the test. The sensor has been installed outside the skier's jacket and, comparing its output with the data from the weather station, it has been verified that the body heating did not affect its records. Each on-snow test mission has been performed by comparing simultaneously two liners made of different materials for each tester, so tester have skied using the same plastic outer shell but two different liners at the same time. This direct comparison resulted the best way to evaluate different liner's behaviour in real skiing conditions.

4.3 Results

4.3.1 Material characterization

The three liners not only differ for the chemical composition as highlighted by FTIR analysis and explained in chapter 4.2; but SEM imaging has shown major differences among the liners also in the cell morphology as explained in Fig. 4.7.



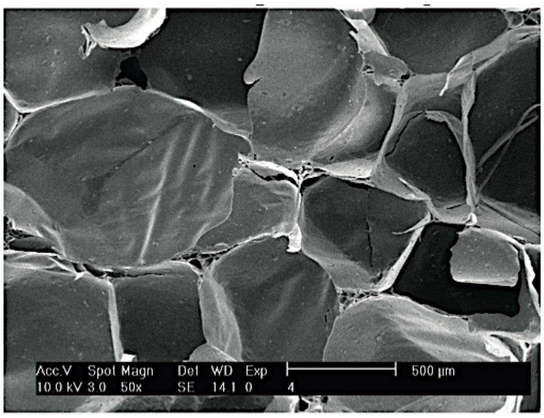


Fig. 4.7 SEM micrographs: from left to right, Liner 1 EVA (200x) and Liner 2 and 3 EVA (50x).

In details, liner 1 is composed entirely of EVA foam with close cell morphology with cell dimensions below 200µm and a wall thickness of 2-5µm. On the contrary the EVA material used for liner 2 and 3 presents cell morphology with both open and closed cells with larger dimension up to 1 mm and diffuse cracks between cell walls. The PE (liner 2) and PVC (liner 3) materials are both compact materials without the cells presence.

4.3.2 Thermal behaviour

Climatic Chamber test

Recent studies have demonstrated that minor differences (below 0.5°C) occur between right and left foot in terms of feet temperature and relative humidity when skiing the same boot setup on both feet [4]. For this reason, it has been assumed that physiological differences between the two feet are negligible compared to those due to the thermal performance of the liners.

Test protocol reproducibility has been evaluated in climatic chamber, comparing the same foot/liner setup in two different days, obtaining reliable results as shown in Fig. 4.8.

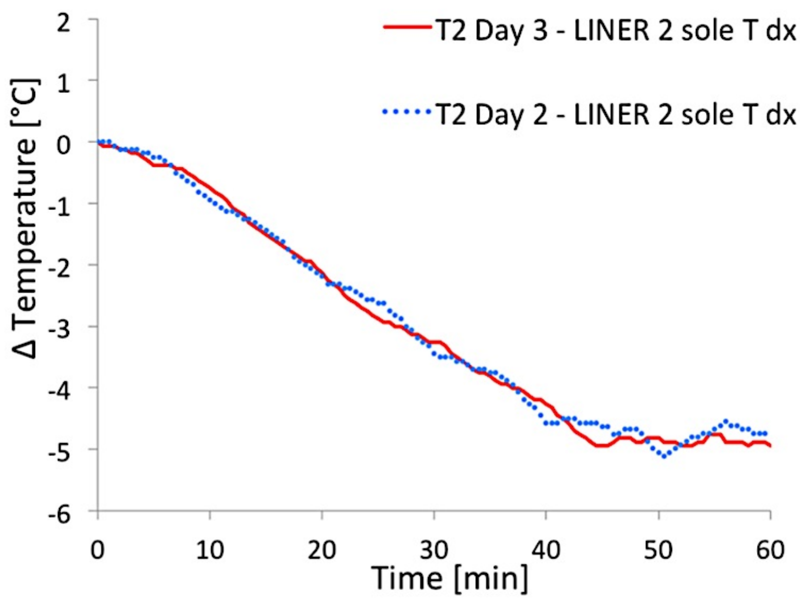


Fig. 4.8 Test protocol reproducibility

In Fig. 4.8, an evident difference between Liner 1 and Liner 2 in terms of thermal behaviour is shown. Liner 1 not only has higher insole temperature values, but also shows a nearly constant trend; Liner 2, on the contrary, is very different if compared to that of liner 2, which is constantly decreasing.

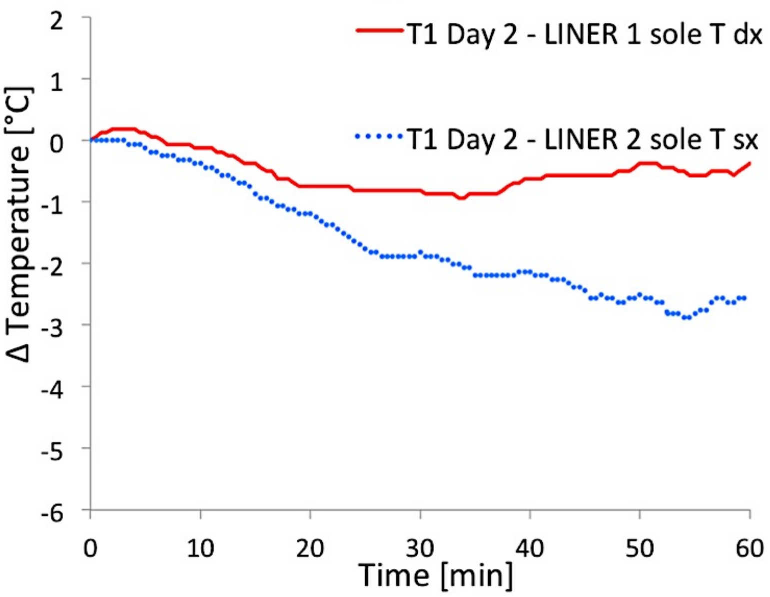


Fig. 4.9 Liner 1 vs. Liner 2, ΔT comparison

The average temperature difference (ΔT), recorded between the beginning and the end of the tests (t60) is reported in Table 4.1, together with the average ΔT recorded by the thermo-camera in the toe area (where the sensor have been installed). In Table 4.2 the average and the maximum relative humidity (RH) measured inside the liner is reported.

Liner	Average ΔT Sensors [°C]	Average ΔT Thermo camera - Toe [°C]
Liner 1	2.99 ± 1.10	1.94 ± 1.72
Liner 2	4.16 ± 1.11	4.61 ± 1.40
Liner 3	4.55 ± 1.34	5.70 ± 1.98

Table 4.1 Average temperature difference (ΔT)

Liner	Average RH [%]	Average time to 80% RH [min]	RH Max [%]	Average time to RH Max [min]
Liner 1	92.94 ± 2.15	3.00 ± 1.3	100.17 ± 0.56	57.2 ± 0.7
Liner 2	94.37 ± 2.27	2.88 ± 1.5	100.57 ± 0.72	54.2 ± 3.3
Liner 3	96.84 ± 2.49	1.00 ± 1.6	101.42 ± 0.58	57.0 ± 2.9

Table 4.2 Average temperature difference (ΔT)

Results proposed in Table 4.3 demonstrate agreement between the data acquired by the thermo-camera and by the sensor, this leads to say that liner 1 seems to offer a more efficient overall thermal insulation, followed by liner 2 and 3. Before the end of the tests, has been recorded that relative humidity reached the saturation limit for all liners.

No significant differences have been observed among the three liners in the time in which they reached the maximum RH and 80% RH, indicating that all liners tested are not sufficiently good in moisture management, at least in the part where the sensor has been located (insole, toe area).

District of the foot	Average initial Thermo-camera temperature [°C]	ΔT Thermo camera [°C] LINER 1	ΔT Thermo camera [°C] LINER 2	ΔT Thermo camera [°C] LINER 3
Toe (T_T)	18.42 ± 2.25	1.94 ± 1.72	4.61 ± 1.40	5.70 ± 1.98
Instep (T_I)	26.31 ± 1.40	1.12 ± 2.61	2.21 ± 0.90	4.13 ± 0.87
Heel (T_H)	19.99 ± 2.81	0.38 ± 2.30	3.33 ± 0.53	5.72 ± 0.09
External (T_E)	20.98 ± 2.66	0.63 ± 4.01	3.38 ± 0.02	6.18 ± 1.73
Medial (T_M)	20.05 ± 2.16	1.21 ± 2.04	3.69 ± 0.77	5.11 ± 4.24

Table 4.3 Average thermo camera ΔT between (t0) and (t60), for each district of the foot

In Fig. 4.10, results show that the toe area is the coldest one, thus in agreement with the results previously reported in the literature [5].

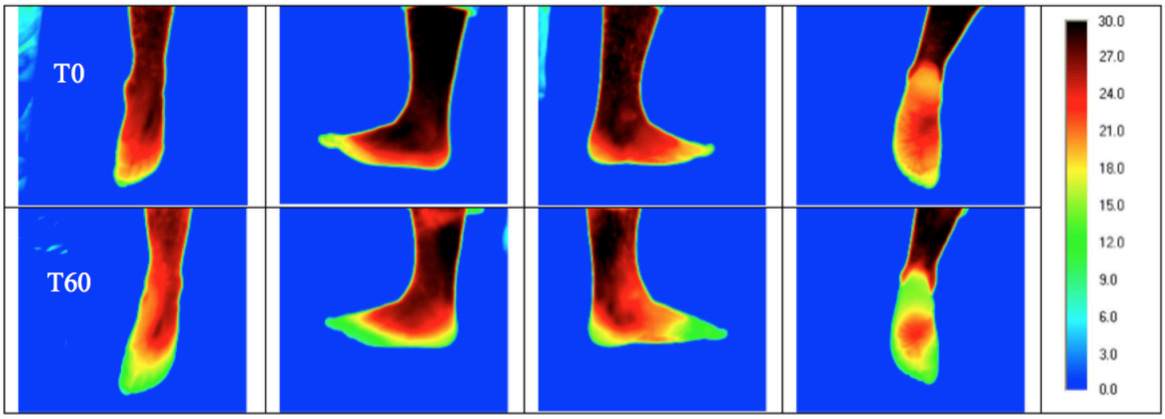


Fig. 4.10 Thermo-graphic camera images at T0 and T60 for liner 1, tester 1, second day of test.

Outdoor Test

Averaging data recorded in different outdoor sessions has not been calculated due to significant differences of the environmental conditions of tests. It follows that only comparative tests between two liners worn in the same time by the volunteer can be used to evaluate liner's thermal properties.

Results from the outdoor tests of liner 1 and liner 3 are reported in Table 4.4.

Liner	Average environmental T [°C]	ΔT Sensors [°C]	Average environmental RH [%]	Average Sensors RH [%]
Liner 1 Test 1	-4.65 ± 1.94	2.51	53.73 ± 5.61	101.45 ± 1.95
Liner 3 Test 1		7.53		99.53 ± 6.32
Liner 1 Test 2	0.95 ± 2.75	-0,50	68.75 ± 9.20	96.22 ± 4.54
Liner 3 Test 2		2,09		96.95 ± 3.63

Table 4.4 Temperature and relative humidity recorder during two on-snow sessions

Again, during on-field trials, liner 1 has ensured the best insulation performance compared to liner 3 and therefore it is possible to assess that results of on-snow tests are in agreement with those obtained in the climatic chamber. The difference between the liners has been more consistent in the coldest of the two days of testing (Test 1). In the warmest testing day, an increase in the final temperature using liner 1 was observed (-0,50 °C), indicating that the insulating behaviour of closed cells EVA used for liner 1 may lead to overheating in the liner in warm environmental conditions. No significant differences in terms of relative humidity inside the liners have been observed also in this case, in agreement with results recorded in the climatic chamber.

4.4 Conclusions

Three different ski boot liners, made of different materials, have been tested to evaluate their insulating behaviour and their moisture management capability. Tests have been conducted in climatic chamber and than repeated in real skiing conditions. Evidences have shown better thermal insulation for liner 1, this behaviour can be ascribed to cells morphology. In fact, closed cell EVA has a more insulating behaviour with respect to the EVA used for liners 2 and 3 that presents larger cells and cracks in the cell walls; the presence of cracks and porosities in the cell walls allows a larger air movement inside the liner, this implies that moisture is able fill up these spaces decreasing insulation [1].

The chemical composition of the outer part of the liner (PE and PVC) seems not to have a significant effect on thermal insulation, causing no changes in both temperature and relative humidity results.

Infrared thermography suggests that specific attention should be addressed to the front part of the foot, resulting the most sensitive to cold exposure.

The use of close cells EVA resulted a proper technological solution to ensure decent overall thermal comfort in colder environment, thus representing the golden choice against frostbite; it has to be said that this solution may lead to slight overheating for warmer skiing conditions.

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5 Thermo-formable ski boots shell for improved ergonomic comfort

Two main functional items compose alpine, ski mountaineering and modern telemark ski boots: inner liner and outer shell. Liners performance in terms of thermal properties and moisture management has been deeply evaluated in chapter 4. The following paragraphs take into account the contribution of the outer shell in achieving ergonomic and thermal comfort. The effect of feet compression inside such a rigid plastic shell has been investigated in terms of its contribution on blood circulation and therefore overall comfort. On the other hand, the chance of developing plastics to manufacture thermo-formable ski boot's shell has been investigated.

Rigid plastic shell, even if from one side provides the highest force transmission and control, offering maximum waterproofness, can produce at the same time dangerous pressure points, pain and blood circulation alterations, causing ergonomic and thermal discomfort.

5.1 Introduction

Plastic ski boots history

Even if the number of ski-lifts and of alpine skiers was dramatically increasing, the ski-boots used in the 1950's were essentially unchanged from those used in the previous centuries, having a thick sole with a thinner upper shell of leather similar to a normal winter boot. However, with the development of new ski bindings like the Kandahar (in 1930) and of the Head standard skis (1950) which allowed a much stronger control of the edges and a more precise and fast skiing [1], new boots became necessary. The first changes were made to improve the boot stiffness to allow for greater control by using stiffer and thicker leather and by soaking the boot in hot water before use. Also the sole was made of harder materials since the boot was clamped on the ski. However, these changes made the boots extremely uncomfortable. The first attempt to use stiffer materials other than leather, was made by Robert Lange that inserted elements made of fiberglass reinforced epoxy resin in 1947 [2]. The first important change was made in 1960 when Lange made the first ski boot made of plastic using ABS plastic [3]. However, the poor low temperature resistance of the plastic used (Royalite from Uniroyal) gave rise to several mechanical failures. In the same years Hans Martin of Henke Speedfit patented the levered buckles for the closure of the boot [4]. The problems with ABS plastic were partially solved using Adiprene, polyurethane manufactured by Dupont in 1965. With this new material it was possible to produce ski boots by injection moulding, the same technique used now. In the same year Rosemount was manufacturing the first composite ski-boots, using fiberglass epoxy resin composite, with a shell that was made in two separate parts to permit the insertion of the foot [5]. The mass production of plastic ski boots started in 1966 with Lange. 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, named Desmopan, that is still one of the most used materials [6]. In 1972 Hanson introduced the rear entry design that was then used by Nordica and Salomon [7]. A former NASA engineer Eric Giese made the last important innovation in ski boot design in 1979. Taking inspiration from the joint of spacesuits, he designed a ski boot that was made of an additional tongue that was controlling the flex of the boot [8]. This construction was named Flexon design and now is also known as 3-piece design or Cabrio Design.

Materials used for structural parts (cuff, shell and tongue)

Several materials are used for the construction of ski boots [9]. Nevertheless, all the materials should comply with several important features:

- Must be resistant at impacts at low temperature
- Must have a long-term stability to thermal and UV aging and to hydrolysis
- Must return to the original position after being flexed
- Must have optimal viscoelastic properties to obtain a progressive flex and an optimized rebound
- Should resist to scratch and to punching
- Should not became too stiff at low temperature

Additional important parameters in the choice of the appropriate materials are density, transparency and the dyeability.

There are few classes of plastics that fulfil all the characteristics reported above. Some of them have some advantages over the others but there is no material that is superior to all the others in every characteristic. The main classes of materials used are showed in Fig. 5.1: thermoplastic polyurethanes (TPU) with polyether and polyester soft-blocks, polyolefines copolymers and blends, polyammide (Nylon) and polyammide-polyether block copolymers (Pebax). TPU can have different composition of both the urethane block and of the soft block. The two most used soft block are polyether (e.g. poly butylene glycol) and poly ethylene glycol) while for the aromatic urethane the most used is that made starting from methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI). The most used polyamides are Nylon 11 and Nylon 12, since present best fatigue properties, lower density and lower water adsorption with respect to the most common polyammides, such as Nylon 6 and Nylon 6,6. Pebax is a block copolymer of a Nylon 11 or 12 with a ether soft block. The presence of the soft blocks or of plasticizers is needed in order to obtain materials with the desired elastic modulus and low temperature impact resistance. Nylon 11 and 12 can be obtained not only from fossil fuels but also from renewable resources (in particular castor oil) thus decreasing the carbon footprint of the material [10].

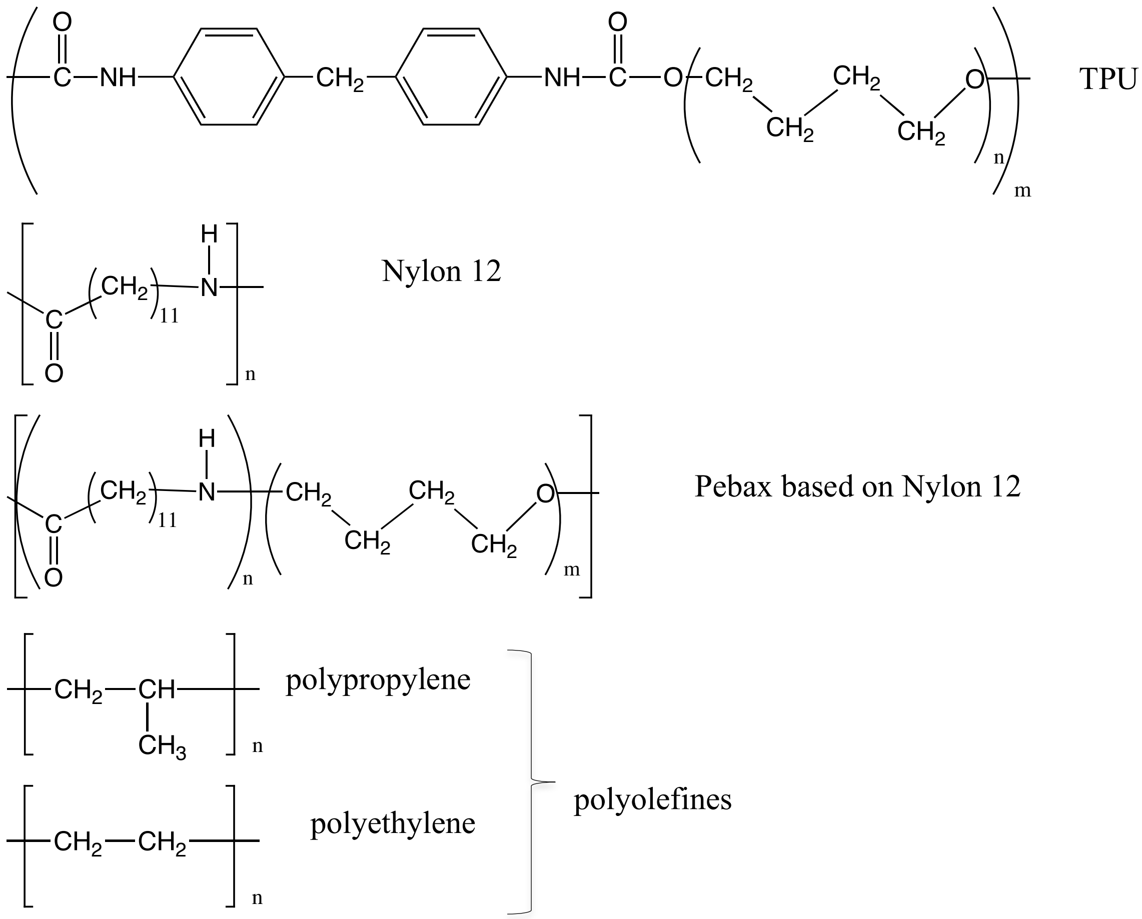

Figure 5.1 polymers used in ski-boot shell and cuff.

5.2 Effect of compression

5.2.1 Introduction

Footwear thermal insulation is one of the most important factors for an efficient protection against cold. Alpine skiing, ski mountaineering and backcountry skiing are performed in cold environmental conditions and skiers are exposed to cold temperatures for long periods of time. Liners are used inside the hard shell of ski boots to provide thermal insulation, cushioning and comfort. The softer parts of the inner boot are made of foamed materials generally based on cross-linked ethylene vinyl acetate (EVA) [11]. The thermal insulation properties of ski boot liners have been reported by Hofer et al [12] that have measured the temperature and humidity inside a ski boot liner during simulated and real skiing actions, finding out that the toe area is the most exposed to cooling. It has also been reported [13] that the insulation properties of shoes and boots are directly proportional to the amount of air trapped inside the fabric and between the foot and the shoe, indicating that convection has a negative effect on heat insulation of boots. Indeed, the measure of the thermal insulation and moisture management of ski boot liners made of different materials, analysed in a climatic chamber and outdoors [14,15], has shown that liners made of closed cell EVA present a higher thermal insulation compared to those made of open cell EVA due to the lower convection in closed cell materials. However, not only the intrinsic thermal insulation properties of the material can affect the overall thermal comfort. In particular, it is well known [16] that blood circulation has an effect on the ability of the body to regulate the temperature of the extremities (hands and feet) and that blood circulation is affected by compression. For this reason, the study of the effect of compression on the thermal comfort of ski boots, comparing ski boots with different internal volumes and feet compressions has been performed.

5.2.2 Materials and methods

Temperature has been measured placing wireless sensors (Hygrochron - Maxim-Dallas) inside the liner. Sensors did not interfere with the skiing action; neither caused pressures on skier's feet. Each boot was equipped with one sensor placed on the innersole in the toe area, considering this as the most critical part from the thermal point of view [12]. Proper slots have been obtained by removing small amounts of material from the liner innersole. The temperature resolution of the sensor is 0.0625°C working with 12-Bit and with a sensor sampling rate of 30 seconds.

Two testers have been used in this study:

- Tester 1 (T1), male, 43 years old, 85 kg, ski boot size 28,5 - expert skier
- Tester 2 (T2), male, 36 years old, 75 kg, ski boot size 28,5 - expert skier

A ski boot, model *Lupo* S.P. from Calzaturificio Dalbello in size 27.5 Mondopoint with a liner entirely made of closed cell EVA foam has been used in all tests. This type of liner has been previously proven [14] to provide better insulation properties with respect to liners made of open cell EVA foams. Tests have been performed with the same set-up (ski boot, liner, buckles closure etc.) reducing the internal volume of 10% (160 mL) using a footboard 5 mm thicker (reduced volume in Fig. 5.2.1) with respect to that commercially sold with the ski boot (correct volume in Fig. 5.2.1). The variation of the internal volume has been measured using water inside an elastic plastic bag, measuring the different amounts of water necessary to fill the boot to the same level. Both testers have declared that it was possible to ski with both configurations (correct and reduced volume) even if a significant sensation of compression was present, especially for tester 1, with the reduced volume configuration. In a compressive comfort scale (from 0 = comfortable to 4 = extremely uncomfortable, according to ISO 10551) both testers have given a ranking of 0 for the correct volume set-up and 2 for the reduced volume set-up.

During measurements, testers have worn the same type of socks (Dalbello ID socks - 95% of polypropylene fibres, 5% Elastane) and clothes they normally use in cold winter skiing conditions. Ski boots have been thermo-stated at 15°C before starting the tests. Testers have performed 60 minutes of simulated skiing, with a continuous alternation of 5 minutes of flywheel half squat (YoYo Squat - YoYo Technology AB) and 5 minutes of rest. Tests took place in a climatic chamber (Albafrigor srl) set to -10°C with a relative humidity of 60%. At the beginning of each session (t0') and after 60 minutes (t60') the skin temperature map of the feet has been acquired by infrared thermo-camera imaging (NEC R300 - NEC Avio Infrared Technologies Co, Ltd., with a temperature resolution of 0.03°C). To describe the temperature in the different foot regions (tiptoe (T_t), instep (T_i), heel (T_h), external (T_e) and medial (T_m)) the punctual temperatures have been averaged according to the procedure previously reported [Ch. 4.2.2]. Every tester has used each configuration at least two times. One test a day was performed, starting at 10.00 AM.

Fig. 5.2.1 Ski boot and footboard employed to modify the internal volume.

The compression on skier's feet has been measured using four resistive pressure sensors (Tekscan A401) placed between the liner and the shell in the positions reported in Fig. 5.2.2. Sensors outputs have been read using a Fluke 175 multi-meter, configured with 1mV resolution, 0.15% accuracy and [-6V; +6V] range. The calibration curve has been extracted with reference pressures generated by a set of weights between 0.3 Kg and 2.7 Kg with steps of 0.5 Kg, using a flat part made of the same material of the boot liner as a soft interface material. Data have been acquired four times and average results have been processed to calculate a second order polynomial curve, which minimizes the RMS error between the known pressure and the sensor output.

Fig. 5.2.2 Pressure sensors positions in the front area of the boot

5.2.3 Discussion

The liner used was made of elastomeric foam with closed cell morphology, composed of cross-linked ethylene vinyl acetate (EVA) containing 14% of vinyl acetate. The choice of this type of material is related with the necessity to separate the effect of the thermal insulation due to the material from the effect of compression. For this reason, it has been chosen the most insulating material, which has been proven [Ch. 4.3.2] to maintain, in the same testing conditions, the toe temperature of approximately 3°C higher than other liners with open cell morphologies. The method used in the present tests has been validated in previous studies [14,15], which have shown its very good repeatability. In particular, tests have been performed twice, in two different days, observing a skin temperature difference between tests with the same configuration below 2°C after 60 minutes of test. The difference between the toe temperatures measured on the left and right foot during the same test (conducted with the same configuration on both feet) was below 0.5°C after 60 minutes of test. Values of the average temperatures drops from T0 to T60, measured using the wireless sensor and the thermo-camera, are reported in Table 5.2.1.

Liner	Average ΔT Sensor [°C]	Average ΔT Thermo-camera (toe) [°C]
Correct volume	2.99 ± 1.10	1.94 ± 1.72
Reduced volume	9.15 ± 1.35	8.53 ± 2.03

Table 5.2.1 Temperature decrease (ΔT) between t0’ and t60’, measured in the toe area using wireless sensors and thermo-imaging.

Results in Table 5.2.1 show that the use of a closed cell EVA foam caused, according to previous results [Ch. 4.3.2], a smaller temperature drop using the ski boot with the correct volume, since both the sensor and the thermo-camera indicate a temperature decrease in the toe area of less than 3°C in 60 minutes. In this case testers did not feel any pain and in a temperature comfort scale (scale from +4 = very hot to -4 = very cold, according to ISO 10551) have given a ranking of -1 ± 1 at the end of the tests. On the contrary, a significant temperature decrease has been observed with the reduced volume configuration and in this case the feeling of comfort was -4 for both testers at the end of the tests. The pain sensation at the end of the tests (according to ISO 10551, with a scale from 0 = no pain to 4 intolerable pain) was 3 ± 1. One of the tester declared that it was not possible to make a longer test in the testing conditions (-10°C). Results in Figure 5.2.3 show a much more consistent temperature decrease for the reduced volume pattern after 60' of test.

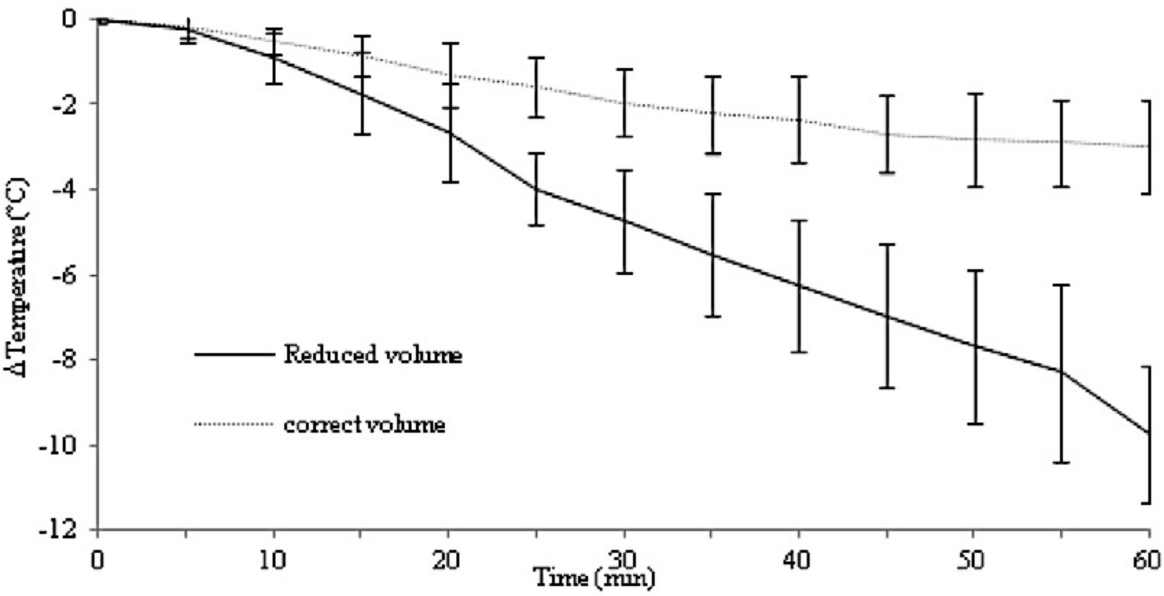

Fig 5.2.3 Temperature decrease during tests with normal and reduced volume

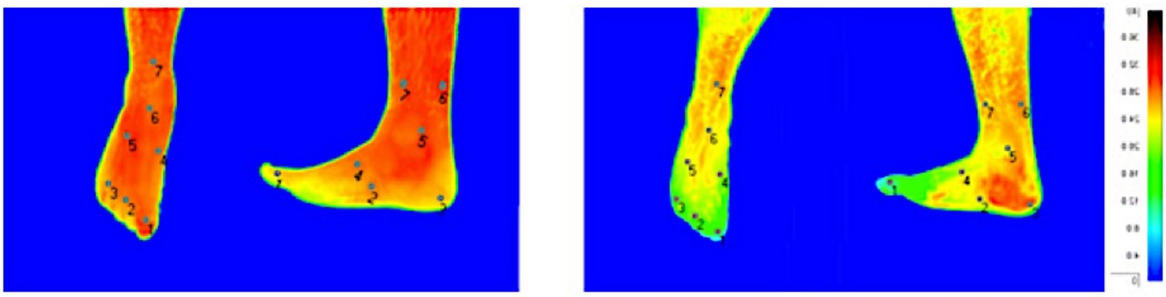

Fig 5.2.4 Tester 1, thermo-graphic images taken at the beginning (t0') and the end (t60') of the test

The comparison of the thermo-graphic images shown in Fig. 5.2.4, taken at the beginning (t0') and at the end of the test (t60') shows that, according to the literature [12,14], the coldest part is the toe area, in particular in the front and front-lateral parts.

An additional test has been performed decreasing the compression after 20 minutes by extracting the liner from the ski boot shell (keeping the foot inside the liner), results are shown in Fig. 5.2.5. In this case the skin temperature has shown a sudden increase of 5°C, reaching in less than 2 minutes, the same temperature of the foot inside the ski boot with the correct volume, which in the case of tester 1 has been similar to the starting temperature (less than 1°C decrease in 60 minutes). After 2 minutes the liner has been inserted again in the shell and the buckles have been closed again. The temperature started again to decrease with a similar trend with respect to the other foot that was not extracted form the shell. The same procedure has been performed a second time after 50 minutes obtaining the same trend with an even larger temperature increase when the compression has been diminished.

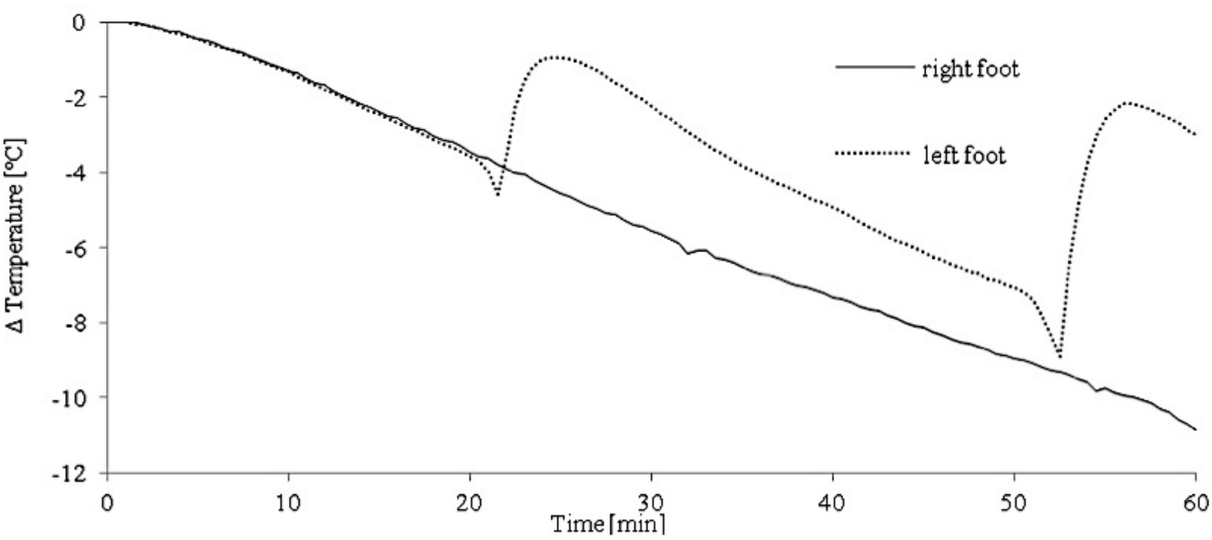

Fig 5.2.5 Tester 1, effect of extraction of the left foot (reduced volume), after 20' and 50' while the right foot was kept inside the ski boot

Compression has been measured using four pressure sensors positioned in the front part of the boot. Two sensors have been placed on the sides in correspondence with the maximum width of the boot and of the foot, while the other two sensors have place placed in the top part of the boot. In all cases the pressure with the reduced volume was higher compared to that measured with the correct volume configuration. The largest difference in pressure was observed in the lateral internal part (Tab. 5.2.2, point 1) for both testers. However, significant differences between the two testers have been observed also in the other parts, due to the different shape of the feet of the two testers. Nevertheless, the lowest pressure difference between the correct and reduced volumes was observed for both testers in point

3 (Tab. 5.2.2), which is in the zone, according to Fig. 5.2.3, with the lowest skin temperature.

Volume pattern	Pressure point 1 [Pa]	Pressure point 2 [Pa]	Pressure point 3 [Pa]	Pressure point 4 [Pa]
Tester 1, correct volume	2868 ± 1055	1131 ± 673	446 ± 429	395 ± 395
Tester 1, reduced volume	5642 ± 1800	5096 ± 1623	863 ± 790	2313 ± 911
Tester 2, correct volume	2168 ± 1944	401 ± 418	1705 ± 666	678 ± 669
Tester 2, reduced volume	7059 ± 743	1382 ± 836	2227 ± 958	2533 ± 580

Table 5.2.2 Pressure sensors output

5.2.4 Conclusions

The comparison between temperatures in the toe area of a ski boots with different internal volumes indicates a consistent temperature decrease (exceeding 9°C) after 60 minutes of test at -10°C with the reduced volume configuration, with a difference of more than 6°C with respect to the correct volume configuration. Moreover, a significant feeling of cold discomfort has been perceived for both testers using the reduced volume configuration. The comparison of these results in comparison with the insulation properties measured with liners made of different materials [Ch. 4.3.2], indicates that the volume reduction effect overcomes the effect of the insulating behaviour of the material used for the construction of the liner. Indeed, a 5.70 ± 1.98 °C decrease in 60 minutes was observed for the liner made of the less insulating material (open cell EVA) while a 9.15 ± 1.35 decrease was observed for the best insulating material (closed cell EVA) with the reduced internal volume.

The measure of the compression on skier's feet, performed using resistive pressure sensors, indicates for all points a significant increase of pressure using the reduced volume configuration compared to the correct volume set-up. The highest pressure and difference between the two configurations have been observed in the lateral internal part (Tab. 5.2.2, point 1), with maximum pressures around 5000-7000 Pa for both testers. These pressures did not cause pain to the skiers but significantly influenced the skin temperature. Inside the liner the heat transfer is ruled by the heat flow from the foot to the liner and from the liner to the shell, by conduction and convection [13]. The lower thickness of the liner caused by its compression should provide less insulation by thermal conduction. However, thermal convection is the main responsible of heat loss in winter shoes [13]. The air inside the cells of foamed materials with closed cell morphologies (as those used in the present study) is trapped and therefore is not able to move and transfer heat by convection. Moreover, the results of the pressure measurements indicate that the coldest part (point 3 in Table 5.2.2), was the one with the lowest pressure difference between the two configurations and therefore with the lower difference in thickness of the liner. For this reason, the lower temperature in the front part of the boot with the reduced volume configuration cannot be ascribed to the reduced thickness of the liner due to compression.

The importance of the effect of compression on blood circulation and therefore on thermal comfort has been proved by the sudden temperature increase when the compression has been eliminated extracting the liner from the shell after 20 and 50 minutes of test. This effect has also been confirmed by the subsequent temperature decrease when the liner was inserted again in the ski boot shell.

Further investigation could be made measuring blood circulation by eco-Doppler analysis.

In conclusion, the results obtained in the present study indicate the fundamental effect of compression on thermal comfort inside ski boots in cold environmental conditions.

5.3 Thermo-formable ski boots shell

5.3.1 Introduction

Ski boots are made of a rigid plastic outer shell that provides protection against impacts and transmit the forces from the skier to the ski and allows controlling the trajectory of the skier. Every foot has a different shape and pressure points could be present when the shape of the foot is inserted in a shell that is not anatomically compatible with its anatomy. For this reason, in he last few years, ski boot producers have developed new materials and methods to adapt the shape of the outer shell of the boot to the skier anatomy (thermo-formation) [17]. The thermoplastic properties of the polymers used for the construction of ski boot shells can be in principle used to modify the shape of the boot [18]; 80°C is the maximum temperature that can be used in this process in order to avoid burns on the skier's feet. It has to be said that thermoplastic polymers decrease their stiffness with temperature differently, depending on their chemical composition, melting temperature and crystallinity [17]. Moreover, all thermoplastic materials present a memory effect and when they are forced to a new shape, they tend to partially return to the initial form in a few days [18]. For this reason, new polymeric systems have been developed in order to obtain materials with optimized softening temperatures and low memory effect. In particular, Salomon Sports has patented [19] the use of a blend of polycaprolactone with polyurethane (called Custom Shell Plastic) in order to decrease the softening temperature of polyurethanes. The DMTA analysis reported in the patent [19] shows that the polymer blend displays a decreased softening point without significantly affecting the stiffness below 40°C. More recently, Fischer GmbH has patented [20] a blend of Nylon with a ionomer (polymer containing ionic groups), named Vacuum Plastic, to obtain a material that becomes very soft at 80°C and could be shaped around the skier's foot applying an external pressure with a dedicated apparatus that involves a sealed bag that produces a pressure from the outside of the ski boot. The difference between this method and the method previously reported by Salomon consists in the fact that the shell is adapted by external pressure on the skier's foot, while in the method patented by Salomon the force to deform the plastic is applied by the foot inside the boot.

It is well known [17] that the polymeric materials used for the construction of shells have a significant effect on the overall performance of ski boots [21]. Dynamical mechanical thermal analysis (DMTA) has been used to predict the flexural and rebound performance of ski boots [21] on the basis of the properties of the plastics employed in the construction of the boot.

A comparison between different plastic materials in the thermoforming process (in terms of deformation and memory effect) of ski boots has never been reported in the literature. For these reasons, in the following chapters have been reported the results of the thermo-formation process of the materials used for the production of thermo-formable ski boots, analysing the contribution of the chemical composition and of the thermo-mechanical properties on the thermo-formation process.

5.3.2 Materials and methods

Four different types of ski boots, which have been claimed by producers to be thermo-formable, have been tested. All boots were in size 26.5 Mondopoint. The plastic name given by the manufacturer, the external maximum width (called *Last* [17]) and the nominal flex index (nFI, the value of the flex index provided by the manufacturer and that has no correlation between different manufacturers [22]) are reported in Table 5.3.1. Boot 1 and 2 have the same internal and external dimensions since have been obtained by the same mould. As shown in Fig. 5.3.1, Boot 3 is composed by two parts with different hardness values, the stiffer on the lower section of the shell (yellow) and the softer in the upper section of the shell (white). The same type of liner was used in all tests. The liner used was not thermo-formable in the testing temperature range.

	Plastic name	External maximum width (mm)	nFI
Boot 1	TPU	109	120
Boot 2	PTL	109	100
Boot 3	Custom shell	110	120
Boot 4	Vacuum plastic	110	130

Table 5.3.1 Characteristics of the ski boots tested

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. Crystallinity and melting temperature have been measured by differential scanning calorimetry (DSC) with a Perkin Elmer DSC6, using a heating rate of 20°C/min from 0°C to 240°C. The Shore D hardness of materials has been measured according to ISO 878, at 23°C.

The softening of the plastic materials has been studied measuring, by DMTA analysis, the storage modulus (E’) in a temperature range from -120°C to 120°C. Tests have been performed with a Rheometrics dynamic mechanic thermal analyser DMTA-3E model with a single cantilever bending geometry on samples of 25x2x6 mm, using a strain of 0.1%, a frequency of 10 Hz and with a scan rate of 3°C/min. DMTA has been performed applying an oscillatory force to the sample and analysing the response as a function of temperature. Due to the visco-elastic nature of the polymers tested, a sinusoidal stress induces a sinusoidal strain consisting of an in-phase or elastic part (E’, storage modulus), and an out-of-phase or viscous part (E”, Loss modulus). The ratio between E” and E’, called tanδ, gives an indication of the damping behaviour of the material. DMTA analysis has also been used to predict ski boot performance (flex and rebound speed) measuring the storage modulus and tanδ of materials [21]. The change in shape of ski boots has been driven using a foot prosthesis (size 26.5 Mondopoint), modified with a deformation in the internal part as shown in Fig. 5.3.1. The prosthesis was inserted in the liner and thus in the ski boot, after heating the shell at 80°C for 10 minutes, according to the suggested thermo-formation time and temperature given by ski boot producers; a K-Tech Oven has been used, model TFHS-1CH, with a power output of 2300W. After the insertion, the prosthesis was kept in the boot at room temperature for 10 minutes and then extracted from the boot. After that, the width of the boot has been measured in 7 different points as described in Fig. 5.3.1, at the end of the process, after 24 hours and after 1 week, in order to determine the memory effect of the material.

Fig 5.3.1 Prosthesis with modified shape used in the tests and points in which the enlargement has been measured

5.3.2 Results

The chemical composition of plastics used for the ski boot shells was analyzed by FT-IR analysis (Fig. 5.3.2). The pattern of the peaks and in particular the presence of a signal at 1591 cm^{-1} indicates that boot 1 and boot 3 are mainly composed of a thermoplastic polyurethane (TPU) based on methylene diphenyl diisocyanate and polyether soft blocks [17]. Both parts (yellow and white) of boot 3 have identical FT-IR patterns, indicating that the two materials have the same chemical compositions. The FT-IR spectrum of boot 2 shows the presence of polyethylene and polypropylene in blend with a rubber containing styrene blocks. In particular, the presence of styrene-based units is evidenced by the presence of signals at 1643 and 698 cm^{-1} [17]. The presence of rubber in the polyolefine-based blend of boot 2 and of polyether blocks in polyurethanes are necessary to have good impact properties at low temperatures. No significant amounts of polycaprolactone were found in boot 3 by FT-IR analysis. Boot 4 presents signals at 1640 and 1542 cm^{-1} typical of polyamides and a peak at 1697 cm^{-1} ascribable to methacrylic acid ionomers. Thermal properties of polymers have been analyzed using DSC (Fig. 5.3.3). This type of analysis provides information on the chemical composition and on the temperature at which the polymer melts. The DSC curves in Figure 5.3.3 show that boot 4 presents two melting peaks, indicating the presence of a blend of two polymers. In particular, the low temperature peak at 69°C can be ascribed to the methacrylate-based ionomer, while the second melting peak at 220°C indicates that the polyamide that compose the polymer blend is based on Nylon 6. The high enthalpy of melting of the low-temperature endothermic peak indicates that the amount of ionomer is consistent in the plastic material used for boot 4. Ionomers are well known to decrease their viscosity in a very narrow temperature range due to the efficient break of the ionic interactions between polymer chains [20]. The plastic used for boot 2 presents a glass transition temperature at 50°C, which can be associated with the presence of styrenic groups in the elastomer used to increase the low temperature impact resistance of polyolefines.

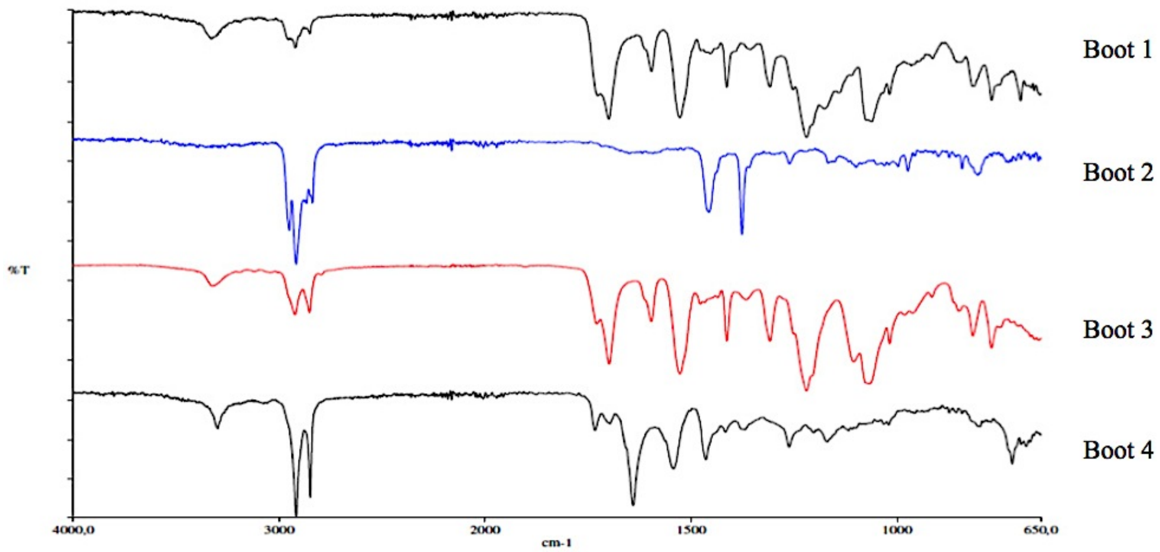

Fig 5.3.2 FT-IR of the plastics used for the tested boots.

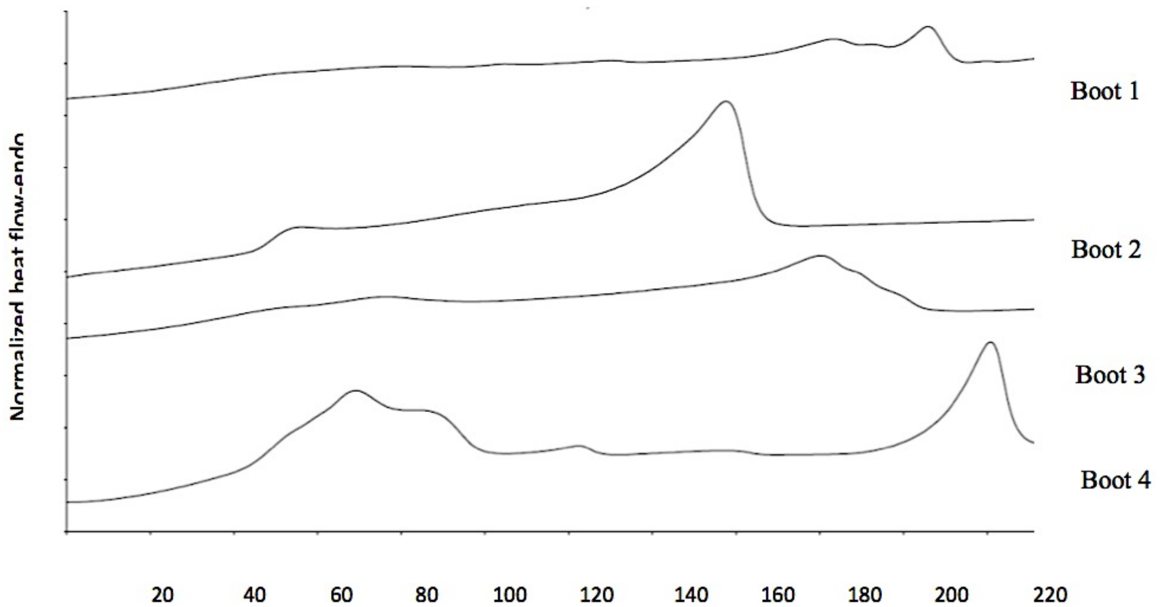

Fig 5.3.3 Differential Scanning Calorimetry, first heating scan at 20°C/min.

The DMTA analysis, which results are shown in Tab. 5.3.2, indicates that all plastics used have similar modulus in the temperature range in which skiing is performed (from -20°C to 20°C) but with a significant difference at 80°C for the plastic used for boot 4, which has a more consistent reduction in stiffness compared to the other materials. The modulus at 0°C and at 80°C are reported in Table 5.3.2. The melting temperatures and melting enthalpies (ΔHm) are reported in Table 5.3.3. Results in Table 5.3.2 and Figure 5.3.4 indicate that at the thermo-formation temperature (80°C), the materials used for Boot 1-3 have similar stiffness while the plastic used for Boot 4 has a modulus that is 25% lower than the other materials. The DSC analysis indicates that polyurethane and polyamides have the highest melting temperatures. The two materials used for boot 3 (that have the same endothermic peaks temperatures and intensities) present a small melting peak at 76°C (with a 64H of 1.5 J/g), which does not significantly affect the behaviour of the material in terms of stiffness decrease at higher temperatures. On the contrary, the material used for boot 4 has a large endothermic transition at 69°C that has a significant effect in decreasing the stiffness of the material above this temperature. The values of the tanδ measured at 0°C are similar for all boots.

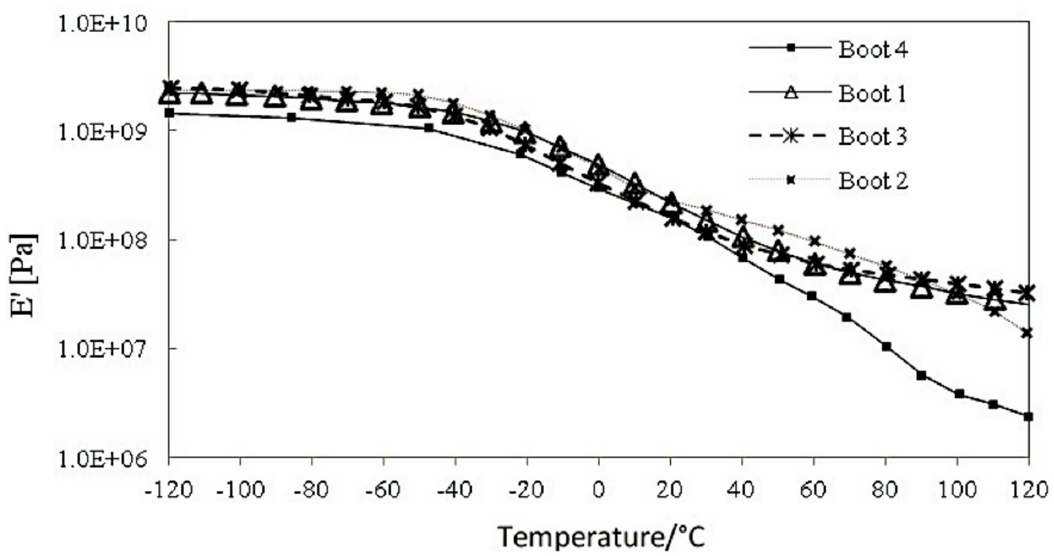

Fig 5.3.4 Storage modulus temperature dependence of the boots' plastics (for boot 3 the white softer part is reported)

Liner	Material	E' at 0°C (MPa)	E' at 80°C (MPa)	Hardness at 23°C (shore D)	Tanδ at 0°C
Boot 1	Polyurethane	485	45	59	0.137
Boot 2	Polyolefin	452	44	53	0.129
Boot 3	Polyurethane	380/470	47/49	55/60	0.162
Boot 4	Nylon/ionomer	370	11	58	0.119

Table 5.3.2 DMTA results

Liner	Tm1 (°C)	ΔH1 (J/g)	Tm2 (°C)	ΔH2 (J/g)
Boot 1	206	9.8	-	-
Boot 2	158	26.1	-	-
Boot 3	76	1.5	180	21.3
Boot 4	69	27.3	221	16.7

Table 5.3.3 DSC results

The enlargements measured after heating the boots for 10 minutes at 80°C are reported in Table 5.3.4 along with the decrease in width of the boots, due to memory effect, after 24 hours and 1 week. Results indicate that all the boots present a significant modification. In particular, a deformation of at least 9 mm was present in all cases in correspondence of the maximum of the deformation in the foot prosthesis (point 7 in Fig. 5.3.1). Results also indicates that boot 4 has had the largest deformation. Nevertheless, the small differences with the other boots indicates that also polyurethane and polyolefines based polymers are suitable for the thermo-formation process as performed in this study. Boot 4 also presents the lowest memory effect compared to the other boots. Boot 3, which is the only one composed of two different stiffness materials, presents the second highest deformation in point 7 and the lowest average deformation. This result indicates that the softer part, where point 7 is located, is more thermo- formable with respect to the stiffer part on lower shell, where other measurements points are located. The softer part also suffers of a more consistent memory effect compared to the hardest part.

Liner	Point 7 after thermo-formation [mm]	Average thermo-formation [mm]	Average recover (24 H)	Average recover (7 days)	Point 7 Recovery (7 days)
Boot 1	9.0	3.0	23%	38%	16%
Boot 2	9.9	3.4	27%	33%	17%
Boot 3	11.4	2.4	30%	33%	26%
Boot 4	11.8	3.4	24%	28%	12%

Table 5.3.4 Enlargement after the end of the thermo-formation process and recovering ratio to the initial shape

Effect of materials

Results have demonstrated that boot 4 presents the lowest memory effect compared to the other boots tested. The memory effect is due to the fact that the polymer chains tend to achieve a random coil conformation that is thermodynamically more stable due to entropic factors [23]. For this reason, the polymer chains that are stretched as a cause of the applied force by the foot prosthesis, tend to return to the random coil conformation (and therefore to the initial shape) when the applied force is released. However, if the temperature is high enough to allow sufficient chain mobility, the polymer chains tend not only to stretch when the force is applied but also to slide one respect to the others and therefore a permanent deformation is achieved. Nevertheless, they partially tends to return to the initial position due to the fact that they must return to the random coil conformation even if they have slide one respect to the others. The reason why the memory process is quite slow is due to the reduced chain mobility at low temperature.

Significant care must be taken in order to don’t overheat the plastic and to maintain a firm stance during the cooling process. Indeed, the company that produces Boot 3 suggests the use of a particular apparatus that stops the movement of the skier during the cooling. The reason of the use of this very thermo-formable material lies in the process used for its thermo-formation that consists in applying a pressure from the outside by means of a pressure bag [24]. In this case, if a more stiff material is used the pressure needed to deform the plastic is too high to be used in a safe and economical way. For this reason, this type of material and process (named Vacuum process) is only used by less than 1% of the total ski boot market. Boot 2 is made of a polyolefine toughened with a styrenic rubber [25]. This type of material is not used in ski boots for racers and advanced skiers due to the lower performances in terms of flex and rebound connected with the visco-elastic properties of this material [21]. For this reason, it is mainly used in boots for junior and beginner skiers. Moreover, the lower market of ski boots made of polyolefines is connected with their low resistance to scratch and abrasion with respect to TPU materials [11]. On the contrary, the most used material for ski boots is TPU that provides the best performances and durability [11].

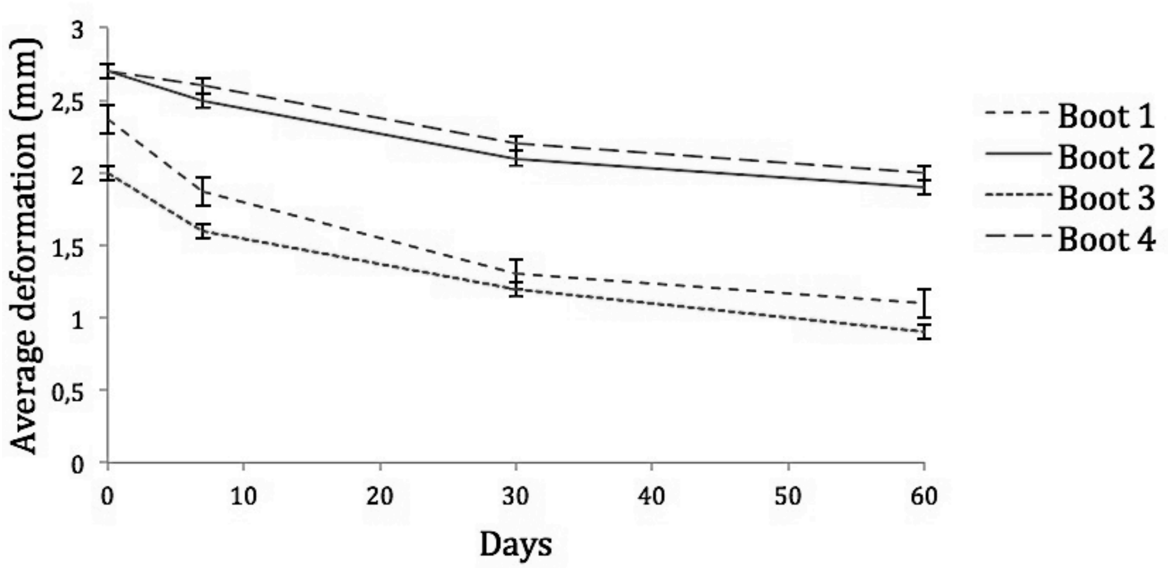

Figure 5.3.5 initial deformation and memory effect of boots made with different polymeric materials (10 minutes heating and 20 minutes cooling at room temperature).

Effect of heating time

The effect of the heating procedure has been analysed performing 4 tests with different heating times ranging from 4 to 16 minutes and cooling for 20 minutes at room temperature. Results in Fig. 5.3.6 show that the heating time has a significant effect on the initial deformation for times up-to 12 minutes. After 12 minutes no significant differences have been observed. The memory effect is similar since all the curves are parallel. This means that the main effect of the heating time is connected with the softening of the plastic and once the deformation is achieved the memory effect is connected with the molecular motions and material's relaxation. The oven has need 4 minutes to reach a stable temperature above 100°C. This means that the external temperature of the plastic is above 80°C only after 5 minutes. The plastic material of the shell is 6 mm thick and therefore the heat needs a certain time to reach the internal part. Indeed, the measure of the temperature inside the shell has shown that after 10 minutes the temperature has been still below 60°C. Therefore, at this temperature the material is still too stiff and the chain mobility not enough to allow a permanent deformation of the plastic. This low temperature in the internal part of the boot is due to the shape of the oven that does not allow a proper heating of the internal part by air convection. Indeed, the internal temperature closing the boot upper opening with a foamed polystyrene cover has been measured, observing a temperature that has been less than 2°C different form that measure without the closing cap. This is a clear indication that the heat transfer is almost completely due to diffusion inside the plastic from the outside to the inside of the shell and that convection has not a significant effect on heat transfer in this heating system. All the ovens commercially available for ski boots thermo-formation are made with similar shape to the one used in the present study, that does not allow to the hot air to reach the internal part of the boot since the boot opening is positioned on the upper part of the oven and the fan is positioned in the back part. The shape of the oven does not allow rotating the boot in order to have the boot opening close to the fan.

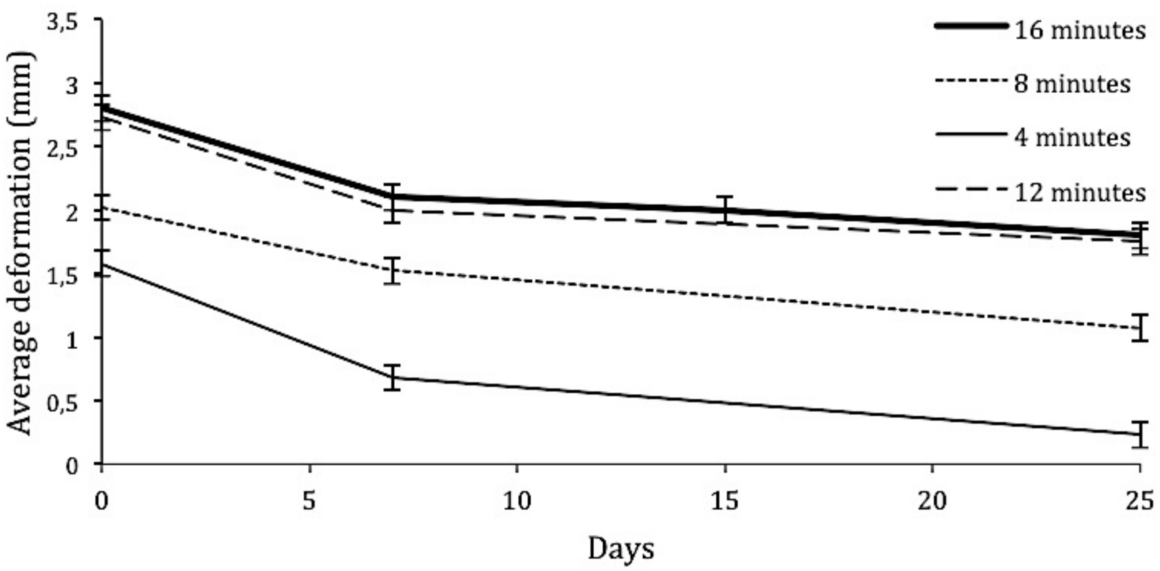

Figure 5.3.6 Effect of heating time on thermo-formation

Effect of cooling procedure

It is a common practice among boot fitter to quench the boot after heating and modifying the shape, putting it in cold water or ice. Moreover, some ski boot producer provides cooling pads to cool down the shell after the foot is inserted. It is well know that polymer chain mobility is affected by temperature and that rapid quenching is able to lock the chains in a disordered position. For this reason, different cooling procedures have been tested in order to assess the temperature effect in the cooling stage with the foot inserted. In all cases a 12 minutes heating has been used and the foot prosthesis has been maintained inside the boot for 20 minutes before taking the prosthesis out and measuring the deformation. Results in Fig. 5.3.7 show that the best results in terms of initial deformation have been obtained cooling at ambient temperature while the worst results occurred using ice as cooling agent, indicating that the procedure suggested by boot-fitters and some ski boot producers could offer a negative effect on the final thermo-formation [19,20]. The reason of this behaviour can be ascribed to the reduced polymer chain mobility at lower temperature. Indeed, in order to achieve a permanent deformation, polymer chains must have enough chain mobility to slide one respect to the others. If the temperature is lowered, the chain mobility is reduced and therefore the chains are not able to slide and give rise to a permanent deformation. The most pronounced effect of ice is due to the fact that liquid nitrogen (that is much colder than ice) tends to evaporate, creating an insulating gas layer on the surface and therefore the cooling effect is less efficient with respect to that observed using ice.

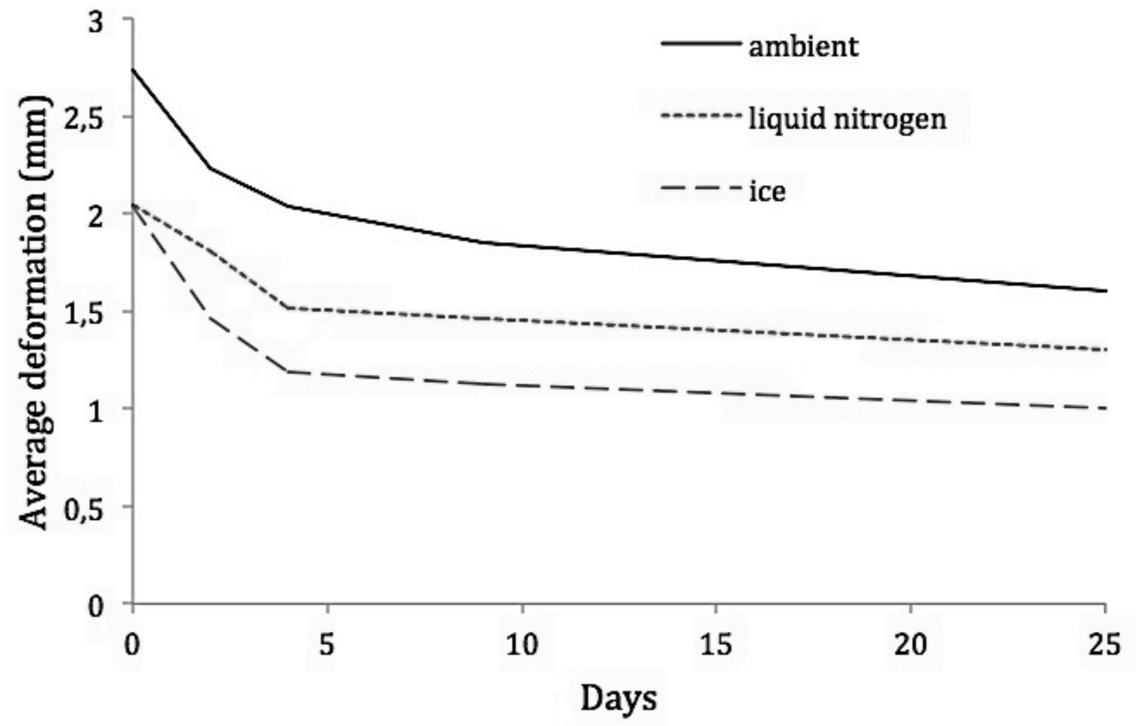

Figure 5.3.7 Effect of different cooling procedure on thermo-formation

Properties of the boot and plastic after thermo-formation

It is well know that thermal annealing can have a significant effect on crystallinity and therefore on the thermo-mechanical properties of thermoplastic polymers [23]. For this reason, the crystallinity of the TPU material used in Boot 1 has been measured before and after the thermo-formation process, with 12 minutes of heating and cooling at ambient temperature and using ice. Results in Fig. 5.3.8 show no significant differences after the thermo-formation process in terms of melting temperature and heat of fusion (ΔHm) of the main melting peak. However, a small secondary peak is present at 130-140°C after thermo-formation, indicating the formation of a second crystalline phase upon annealing.

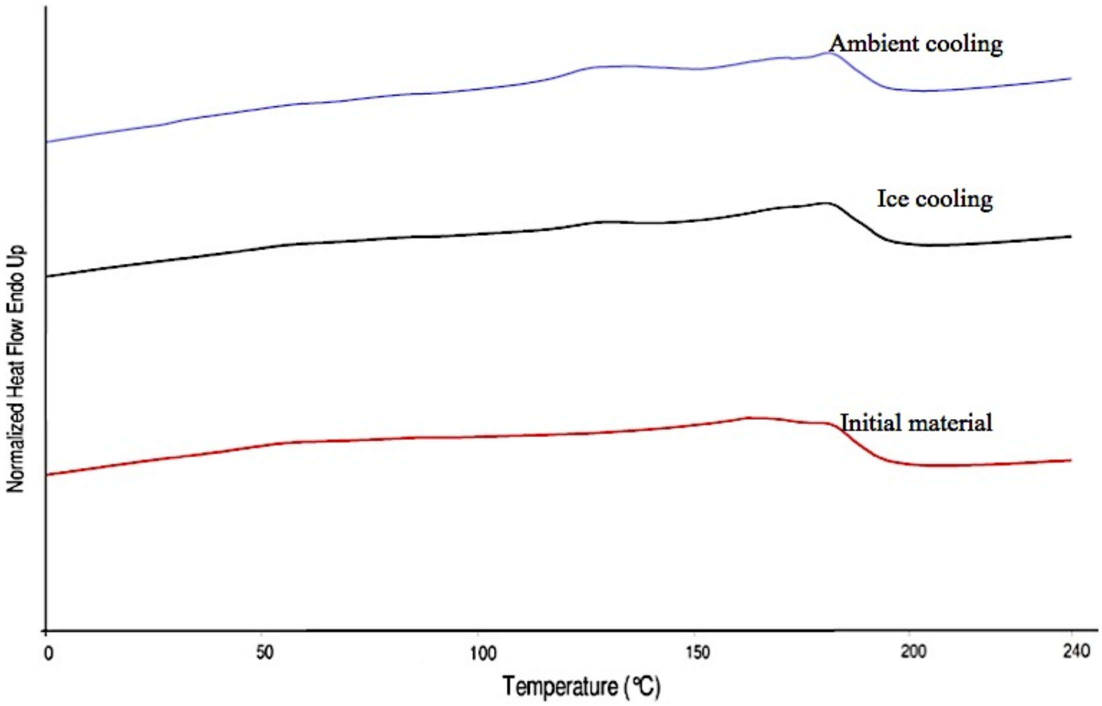

Fig. 5.3.8 DSC analysis (first heating scan) of TPU before and after the thermo-formation

Results of the measure of the flexural stiffness of Boot 1 before and after thermo-formation are shown in Fig. 5.3.9: there are no changes in performances after the thermo-formation process, indicating that the thermal treatment does not affect the mechanical properties of the material.

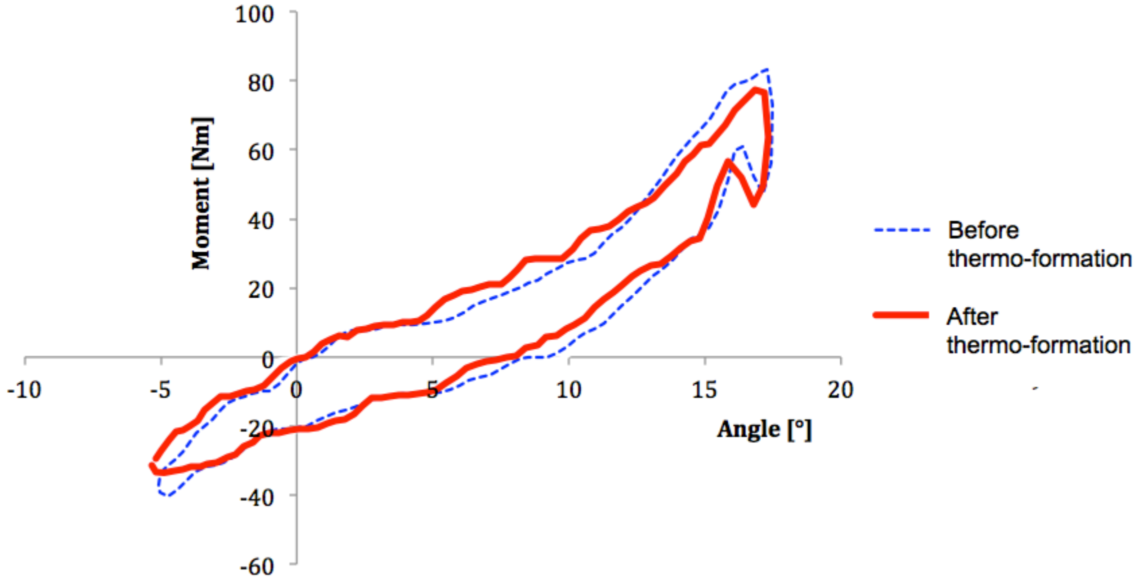

Figure 5.3.9 Flex measurements at -2°C of a ski boot before and after the thermo-formation process

5.3.2 Discussion and Conclusions

Boots tested in this chapter have been chosen from different manufacturers with the aim to gather products with similar width in the largest part of the boot and similar nominal flex index (even if this value has no quantitative significance [22]). FT-IR analysis has defined the exact chemical composition of polymers, while DSC analysis has defined that the plastic of boot 4 presents a melting peak at 69°C that decrease the stiffness of the material at higher temperatures. All the other materials have their main melting peak above 150°C. For these reasons, material used for boot 4 has a more significant decrease of modulus form 0°C to 80°C and present a modulus at 80°C that is 25% lower with respect to those of the plastics used for boots 1-3. This behaviour can be ascribed to the chemical composition of boot 4 that is a blend of a ionomer (that becomes very soft at temperatures above 70°C) and of a polyamide with a high melting temperature (220°C). Therefore, the material decreases its stiffness above 70°C, but retains a sufficient dimensional stability due to the presence of the polyamide part. Boots 1 and 3, based on TPU, have the highest melting temperatures and the highest stiffness at 120°C. This indicates that, if temperature exceeds the correct thermo-formation temperature due to malfunctions of the heating systems, these boots suffer of the lowest probability to be damaged due to the partial or complete melting of the plastics. Moreover, they should suffer of less deformation in the thicker zones of the boot, especially those in contact with the binding, which must respect specific dimensions according to ISO 5355. All the boots have similar storage modulus in the range from -20°C and +20°C and similar tanδ values at 0°C and therefore, according to the literature [21], similar flexural stiffness and rebound behaviour of the boots are expected at those temperatures.

Results of the thermo-formation process conducted using a modified prosthesis indicate that the boot made of the material with the lower modulus at 80°C (boot 4) is the one thet can achieve the largest deformation after the process. Nevertheless, also the other three boots present significant shape modifications, in particular in the point of maximum width of the prosthesis (point 7). Results have also shown that in a thermo-formation process conducted only using the pressure exerted by the foot inside the boot, also materials like those used in boots 1-3 can produce significant shape modifications. On the contrary, in a process based on the application of an external force it is necessary to obtain a more significant stiffness reduction at 80°C due to the lower pressure of the process. However, the material used for boot 4, due to its low stiffness at 80°C could suffer of deformation also of the parts in contact with the binding. The comparison of the two parts with different stiffness of boot 3 indicates that softer materials present a more significant shape modification after the process. However, softer parts also present a more consistent memory effect.

It has been also demonstrated that thermo-formation process in terms of initial deformation and memory effect is strongly influenced by the thermoplastic material used, heating time, and cooling procedure. In particular, it has been found that the heating time with a conventional oven used for the thermo-formation must be of at least 12 minutes and that a cooling at room temperature for 20 minutes must be preferred with respect to other rapid cooling procedures using ice or liquid nitrogen.

It has also been demonstrated that the thermo-formation process does not affect the performances of the ski boot. Finally, it must to be said that the method can be applied not only to plastic shells for ski boots but also for other winter sports equipment (e.g. cross-country skiing, ice-skating, ice-climbing, high altitude climbing, snowboarding etc.) and summer sports (e.g. inline skating).

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6 Ski boot soles: the use of fiberglass inserts to increase safety and grip performance

Sometimes, sport equipment design should accomplish specific tasks that can be related not only to pure performance but also to user's safety, this is the case of ski boots soles. Ski boots soles for alpine skiing are often made of the same plastic material of the boot shell, thus ensuring to meet the mechanical standards to fit the bindings, but offering very poor traction on wet and icy surfaces. Since ski boots, apart from telemark boots, which have a plastic bellow in the front part of the foot, don't allow the feet to flex, it follows that become really difficult to make soles to work properly. Indeed, pressure can only be applied into little sole surface and for a short time, hence achieving poor grip performance especially on the most common wet and icy surfaces that characterize ski areas. Nevertheless, also indoors wet floors, such as huts, restaurants and ski shops ones, represent a very common scenario in which slips and falls can occur.

6.1 Introduction

Ski boot sole 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 [1]. Several ski boot manufacturers have started to produce soles with softer inserts with respect to the plastic used for the main body of the boot [2], with the aim to improve the anti-slip properties. In particular, soles used for ski touring and freeride skiing boots are completely or partially made of thermoplastic elastomers or rubber, in order to improve the grip when hiking and climbing [1].

A significant work has been performed in recent years in order to understand and model the friction behaviour of elastomers on wet and icy surfaces. For example, Gronqvist et al [3] have tested 49 types of winter footwear on dry and wet ice, determining the most important parameters that influence grip performance. From their evaluation, material type, hardness and cleat design have been defined as the most important parameters for grip on dry ice. On the other hand, on wet ice, only the tread design has an influence on the friction properties. The high slipperiness of ice has been also analyzed by Gao et al [4], who have measured the effect of sole abrasive wear on the coefficient of friction on dry and melting ice.

Factors that influence the coefficient of friction (COF) of the materials used for the production of soles for ski boots on wet floors and icy surfaces have been also investigated [5]. Results have pointed out that material stiffness and roughness used for the sole have a fundamental effect on grip performances [5]. In particular, results obtained have shown that softer materials provide more grip with respect to harder materials and that the surface roughness has a negative effect on friction, since the materials with the highest Sa (arithmetic mean height) and with the lowest number of contact points with the surface have the lowest COF. The grip measurement on inclined wet surfaces (according to DIN 51130-R ramp test) has also shown a relation between hardness and grip, the softer materials having the higher grip [5]. The performance ranking of different materials has been the same for the COF and for the slip angle ramp tests, indicating that COF can be used as a parameter for the choice of the optimal material to be used for ski boots soles. The comparison of different sole treads indicates that the best results in terms of anti-slip behaviour can be obtained reaching the wider contact area with floor. However, even the most performing thermoplastic polymer or rubber tested so far (complying with ISO 5355 standard for ski boots) did not possess a coefficient of friction on icy surfaces above 0.15 and therefore the soles actually present on the market do not posses an sufficient grip on those surfaces.

For this reason, in the last few years, researchers and producers of boots for winter sports have started to study the application of hybrid soles containing components with improved friction on icy surfaces. Recently, Rizvi et al [6] have reported a study on polyurethane/glass fibre composites, finding a significantly increased COF on ice for the materials containing these fibres. Treksta™ has recently developed, using a proprietary patented technology named Ice-Lock™, soles for shoes for outdoor sports with parts made of a composite materials based on a rubber matrix containing aligned glass fibres that are perpendicular to the base of the sole. According to Treksta™, the purpose of the rigid glass fibres is to increase the mechanical grip on ice, while the creation of a micro-structured surface should have an effect on grip performances on wet surfaces, since it should modify the water repellence of the surface. However, no scientific data have ever been reported and no scientific study has ever investigated the mechanism of action of this type of rubber/glass fibres composite. For this reason, this chapter contains a study in order to assess the performances of this type of composite material and to understand the fibres behaviour in the rubber matrix. Moreover, a ski boot sole complying with ISO 5355 norm has been prepared, containing parts made of rubber/glass fibres composite, comparing its grip performances with those of a standard rubber sole.

6.2 Materials and Methods

The rubber/glass fibres composite (Material 1) and the rubber material used as matrix for the composite (Material 2) have been kindly provided by Treksta™. Indeed, Material 2 is made of the same rubber of Material 1 without the glass fibres.

Soles have been produced by over-injection moulding of polyurethane on the rubber and rubber/glass fibres composite and they all meet the ISO 5355 norm. Only the heel soles parts have been tested since this is the most flat and regular compared to the front part due to the constraints of ISO 5355 norm. In this way it has been possible to apply a more distributed pressure on the entire surface of the sole. A sole (Sole 3) containing two inserts of 3.7 cm^2 each of Material 1, the rubber/glass fibre composite, has been tested and compared with an identical sole without the composite inserts in Material 1 (Sole 2). A sole made of thermoplastic polyurethane (TPU) has also been used as a reference (Sole 1).

Figure 6.2.1 Soles tested; rubber/fibre composite insert in Sole 3.

The chemical composition of the soles has been determined using Fourier Transform Infrared Analysis (FTIR), performed directly on the surface of the materials using a Perkin Elmer Spectrum One instrument equipped with an Attenuated Total Reflectance (ATR) detector. The glass fibre content has been measured by thermo-gravimetric analysis (TGA) using a Perkin Elmer TGA 7 instrument with a scan rate of 20°C min and an air flux of 30 mL/min.
Shore D hardness of the materials and of test surface (Surface 1) has been measured according to ISO 878 norm at 23°C.
Morphology of the rubber/glass fibre composites has been analysed by Scanning Electron Microscopy (SEM), using a ZEISS Model EVO 50 EP working with a pressure of 90 Pa in the chamber. Observations of the surfaces have been taken without any particular specimen preparation. Micrographs have been taken with a backscattered electrons detector that permits to distinguish the fibres (white) from the darker plastic substrate. Fibres composition has been analysed using an EDS detector (OXFORD INCA 350). The height of fibres from the rubber surface has been measured using a Hirox model 7700 multifocal digital microscope.
The wettability of the soles has been evaluated by measuring the static contact angle with a DSA30S instrument, using water drop phase.
The coefficient of friction has been measured on ice and on hard surface (Surface 1) using an Instron 1011 dynamometer connected to the sole with a screw by steel cable. A pulley system was used in order to drag soles horizontally with respect to the testing surface. A weight of 15 kg evenly distributed on specimens (surface 145 cm^2). Experiments have been repeated 5 times and averaged. Experiments have also been performed on a solid surface that mimics the surface of mountain huts floor and rental shops (Surface 1). The temperature on the ice surface has been measured using a digital infrared thermometer. Tests have been conducted on ice at -10°C and at -1°C. In the second case 10 mL of water have been added uniformly on the ice surface in order to obtain a wet surface. A maximum difference of 1°C has been measured during the duration of the test. After each test the ice block has been cooled in a refrigerator at the set temperature for at least 1 hour before the next test.

6.3 Results and discussion

Chemical composition (confirmed by FTIR analysis) and hardness of the different parts of the soles are reported in Table 6.3.1 and 6.3.2.

The FTIR analysis have confirmed that the composition of the dark and grey parts of the composite (Material 1) have the same chemical composition (vulcanized polyisoprene rubber) and the different colouring is due only to marketing and aesthetic reasons. Hardness measurements of the rubber parts of Sole 2 and 3 indicates that they have similar Shore D hardness, while Sole 1 is harder. Soles 2 and 3 also have an internal part (orange in Fig. 6.2.1) made of a rigid (59 Shore D) TPU material that is necessary to achieve the correct release of the boot from the binding in case of fall, according to ISO 5355 norm. The comparison of Material 1 with Material 2 shows that the presence of the glass fibres does not have a significant effect on the hardness. Moreover, results show that Material 1 and 2 are softer compared to the main rubber material used for Soles 2 and 3.

Material	Chemical Composition	Shore D hardness
Material 1 (black part)	Rubber/Glass Fibre	19
Material 1 (grey part)	Rubber/Glass Fibre	20
Material 2	Rubber	21

Table 6.3.1 Chemical composition and hardness of materials

Material	Chemical Composition	Shore D hardness
Sole 1	TPU	38
Sole 2	Rubber/TPU	33/59
Sole 3	Rubber/TPU	30/59

Table 6.3.2 Chemical composition and hardness of the specimens (soles)

TGA analysis measurements, have shown the difference between the residue weight above 800 °C for Materials 1 and 2, allowing to determine that the composite Material 1 has approximately 4 wt% of glass fibres content.

Composite surface morphology has been evaluated by Scanning Electron Microscopy (SEM) with backscattered electrons detector, able to perform an easier imaging of the glass fibres thanks to the presence of silicon atoms (bright contrast), with respect to the purely hydrocarbon plastic matrix (dark contrast), as shown in Fig. 6.3.1.

SEM analysis with EDS detector has confirmed that fibres inserted in the rubber matrix have a purely SiO2 composition. SEM micrographs in Fig. 6.3.1 indicate that glass fibres have an average diameter of approximately 10 μm with an average distance between fibres of 150 μm. Micrographs have also shown that part of the fibres are bended on the surface and, probably due to the pull out of the fibres during the cutting process, some voids are present. Multifocal analysis has shown that fibres protrude from the surface of less than 10 μm.

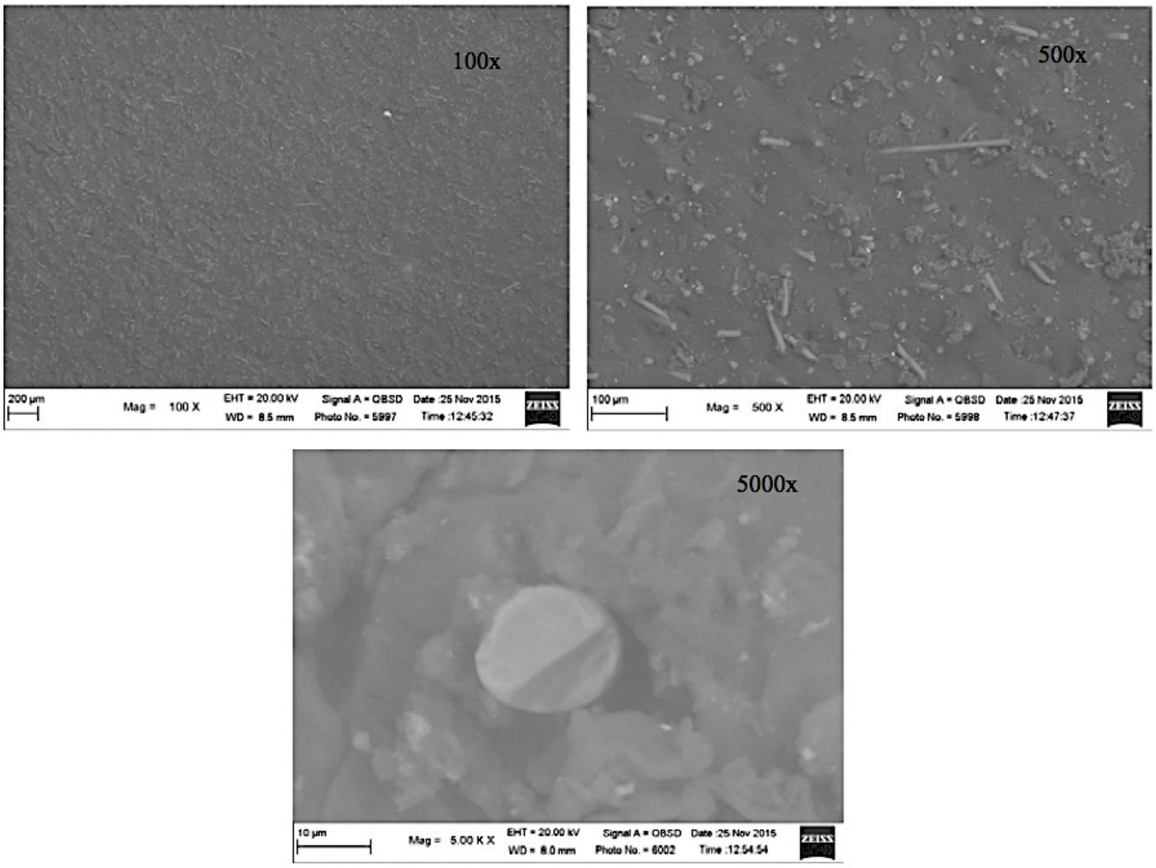

Figure 6.3.1 SEM analysis of the surface of the rubber/glass fibber composite (Material 1) at 100X, 500X and 1000X magnification

The effect of glass fibres on water repellence properties has been evaluated by contact angle analysis. Indeed, studies on the gliding performances of skis [7] have shown that the formation of a water layer below the ski surface, significantly affects the friction of plastic materials on snow and ice. The results of contact angle measurements in Tab. 6.3.3 and Fig. 6.3.2, demonstrate that the composite material has a higher contact angle (and therefore more water repellence) compared to the rubber material used for the composite matrix.

Material	Contact Angle*
Material 1 (black part)	89 ± 5
Material 1 (grey part)	87 ± 5
Material 2	68 ± 3

Table 6.3.3 Water contact angles (*drop volume 4μL)

Wettability is a very important property of materials, especially when gliding or traction performance involves surface contact with liquid or icy water layers. Wettability is partially due to an intrinsic materials property, depending on their specific surface chemistry, but it can be easily manipulated by tailoring the surface roughness.

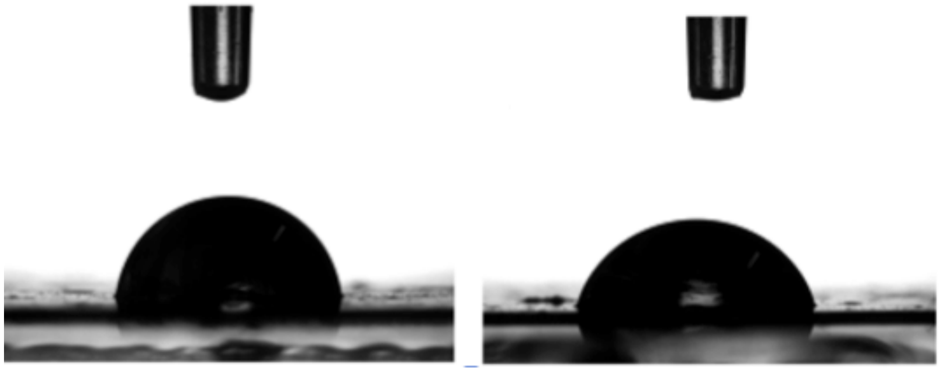

Fig. 6.3.2 Contact angle: rubber with glass fibres (left) and without glass fibres (right)

The wettability of smooth hydrophilic surfaces is improved by roughening them; the contrary effect is observed with smooth hydrophobic surfaces since by roughening, the contact angle will increase [8]. It has been observed that the polyolefinic nature of rubber material induces its mainly dispersive behaviour, giving rise to quite hydrophobic surfaces. The insertion of glass fibres in the Rubber matrix, notwithstanding the polar character of SiO_2 that should induce a wettability increase, generates a morphological effect of roughening that overcomes surface chemistry, and gives rise to a general increase in hydrophobicity. The purely morphological effect has further been confirmed by measuring the contact angle with water drops of different volume, ranging from 1 μL to 4μL; no significant differences were recorder in the different cases, confirming that the reported contact angle values are meaningful and can be interpreted because the drops used were sufficiently large compared with the scale of roughness [9].

Previous work [5] has shown that the COF value can be used to rank grip performances of different materials used for ski boots soles, in real conditions on wet surfaces. For this reason, the COF on icy surfaces and on a surface that can mimic the internal floor of alpine huts (Surface 1), where slip and falls can also occur, has been measured (Fig. 6.3.3a, Fig. 6.3.3b). Tests on Surface 1 (Shore D hardness of 73) have been conducted at 23°C while those on ice has been conducted at -10°C on dry ice and at -1°C on wet ice.

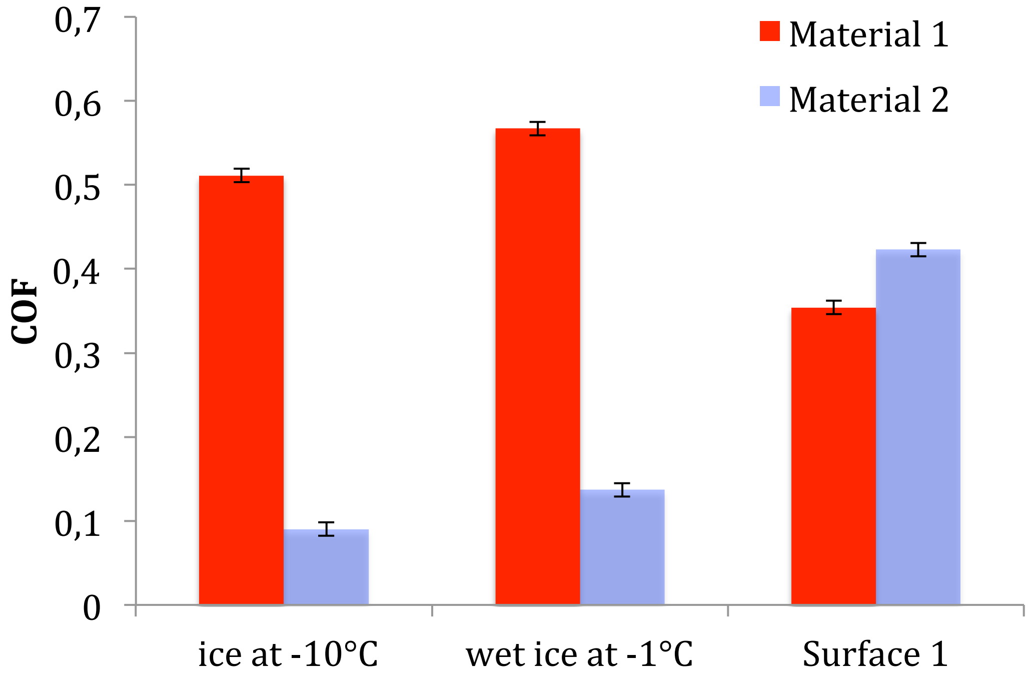

Figure 6.3.3a COF of materials on ice and on Surface 1

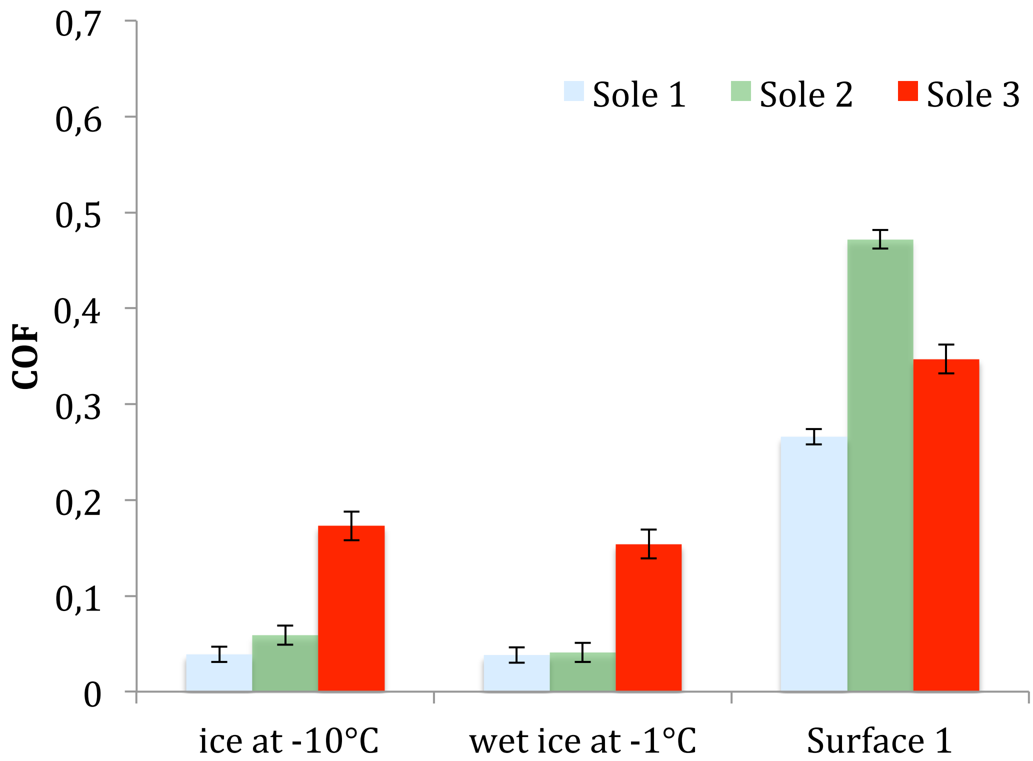

Figure 6.3.3b COF of soles on ice and on Surface 1

In previous studies [5], it hasn't been observed significant differences between several elastomeric materials on ice, with very low COF (below 0.15) in all cases. On the contrary, in this case Material 1 (containing glass fibers) has a COF more than 5 times higher than Material 2, which is made of the same rubber material without the glass fibers functionalization. These results clearly indicate a very positive effect of the glass fibres on friction performance on icy surfaces. This increased friction is due to the mechanical grip of rigid glass fibres on the ice surface. Indeed, glass fibres have an elastic modulus between 60 and 90 GPa [10] while the rubber matrix has an elastic modulus below 100 MPA [11], even at low temperatures (-20°C). Results in Figure 6.3.3 also show that the COF at -1°C on wet ice for Material 1 (with glass fibres) is significantly higher compared to that measured for Material 2. In addition to this, the value measured for Material 1 at -1°C on wet ice is higher compared to the value obtained on dry ice at -10°C for the same material. This behaviour can be ascribed to the fact that fibres are able to have a contact with the ice surface even if a water layer is formed, since they protrude of a few microns from the surface of the rubber (Fig. 6.3.4).

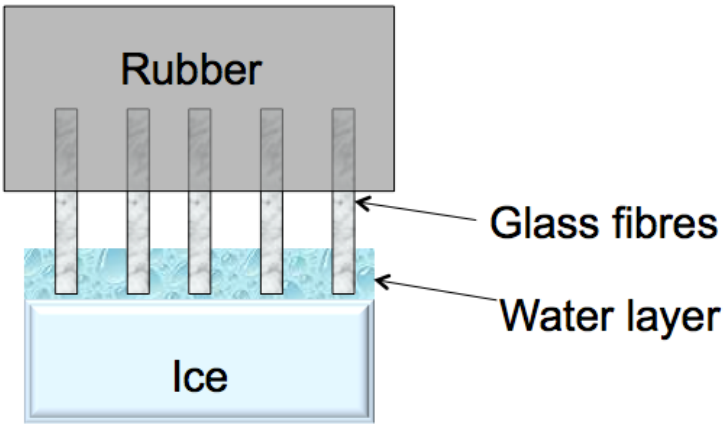

Fig. 6.3.4 Fibres are in contact with the ice surface even if a water layer is formed

Moreover, fibres mechanical grip is more efficient due to the lower hardness of the ice at -1°C with respect to the hardness at -10°C. The higher hydrophobicity of Material 1 compared to Material 2, as measured by contact angle analysis, also affects the grip performances. Indeed, it is well known that friction on ice is ruled by the formation of a water layer between the ice and the material [7]. The higher contact angle and hydrophobicity of Material 1 with respect to Material 2, allows a more efficient water removal below the surface, therefore glass fibres of Material 1, that protrude from the surface, are able to have a more efficient contact with the ice surface.

The comparison of the different soles in Figure 6.3.3 shows that the COF on icy surfaces of Sole 3 (that has two inserts containing Material 1, the rubber/glass fibres composite) is at least 3 times higher with respect to that of the sole that dos not contain the insert in Material 1 (Sole 2). This result indicates again the positive effect of the fibres on icy surfaces friction. The smaller COF value of Sole 1 can be ascribed, according to previous results [5], to the higher stiffness of the material used for that sole.

Results obtained on Surface 1 do not follow the same trend observed on icy surfaces. In particular, Material 1 has a lower COF compared to Material 2, indicating that glass fibres have a negative effect in this case. The reason of this behaviour can be ascribed to the fact that for Material 1 mainly the glass fibres are touching the surface and therefore there are less contact points between material and surface. Indeed, it has been previously found [5] that the surface roughness has a significant effect on the COF; in particular, materials with higher roughness and less contact points have less grip compared to materials with more contact points and less roughness. The comparison of Sole 2 with Sole 3 on Surface 1 is in agreement with what observed on the Materials 1 and 2. The lower COF of Sole 1 can be again ascribed to the higher stiffness of the material used for Sole 1 compared to materials used for the other two soles.

Another comparison has possible between the above mentioned glass fibres (oriented) and some randomly aligned ones (Fig. 6.3.5). Morphological differences among the two are highlighted in Tab 6.3.4.

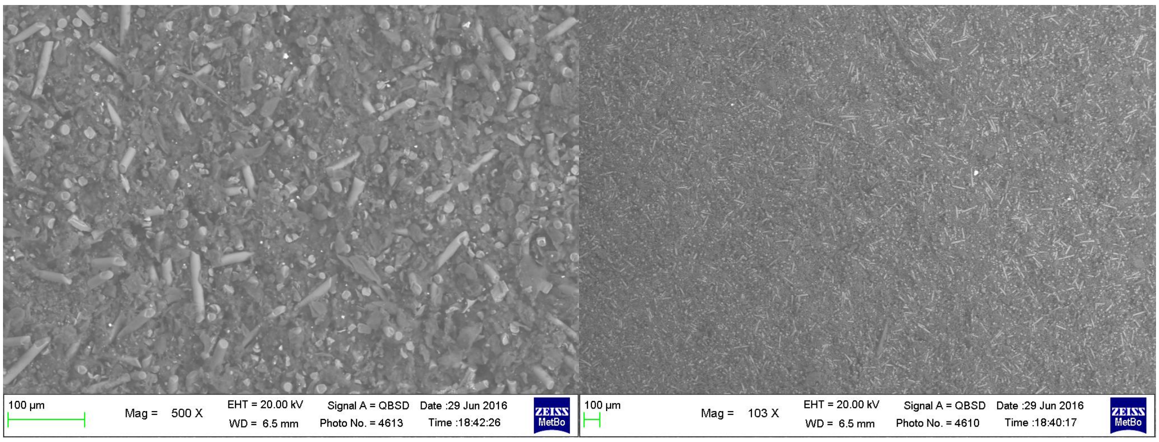

Figure 6.3.5 SEM analysis of the surface of the randomly aligned rubber/glass fibber composite at 100X and 500X magnification

	Aligned Fibres	Randomly aligned fibres
Avg fibres distance [μm]	150	55
Avg fibres diameter [μm]	10	20
Avg fibres length [μm]	10	200

Tab. 6.3.4 Fibres morphological differences

Results of composite comparison are shown in Fig. 6.3.6, showing that glass fibres alignment has a positive effect on grip performances on dry and wet ice and there are no significant friction improvements using randomly aligned fibres.

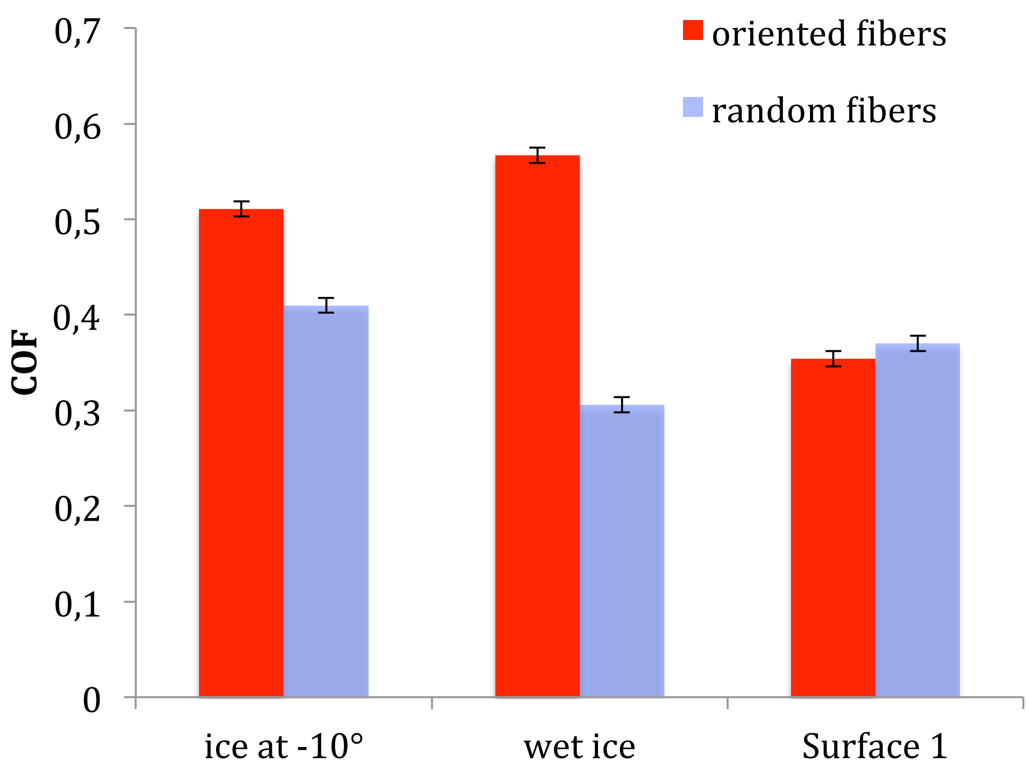

Figure 6.3.6 COF of materials on ice and on Surface 1

6.4 Conclusions

Previous works [5,12] have investigated the friction behaviour of ski boot soles for alpine skiing, showing that the dynamic coefficient of friction depends on the roughness and on the crystalline structure of the materials, with the smother surfaces and the softer materials having the best grip properties.

It is well known [13] that the length of copolymers blocks and molecular weight in polyurethane can have a significant effect on the thermal and mechanical properties of the materials. In particular, the copolymers block composition determines the crystalline structure that is responsible for the overall thermo-mechanical characteristics of the material and consequently, as demonstrated experiments, also for the surface frictional properties. It has also been demonstrated [5,12] the role of surface roughness at the micrometric scale, that is a parameter generally neglected in the design of this kind of product. Its role is as important as the material mechanical stiffness. Thus, also the wear behaviour must be properly taken into account, since the progressive flattening of the surface may conduce to major grip properties alterations.

Thermoplastic polyurethane soles have demonstrated grip on glass compared to porcelain stoneware surfaces; instead, the grip on ice has been significantly lower than wet surfaces one, amplified by the low temperature that has increased the polyurethane stiffness [5,12]. Therefore, materials that limit their hardness increase at low temperature should be preferred. In addition to this, it has been demonstrated in this chapter that the use of rubber/fiberglass inserts on ski boot sole can dramatically increase grip performance on icy surface, offering increased safety when moving in alpine winter environment.

Indeed, results obtained indicate a significant effect of glass fibres on the grip on ice. The increased grip on icy surfaces can be ascribed to glass fibres stiffness, which is able to generate a mechanical grip on ice surface; moreover, the increased contact angle and water repellence contribute to decrease the formation of a water layer below the sole. The opposite effect, observed on hard surface (Surface 1), can be explained because of the higher surface roughness (less contact points) with respect to others surfaces. It has also been demonstrated that there are no significant grip improvements using randomly aligned fibres, while oriented fibres offer the maximum grip performance on both ice and wet ice.

Results of the present study can be also proficiently applied to a wider footwear range to be used in winter environments.

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7 Hiking and mountain boots: safety properties, ergonomic and thermal comfort

Hiking and mountain boots have become proper pieces of high technology but in some cases they still retain their old-fashioned style since excellence production is still a hand-made process. Since the very first leather mountain boots, in terms of functional aspects, nothing has really changed over the years: they still have to provide protection, ankle support, waterproofness, breathability etc.

These are product that must offer reliability over long exposure to water, impacts, strains, scratches and environmental aging. Key producers are now offering a wide range of products and price, covering nearly all kinds of terrain, altitude and activity possible in the outdoors. Specific performances have been achieved through the use of specific parts such as uppers, paddings, lacing systems and soles materials.

Since one of the most relevant uses of footwear is the protection from physical trauma and environmental extremes, more and more attention in hiking and mountain boots design must be addressed to their thermal comfort and shock absorbing properties.

Indeed, the aim of this chapter is to take into account the two above mentioned aspects to build a comfort and performance driven hierarchy among three high-end mountain boot models.

Thus, their response in terms of thermal and ergonomic comfort has been deeply evaluated.

7.1 Thermal properties

7.1.1 Introduction

Three different pair of mountaineering boots have been submitted to in vivo test for the evaluation of thermo-physiological comfort. Three volunteers have performed controlled physical activity on a treadmill under constant environmental conditions (-10°C; 60% RH) inside a climatic chamber. During the test physiological and environmental parameters have been recorded as well as subjective comfort perception of footwear worn. Data have been statistically processed and analyzed to evaluate the boots thermal insulation.

7.1.2 Materials and Methods

Materials

In Fig. 7.1.1 the tested boots are shown. All boots tested belong to the category of mountaineering boots; they all have the feature to operate with semi-automatic crampons, they all use Vibram sole and Gore-Tex PTFE (Polytetrafluoroethylene) membrane in order to guarantee waterproofness and breathability.

Boot 1	Boot 2	Boot 3
		
675 g	690 g	600g

Fig. 7.1.1 Tested boots and their weight

Volunteers

Three male volunteers have participated to trials. Volunteers are aged between 30 and 33 years and fit size 42.5 boot (8 UK).

	Age (years)	**Height (m)**	**Wheight (Kg)**	**Body Mass Index**
Tester 1	32	1.70	59	20.4
Tester 2	33	1.68	58	20.5
Tester 3	30	1.78	68	21,5

Tab. 7.1.1 Volunteers

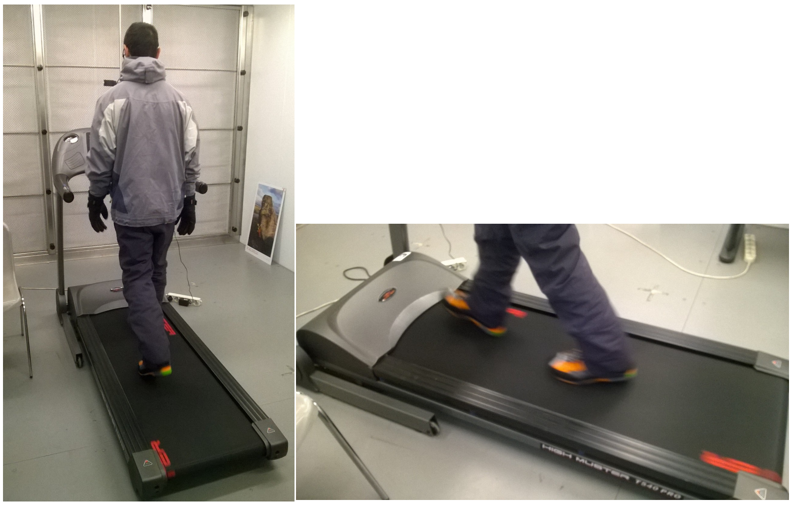


Fig. 7.1.2 Volunteer during the test

Testing Protocol

Each volunteer performed three tests, carried out in three different days at the same hour, in order to minimize the effects of circadian cycles on human physiology. During the tests, volunteers have worn cotton underwear, ski padded pants, thermal synthetic second layer and ski-padded jacket. Clothing worn by each volunteer did not changed during the three tests. All three volunteers used the same ski socks model (45% Acrylic, 19% Nylon, 15% Wool, 12% Polyester, 6% Polypropylene, 3% Elastane).

Boots have been thermo-stated at 20 °C before each test; also volunteers have spent 10 minutes inside a conditioned environment at 20 °C, wearing socks but no shoes, before starting the test.

The tests have been carried out in three phases:

- First phase of acclimatization in climatic chamber during which the voluntary walks for 15 minutes on the treadmill at a speed of 3.5 km/h without any ramp inclination;
- Second phase in which the volunteer performs a walk at 4 km/h, with alternating phases of the ramp tilting, according to Fig. 7.1.3;
- At the end of physical activity, the volunteer remains at rest for 10 minutes inside the climatic chamber.

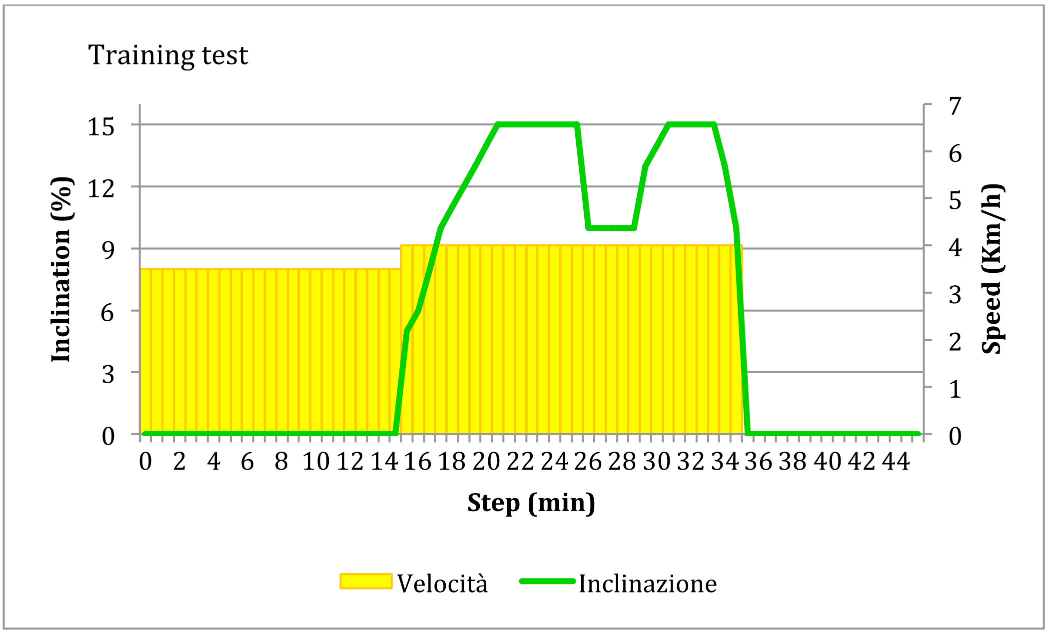


Fig. 7.1.3 Speed and inclination of the treadmill during the test

Microclimate Recording

Microclimate represents the thin air layer formed between fabric and skin. Chest microclimate temperature and relative humidity have been monitored during the duration of each tests through a wireless sensor MSR (Fig. 7.1.4), attached the volunteers chest, with sampling rate of 10 seconds.

Fig. 7.1.4 Chest wireless temperature and RH sensor

Chest microclimate has been monitored in order to verify that the three tests carried out by each tester took place in comparable thermal comfort conditions. In other words, if chest microclimate significantly changed during one of the test, data coming from test would be discarded because physiological parameters and subjective assessments would be conditioned by a different thermal situation which not comply with the other tests.

Microclimate temperature and relative humidity inside the boots have been monitored by inserting in each insole a miniaturized wireless I-Button sensor (Fig. 7.1.5), in correspondence of the front part of the foot (Fig. 7.1.6). Sensors have been installed in the boot insole, housed in a hole of the same diameter obtained by means of a die. The sensor has been positioned with the inlet for the air upward, so that the RH% measured is that coming from the foot.

The sensor is fully integrated into the insole and thanks to its miniaturized size and its position, the volunteer does not perceive any discomfort during the walk.

Fig. 7.1.5 I-Button sensor

Fig. 7.1.6 Sensors position in the insoles

Questionnaire

Volunteers have been asked to answer a questionnaire four times during the course of the test in order to acquire the subjective feelings in relation to the thermo-physiological comfort of the boots worn and the overall thermal sensation. Questions have been asked at: 15 minutes (at the end of the acclimatization period), 25 minutes (after ten minutes of physical activity), 35 minutes (at the end of physical activity) and 45 minutes (at the end of the test).

Environmental Conditions

Tests have been carried out in a climate chamber in order to achieve stable and constant environmental conditions throughout the test campaign.

Temperature and relative humidity have been monitored during the whole duration of the tests using a wireless temperature and humidity sensor (Fig. 7.1.4) with acquisitions every 5 minutes. Temperature and relative humidity values, averaged among all test for each type of boot and along with relative standard deviation, are reported in Tab. 7.1.2.

Boot	Environmental temperature (°C)	Environmental RH (%)
Boot 1	-9.77 ± 0.46	72.41 ± 4.51
Boot 2	-9.87 ± 0.21	71.58 ± 5.54
Boot 3	-9.88 ± 0.35	71.75 ± 5.28

Tab. 7.1.2 Averaged environmental parameters

Expanded PTFE applications

In the last three decades, several companies have started the development of waterproof, yet breathable footwear using ePTFE W. L. Gore technology. Over the years, Gore has placed on the marker a wide range of laminated textiles to be used from everyday life to the most challenging outdoors conditions such as skiing, hunting and mountaineering [1].

Polytetrafluoroethylene or PTFE is the chemical name of a plastic material with unique properties, most commonly known for its use as a material within the DuPont Teflon® brand of non-stick cookware [2]. Discovered in 1938 by Roy Plunkett as unintended consequence of a “failed” refrigeration gas experiment [2], PTFE has revolutionized plastics industry, and led to major innovations in the outdoor industry.

PTFE is produced by polymerization of a C_2F_4 (tetrafluoroethylene) monomer to produce a very long chain macromolecule (Fig. 7.1.7). The Carbon-Fluorine chemical bond is very strong, providing superior protection against chemical attack [2].

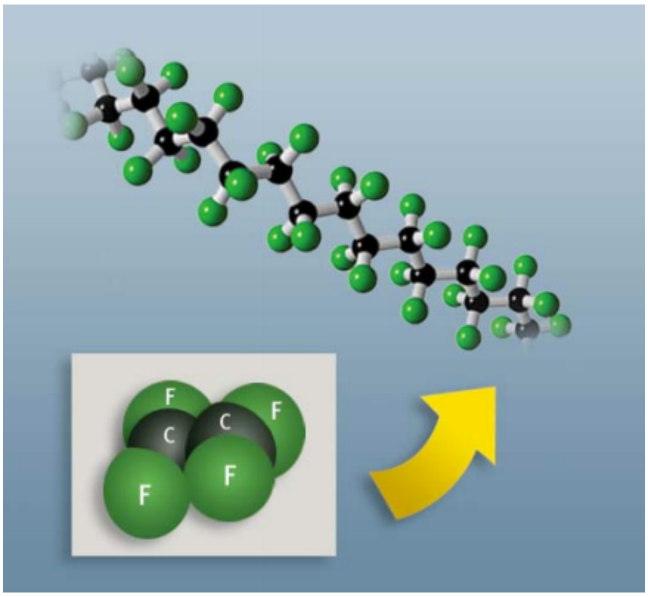


Fig. 7.1.7 Polymerization of a C_2F_4

PTFE is renown for some major advantages, such as:

- Chemically inert to nearly all media (pH 0-14)
- Wide range of thermal resistance -268˚C to +315˚C (-450˚F to +600˚F)
- Non-aging, weather and UV resistant
- Low coefficient of friction
- Physiologically harmless
- Wide application versatility

But there is also a major disadvantage, represented by mechanical weakness. In 1969, Bob Gore discovered expanded PTFE by mean of a unique process, improving significantly the mechanical properties while maintaining all the positive chemistry attributes of the base PTFE material [2].

Boots tested in the present chapter adopt GORE-TEX Performance Comfort technology (Fig. 7.1.7), suitable for outdoor use in a wide range of climate conditions, while GORE-TEX Extended Comfort is designed for indoor and outdoor use in moderate and warmer conditions and GORE-TEX Insulated Comfort is suitable for outdoor use in rain, snow and cold conditions [3].

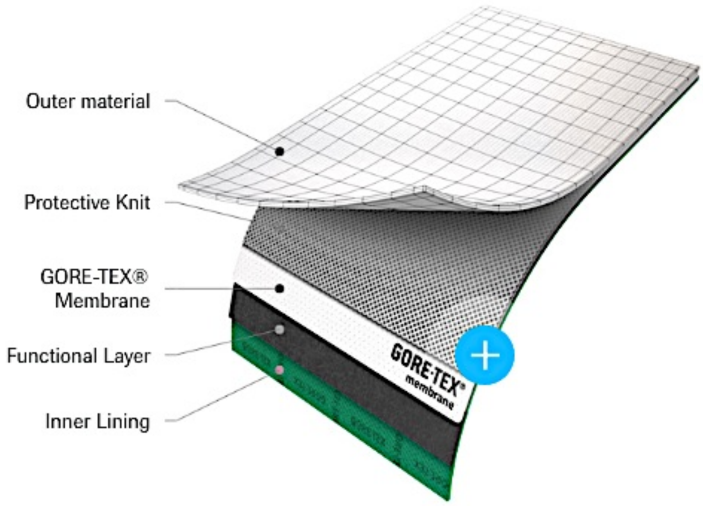


Fig. 7.1.8 GORE-TEX Performance Comfort, construction

All the above-mentioned technologies, combine waterproofness and effective breathability. Water and snow remains on the outside while moisture generated by perspiration escapes from the inside [1]. As shown in Fig. 7.1.8, in addition to ePTFE membrane, there are other textile layers in footwear that contribute to ensure durable waterproofness.

All materials must also be non-wicking or treated with DWR (durable water repellency), to prevent water from being transported into the boot [1].

Reliable weather protection for the useful life of the shoe, thermal comfort and ergonomic comfort complete the frame for an optimal footwear design. In the following paragraphs a deep investigation on how waterproof mountaineering boots perform in simulated cold environment is reported

Heat loss evaluation

The determination of punctual heat dispersion from specific footwear parts such as the upper and the sole, can be useful to asses the boot thermal behavior, giving precise information on how materials used to product assembly retain heat. For example, it is well know that that the toe area is the coldest one [4]. Thus, identifying some mayor heat dispersion in the front part of the boot could suggest designer and product managers to add insulation layers or redesign the boot part.

To achieve this task, each boot has been filled with solid material in dissolved form (grains, 700 g) preheated for 12 hours in a stove at 50 °C. Thermographs have been recorded under controlled environmental conditions (20 °C, 50% RH), generating a thermal gradient of 30° from the inside of the boot and the external environment.

Thermal images have been recorded in 3 phases:

- After 4' from filling the boot with the preheated material
- After 17' from filling the boot with the preheated material
- After 25' from filling the boot with the preheated material

High resolution infrared thermo camera Thermo Tracer TH9100MW (NEC Avio Infrared Technologies Co., Ltd, Tokio, Japan), working in the wave length band 8–14 μm with a resolution of 0.02°C, has been used to record thermo graphic images.

For each boot, five thermo graphic images have been recorded as shown in Fig. 7.1.9 (front, internal side, back, external side, bottom).

Fig. 7.1.9 From left to right: front, internal side, back, external side, bottom

7.1.3 Results and discussion

Chest Microclimate

As mentioned above, chest microclimate temperature and relative humidity have been monitored in order to highlight substantial variations of the general volunteer comfort during each test.

In Fig. 7.1.10 averaged results of chest microclimate temperature are reported for the three boots; while in Fig. 7.1.11 averaged results of chest microclimate relative humidity are reported for the three boots.

In order to assess whether the observed differences are significant, a statistical test type "Paired t-test" have been performed. In Tab. 7.1.3 the "p-value" (confidence interval = 90%) are reported.

The statistical analysis shows a significant variation in the humidity of the microclimate between tests with Boot 2 and Boot 1. This variation will have to be taken into account in the subsequent data analysis if variations inside the boots will be found.

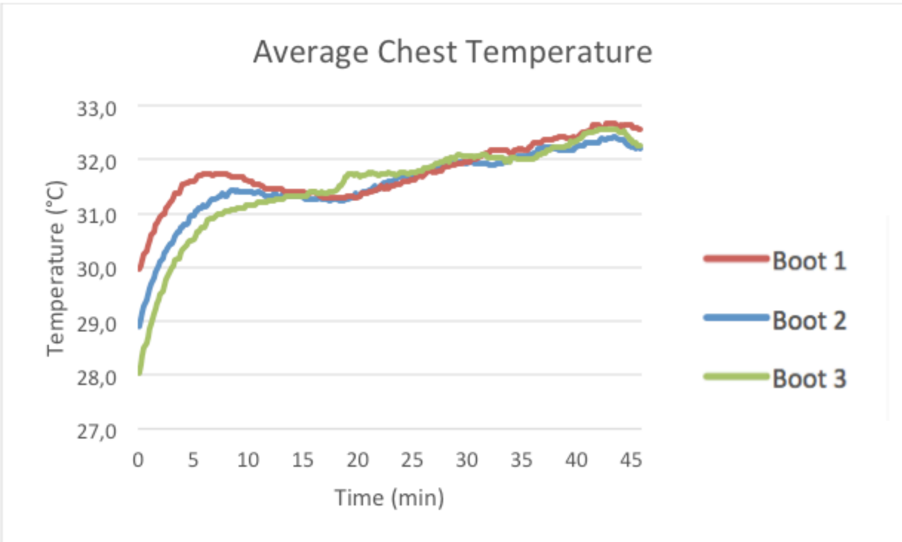


Fig. 7.1.10 Average chest microclimate temperature

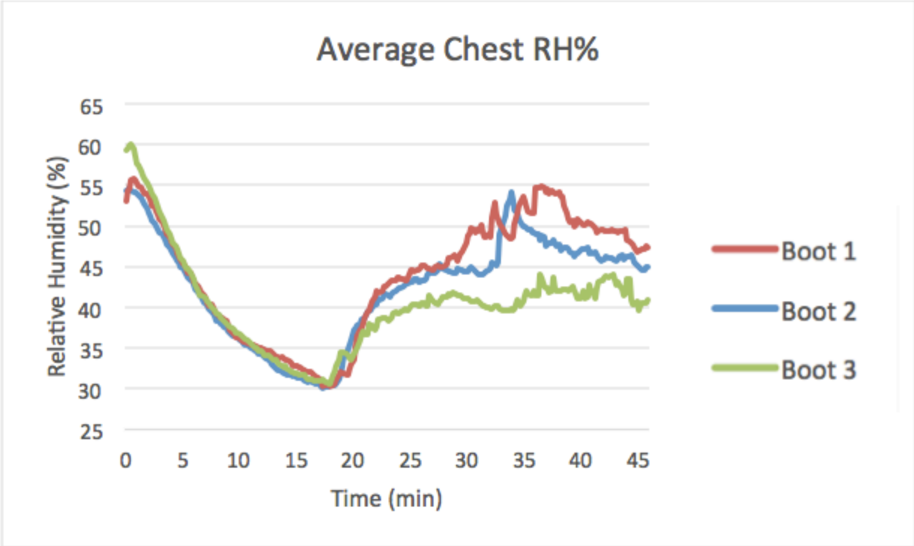


Fig. 7.1.11 Average chest relative humidity

Boot	*p - value* Avg Temperature	*p - value* Avg RH%
Boot 2 – Boot 1	0.439	**0.040**
Boot 2 – Boot 3	0.828	0.624
Boot 1 – Boot 3	0.515	0.397

Tab. 7.1.3 P–values for chest microclimate parameters

Boot Microclimate

In Fig. 7.1.12 averaged results (both feet, all volunteers) of boot microclimate temperature are reported for the three boots; while in Fig. 7.1.13 averaged results (both feet, all volunteers) of boot microclimate relative humidity are reported for the three boots.

In Tab. 7.1.4 are reported the "p-value" relating to the statistical analysis performed with "Paired t-test" method, in order to assess whether the variations observed in the microclimate inside the boots are due to the type of boot and its construction. P-values less than or equal to 0.1 indicate a significant change in the observed parameter with respect to the type of boot worn, while values of p greater than 0.1 indicate a non-significant variation. The confidence interval used is 90%.

The analysis has been performed on the average temperature and relative humidity values, between the right foot and left foot. Values that indicate significant variations are shown in bold characters.

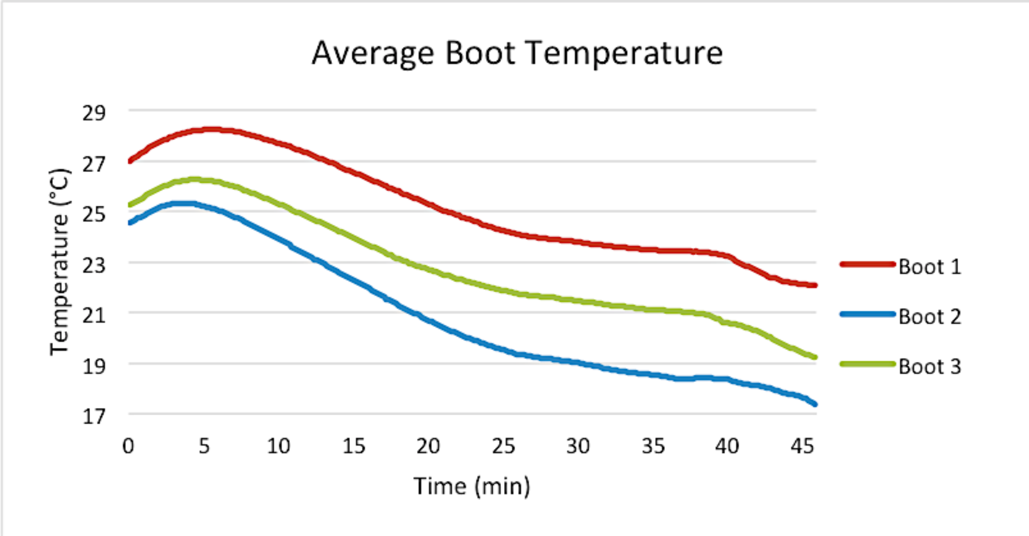


Fig. 7.1.12 Average boot microclimate temperature

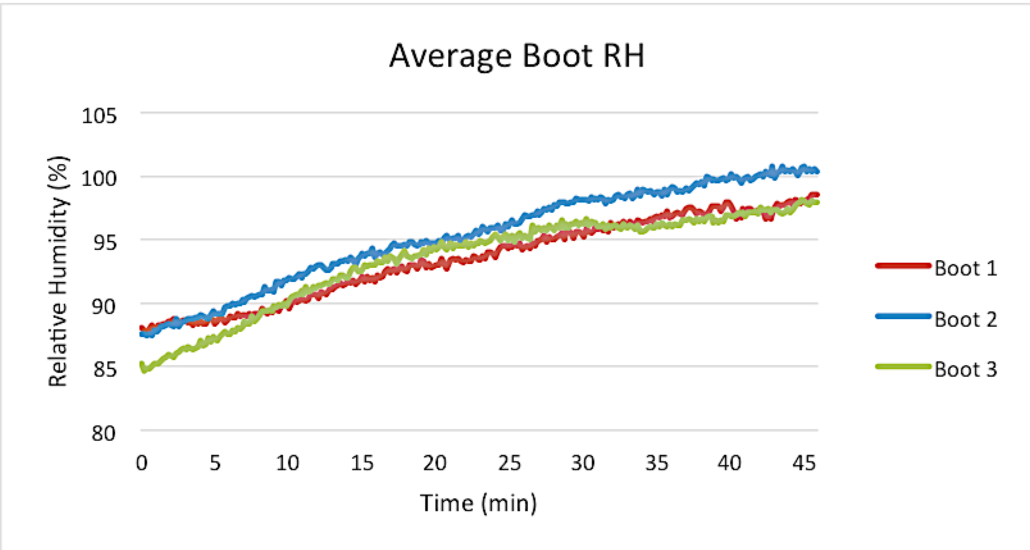


Fig. 7.1.13 Average boot microclimate relative humidity

Boot	***p - value*** **Avg Temperature**	***p - value*** **Avg RH%**
Boot 2 – Boot 1	**0.100**	0.175
Boot 2 – Boot 3	0.130	0.261
Boot 1 – Boot 3	**0.082**	0.980

Tab. 7.1.4 P–values for boot microclimate parameters

Boot 1 results statistically different from the other boots tested, with a microclimate temperature inside the boot, which is always higher. Relative humidity inside the boots, however, does not show significant variations among the tested boots.
In Tab. 7.1.5 average temperature values and variations with respect to Boot 1 are shown

Boot	Average temperature (°C)	Δ respect to Boot 1 (°C)
Boot 1	25.17	–
Boot 2	20.90	- 4.27
Boot 3	22.80	- 2.37

Tab. 7.1.5 Average temperature values and variations with respect to Boot 1

Questionnaire

Specific designed questionnaire has been prepared in order to detect subjective feelings about the thermo-physiological overall comfort, wearing boots in winter-simulated conditions. The questionnaire was proposed to volunteers four times during the test:

- Q1: After the initial acclimatization (t = 15 min);
- Q2: In the middle of the stage of physical activity (t = 25 min);
- Q3: At the end of physical activity (t = 35 min);
- Q4: At the end of the test (t = 45 min).

Questions about the overall comfort have been used to verify that volunteers have been in a total state of comfort and that feelings between the two feet have been equal. After this first verification, answers feet sensations and feelings related to the boots have been evaluated. For each question the frequency of each response has been rated. The following are the graphs for each question and by type of boot.

Acceptability (Fig. 7.1.14): indicates whether the feeling of the feet temperature is acceptable or if the discomfort is such that the feeling is not acceptable. All boots tested have kept the feet in a general situation of comfort for the entire duration of the tests.

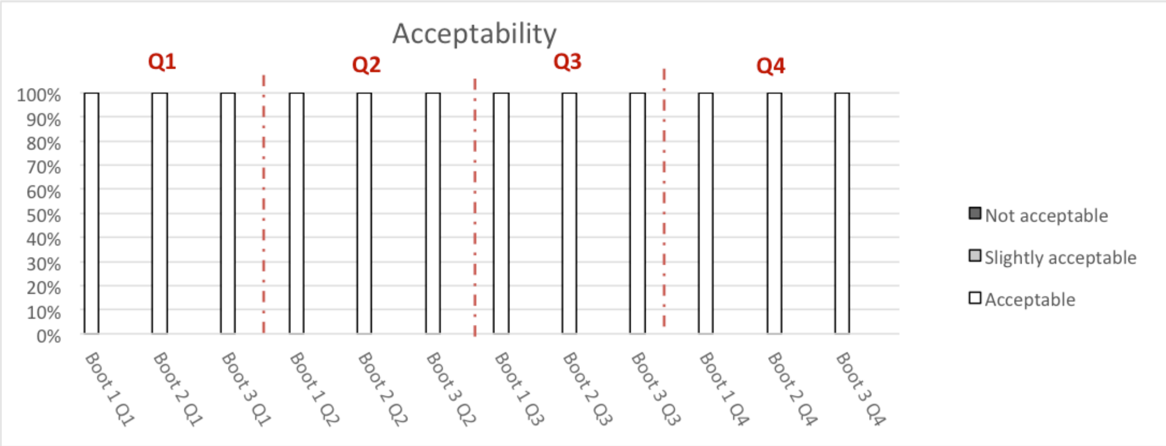


Fig. 7.1.14 Acceptability

Feet temperature (Fig. 7.1.15): indicates feet temperature sensation perceived by volunteers during the test.

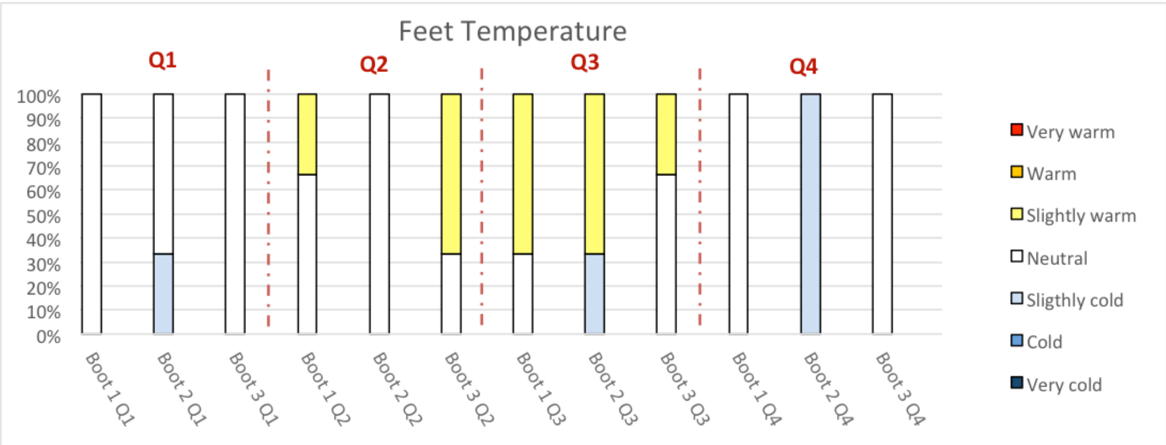


Fig. 7.1.15 Feet temperature

Wearing Boot 2 all volunteers have experienced a feeling of slight cold at the end of the test (Q4), while with the other boots the sensation remains neutral. Boot 1 and Boot 3 have given sensations of light warm during the physical activity (Q2 and Q3). Boot 2, instead, at the end of physical activity has given a discordant feeling of slightly warm and slightly cold between the different volunteers, as consequence of different amount of metabolic heat produced.

Feet relative humidity (Fig. 7.1.16): indicates feet humidity sensation perceived by volunteers during the test.

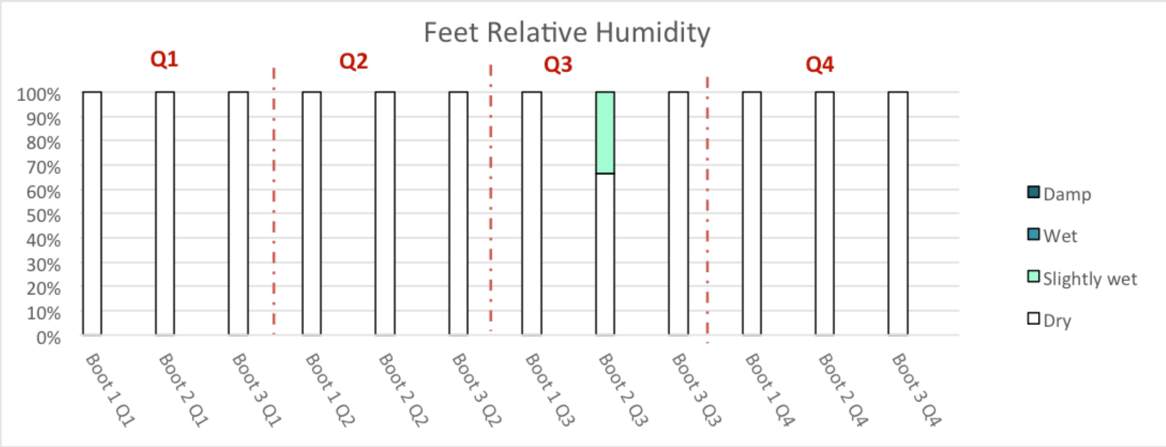


Fig. 7.1.16 Feet relative humidity

All tested boots have given a dry feeling in all test phases. Only with Boot 2, one voluntary sensed a feeling of slightly damp at the end of the phase of physical activity (Q3).

Warmth of the boot (Fig. 7.1.17): indicates the sensation perceived by volunteers about the boot warmth.

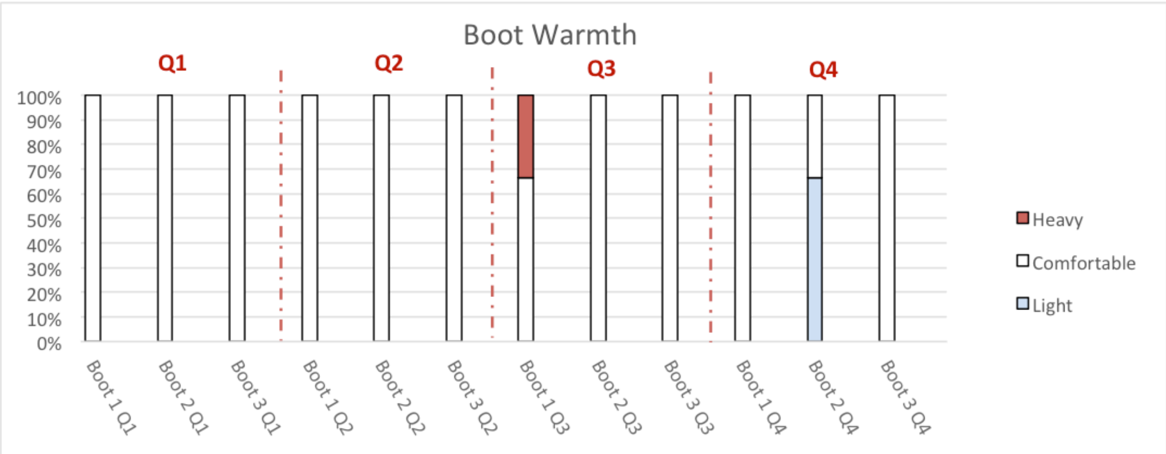


Fig. 7.1.17 Warmth of the boot

Overall, boots tested have been judged warm enough to deal with this specific environmental situation. At the end of physical activity (Q3) a volunteer has judged Boot 1 to be too warm, while at the end of the test (Q4) two volunteers have considered Boot 2 to be to light, with respect to the perceived sensation of cold to the feet.

Boot breathability (Fig. 7.1.18): indicates the sensation perceived by volunteers about the boot breathability.

Breathability feeling has been rather difficult to perceive and define by volunteers. Only one volunteer has defined Boot 1 to be always non-breathable, while for the others, all boots have been breathable enough in the test environmental conditions.

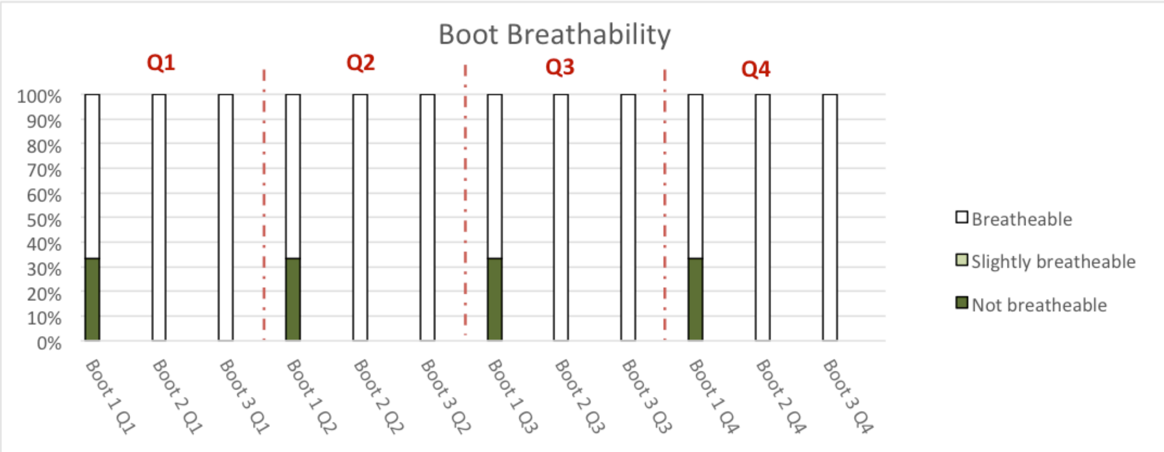


Fig. 7.1.18 Boot breathability

Boot temperature (Fig. 7.1.19): indicates the sensation perceived by volunteers about the boot temperature.

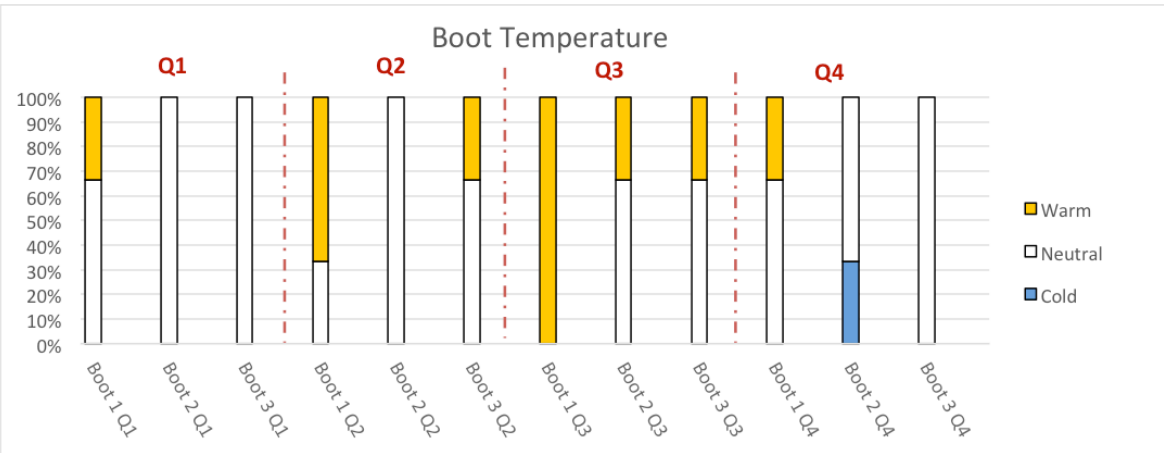


Fig. 7.1.19 Boot temperature

Boot 1 has founded warm by all volunteers at the end of exercise (Q3). Overall, during all tests, Boot 1 has been defined neutral or warm. For Boot 3, the predominant feeling is neutral. Wearing Boot 2, one volunteer has had cold temperature feeling at the end of the test (Q4).

Boot relative humidity (Fig. 7.1.20): indicates the sensation perceived by volunteers about the boot humidity.

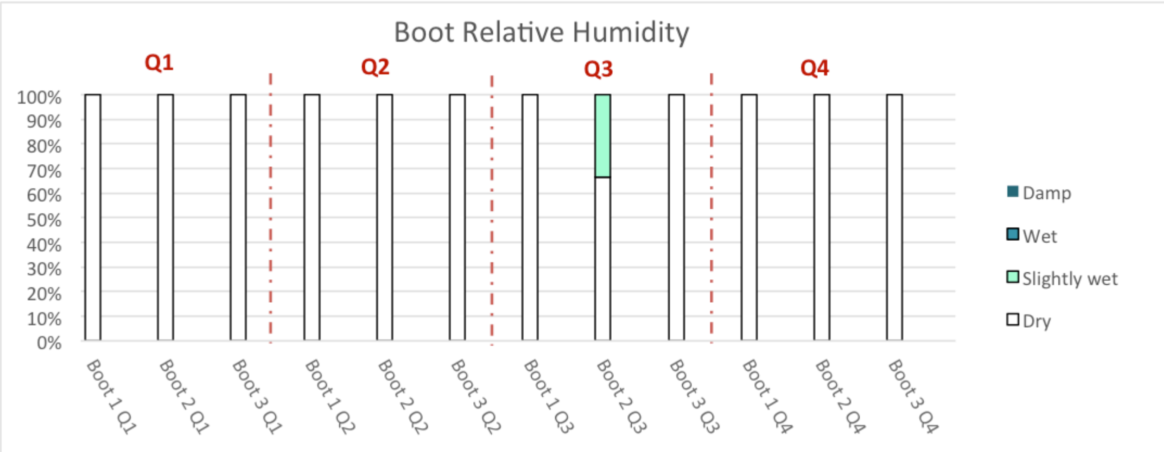


Fig. 7.1.20 Boot relative humidity

In general, the feeling perceived inside the boots has been dry. At the end of exercise (Q3), one voluntary detects a feeling of slight wet inside Boot 2.

Finally, the average ratings (from 1 to 10) given by volunteers for each boots worn are reported in Tab. 7.1.6.

	Boot 1	Boot 2	Boot 3
Avg Score	7	7	8.3

Tab. 7.1.6 Average ratings for each boot

Each answer has been associated with a numerical scale, giving a value 1 to greater discomfort and increasing to reach the maximum value for the best feet and boot comfort sensation. As an example, the question: "What is your feeling of moisture on the feet?" It has been assigned value 1 to the answer "Wet", value 2 to "damp", value 3 to "slightly damp" and value 4 to "dry."

The value of each answer has been multiplied by its frequency, thus obtaining a single numerical value associated with each question. The greater the value, the greater is the comfort perceived by volunteers, since it increases with the number of volunteers who have chosen answers on top of the numerical scale.

In order to give an overall assessment of sensations perceived by volunteers during the test, the numerical values have been added together for the four questionnaires answered at different times.

For each question, the numerical value has been normalized to 10: it has been given score 10 to answer with greater numerical value and the others have been calculated in proportion. This has been made to give the same weight to the contribution of each question. The radar plot with global scores for each survey question is reported in Fig. 7.1.21.

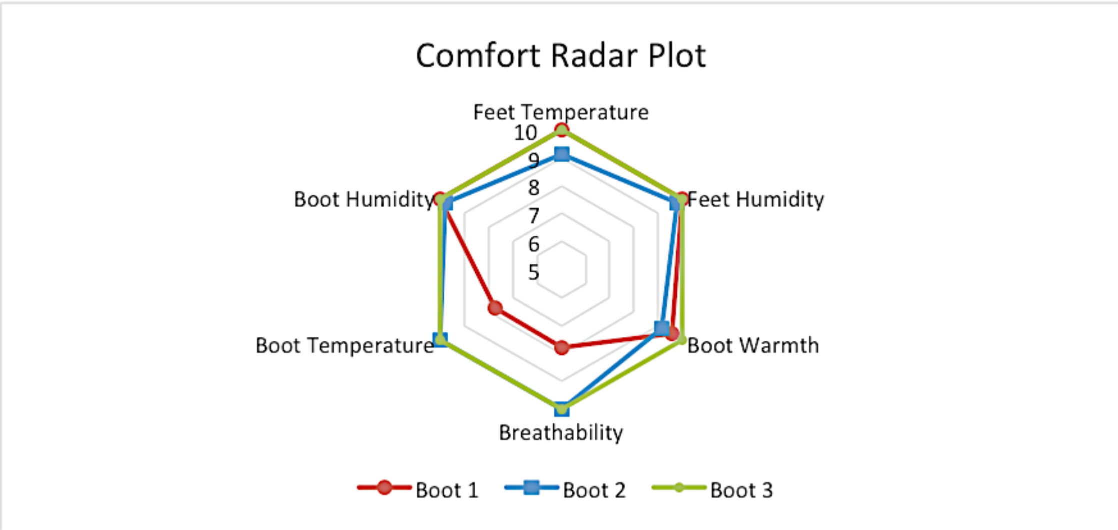
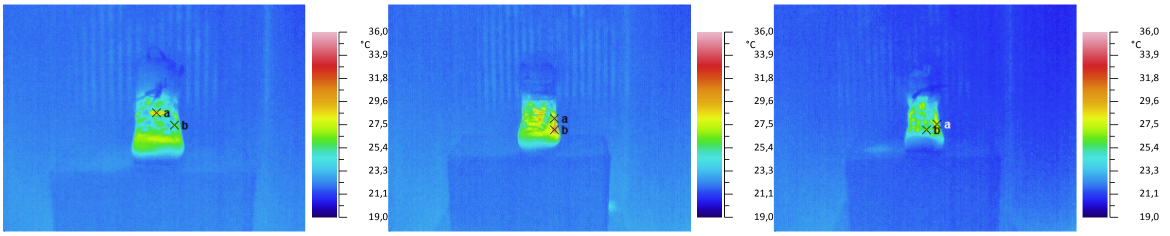


Fig. 7.1.21 Comfort radar plot

Thermo graphic images

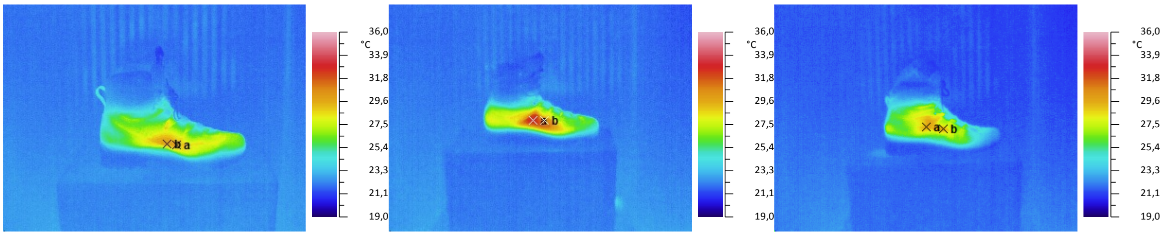
In Fig. 7.1.22, thermo graphic images of the front part of the boot after 4’ are reported.



Boot 1	T[°C]	Emiss.	T_{Envi} [°C]	Boot 2	T [°C]	Emiss.	T_{Envi} [°C]	Boot 3	T [°C]	Emiss.	T_{Envi} [°C]
a	29,4	0,9	20,0	a	30,4	0,9	20,0	a	28,5	0,9	20,0
b	27,6	0,9	20,0	b	30,3	0,9	20,0	b	28,0	0,9	20,0

Fig. 7.1.22 Thermo graphic images, font part after 4’

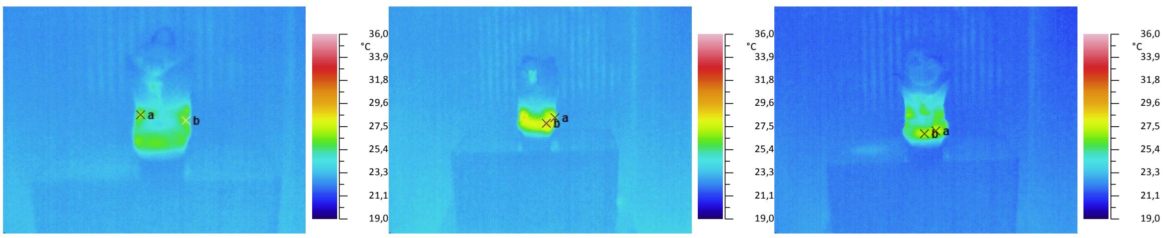
In Fig. 7.1.23, thermo graphic images of the internal side of the boot after 4’ are reported.



Boot 1	T[°C]	Emiss.	T_{Envi} [°C]	Boot 2	T [°C]	Emiss.	T_{Envi} [°C]	Boot 3	T [°C]	Emiss.	T_{Envi} [°C]
a	30,2	0,9	20,0	a	32,8	0,9	20,0	a	30,1	0,9	20,0
b	30,1	0,9	20,0	b	31,4	0,9	20,0	b	29,8	0,9	20,0

Fig. 7.1.23 Thermo graphic images, internal side after 4’

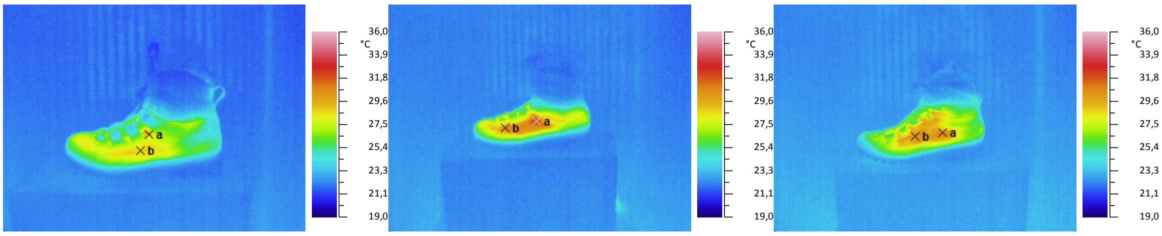
In Fig. 7.1.24, thermo graphic images of the back part of the boot after 4’ are reported.



Boot 1	T[°C]	Emiss.	T_{Envi} [°C]	Boot 2	T [°C]	Emiss.	T_{Envi} [°C]	Boot 3	T [°C]	Emiss.	T_{Envi} [°C]
a	27,5	0,9	20,0	a	29,4	0,9	20,0	a	27,8	0,9	20,0
b	26,7	0,9	20,0	b	28,9	0,9	20,0	b	27,5	0,9	20,0

Fig. 7.1.24 Thermo graphic images, back part after 4’

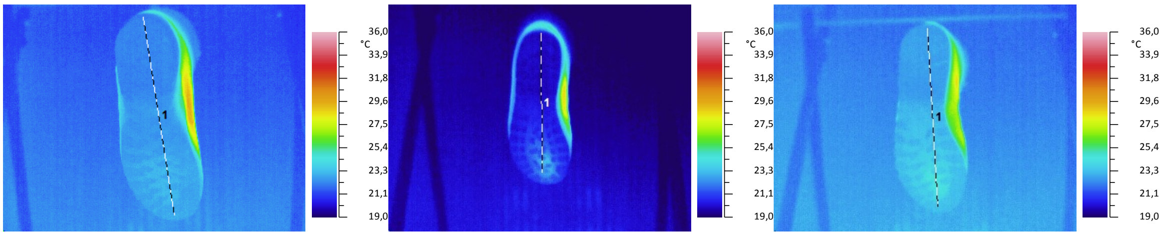
In Fig. 7.1.25, thermo graphic images of the external side of the boot after 4’ are reported.



Boot 1	T[°C]	Emiss.	T_{Envi} [°C]	Boot 2	T [°C]	Emiss.	T_{Envi} [°C]	Boot 3	T [°C]	Emiss.	T_{Envi} [°C]
a	31,2	0,9	20,0	a	32,3	0,9	20,0	a	31,2	0,9	20,0
b	31,0	0,9	20,0	b	31,1	0,9	20,0	b	31,0	0,9	20,0

Fig. 7.1.25 Thermo graphic images, external side after 4’

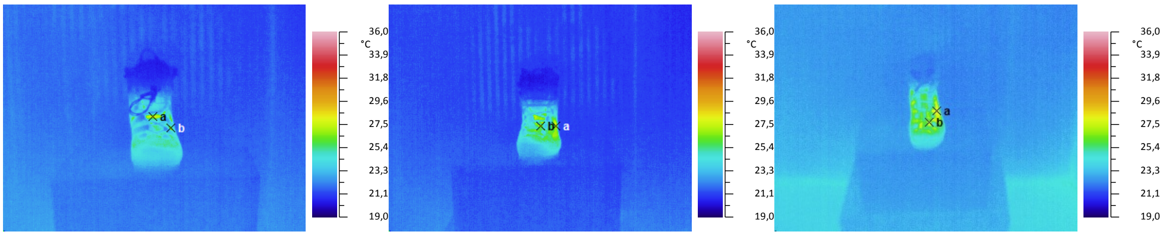
In Fig. 7.1.26, thermo graphic images of the boot sole after 4’ are reported.



Boot 1	Min [°C]	Max [°C]	Avg [°C]	Boot 2	Min [°C]	Max [°C]	Avg [°C]	Boot 3	Min [°C]	Max [°C]	Avg [°C]
Line 1	21,7	23,4	22,5	Line 1	19,7	23,1	20,6	Line 1	22,3	24,8	23,2

Fig. 7.1.26 Thermo graphic images, sole after 4’

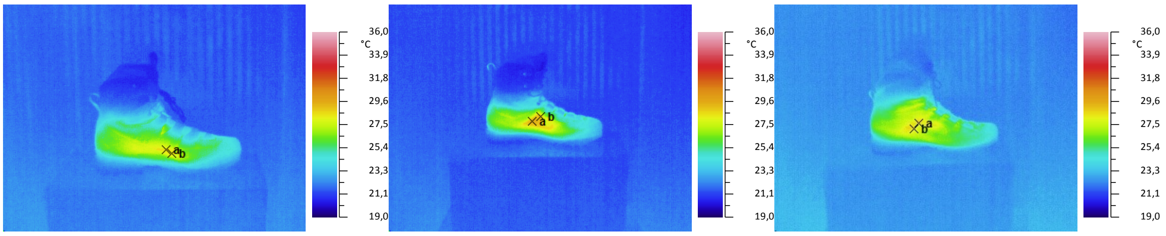
In Fig. 7.1.27, thermo graphic images of the front part of the boot after 17’ are reported.



Boot 1	T[°C]	Emiss.	T_{Envi} [°C]	Boot 2	T [°C]	Emiss.	T_{Envi} [°C]	Boot 3	T [°C]	Emiss.	T_{Envi} [°C]
a	27,8	0,9	20,0	a	28,1	0,9	20,0	a	28,8	0,9	20,0
b	27,5	0,9	20,0	b	27,5	0,9	20,0	b	28,3	0,9	20,0

Fig. 7.1.27 Thermo graphic images, front part after 17’

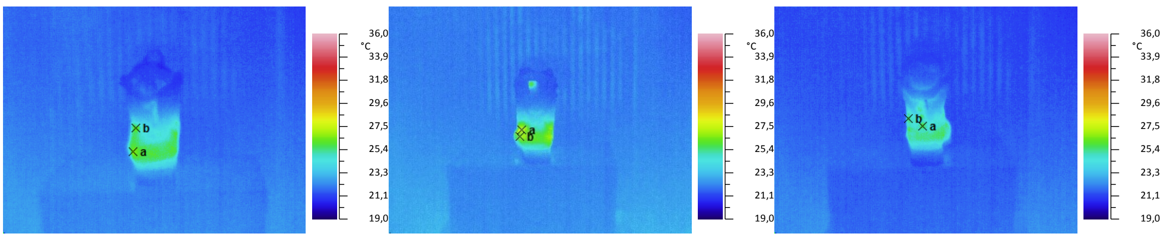
In Fig. 7.1.28, thermo graphic images of the internal side of the boot after 17’ are reported.



Boot 1	T[°C]	Emiss.	T_{Envi} [°C]	Boot 2	T [°C]	Emiss.	T_{Envi} [°C]	Boot 3	T [°C]	Emiss.	T_{Envi} [°C]
a	28,6	0,9	20,0	a	29,8	0,9	20,0	a	28,9	0,9	20,0
b	28,6	0,9	20,0	b	29,3	0,9	20,0	b	28,8	0,9	20,0

Fig. 7.1.28 Thermo graphic images, internal side after 17’

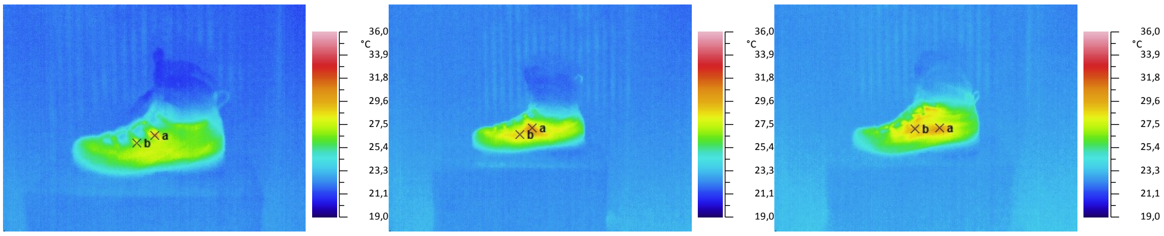
In Fig. 7.1.29, thermo graphic images of the back part of the boot after 17’ are reported.



Boot 1	T[°C]	Emiss.	T_{Envi} [°C]	Boot 2	T [°C]	Emiss.	T_{Envi} [°C]	Boot 3	T [°C]	Emiss.	T_{Envi} [°C]
a	26,8	0,9	20,0	a	27,9	0,9	20,0	a	25,9	0,9	20,0
b	26,3	0,9	20,0	b	27,0	0,9	20,0	b	25,8	0,9	20,0

Fig. 7.1.29 Thermo graphic images, back part after 17’

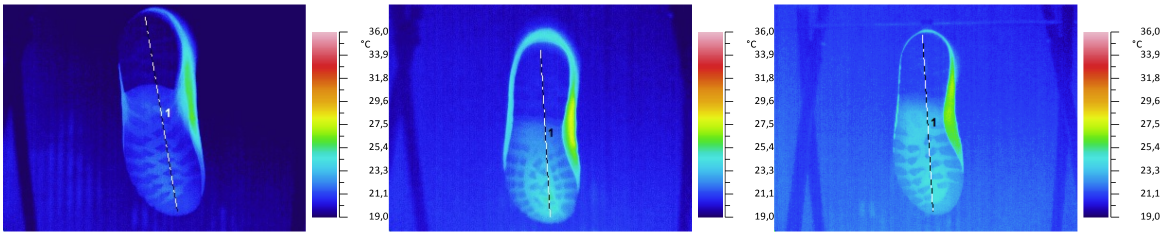
In Fig. 7.1.30, thermo graphic images of the external side of the boot after 17' are reported.



Boot 1	T[°C]	Emiss.	T_{Envi} [°C]	Boot 2	T [°C]	Emiss.	T_{Envi} [°C]	Boot 3	T [°C]	Emiss.	T_{Envi} [°C]
a	29,4	0,9	20,0	a	30,4	0,9	20,0	a	30,2	0,9	20,0
b	28,1	0,9	20,0	b	28,9	0,9	20,0	b	29,6	0,9	20,0

Fig. 7.1.30 Thermo graphic images, external side after 17'

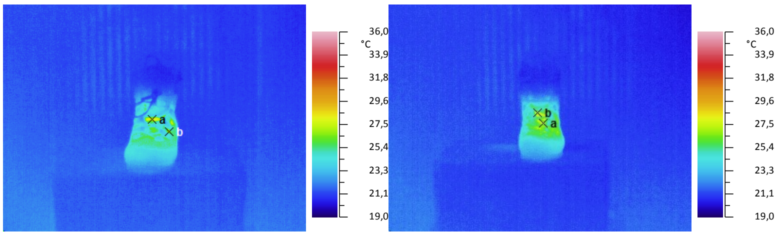
In Fig. 7.1.31, thermo graphic images of the sole of the boot after 17' are reported.



Boot 1	Min [°C]	Max [°C]	Avg [°C]	Boot 2	Min [°C]	Max [°C]	Avg [°C]	Boot 3	Min [°C]	Max [°C]	Avg [°C]
Line 1	18,9	22,0	20,5	Line 1	20,1	25,3	22,0	Line 1	20,7	24,5	22,6

Fig. 7.1.31 Thermo graphic images, sole after 17'

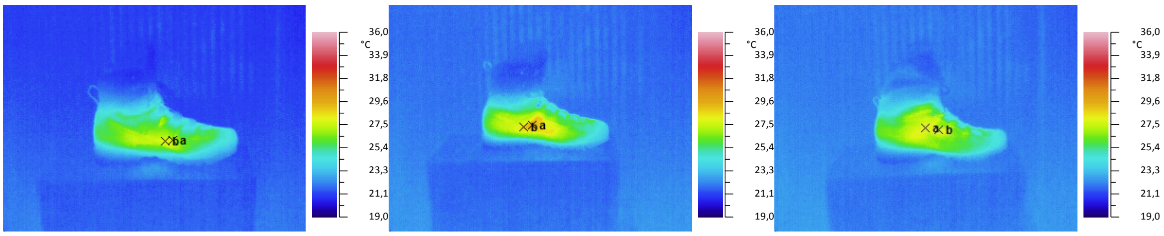
In Fig. 7.1.32, thermo graphic images of the front part of the boot after 25’ are reported.



Boot 1	T[°C]	Emiss.	T_{Envi} [°C]	Boot 2	T [°C]	Emiss.	T_{Envi} [°C]
a	28,6	0,9	20,0	a	28,2	0,9	20,0
b	27,7	0,9	20,0	b	27,8	0,9	20,0

Fig. 7.1.32 Thermo graphic images, front part after 25’, for Boot 3 the image is missing due to thermo camera failure

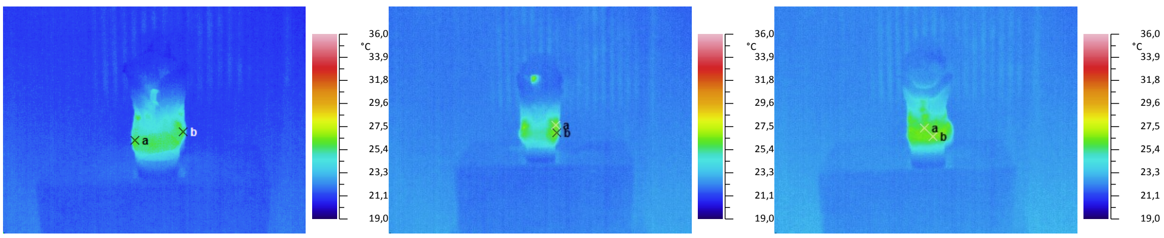
In Fig. 7.1.33, thermo graphic images of the internal side of the boot after 25’ are reported.



Boot 1	T[°C]	Emiss.	T_{Envi} [°C]	Boot 2	T [°C]	Emiss.	T_{Envi} [°C]	Boot 3	T [°C]	Emiss.	T_{Envi} [°C]
a	28,1	0,9	20,0	a	29,6	0,9	20,0	a	28,6	0,9	20,0
b	28,1	0,9	20,0	b	29,3	0,9	20,0	b	28,4	0,9	20,0

Fig. 7.1.33 Thermo graphic images, internal side after 25’

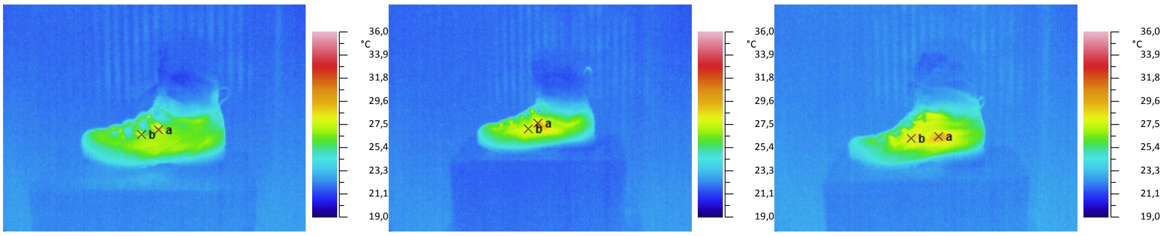
In Fig. 7.1.34, thermo graphic images of the back part of the boot after 25’ are reported.



Boot 1	T[°C]	Emiss.	T_{Envi} [°C]	Boot 2	T [°C]	Emiss.	T_{Envi} [°C]	Boot 3	T [°C]	Emiss.	T_{Envi} [°C]
a	26,2	0,9	20,0	a	26,7	0,9	20,0	a	26,8	0,9	20,0
b	26,2	0,9	20,0	b	26,7	0,9	20,0	b	26,7	0,9	20,0

Fig. 7.1.34 Thermo graphic images, back part after 25’

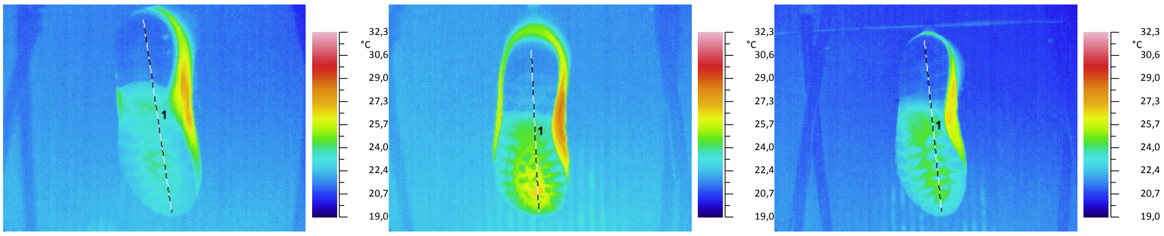
In Fig. 7.1.35, thermo graphic images of the external side of the boot after 25’ are reported.



Boot 1	T[°C]	Emiss.	T_{Envi} [°C]	Boot 2	T [°C]	Emiss.	T_{Envi} [°C]	Boot 3	T [°C]	Emiss.	T_{Envi} [°C]
a	29,4	0,9	20,0	a	29,4	0,9	20,0	a	29,8	0,9	20,0
b	28,5	0,9	20,0	b	28,0	0,9	20,0	b	28,8	0,9	20,0

Fig. 7.1.35 Thermo graphic images, external part after 25’

In Fig. 7.1.36, thermo graphic images of the external side of the boot after 25’ are reported.



Boot 1	Min [°C]	Max [°C]	Avg [°C]	Boot 2	Min [°C]	Max [°C]	Avg [°C]	Boot 3	Min [°C]	Max [°C]	Avg [°C]
Line 1	21,0	24,1	22,7	Line 1	21,5	26,9	23,8	Line 1	20,7	24,9	22,9

Fig. 7.1.36 Thermo graphic images, sole after 25’

7.1.4 Conclusions

After checking, by comparing microclimate temperature, that tests have been conducted in the same conditions and that each volunteer has been in comparable thermal condition, it can be said that the differences highlighted on the boot comfort are strictly connected to the boot characteristics.

From the evaluation of temperatures measured inside the boots, it can be deduced that Boot 1 is on average warmer than the Boot 2 (+ 4,27 °C) and Boot 3 (+ 2,37 °C), guaranteeing reduced heat dispersion as confirmed by thermo graphic images.

On the contrary, there is no indication about significant differences on the effect of relative humidity and microclimate moisture inside the boots.

Beside the fact that the assessment of subjective comfort and different comfort perception is related to a small number of volunteers, it is possible to affirm that all the boots have kept the feet in a condition of comfort during the whole duration of the test. Feet humidity and boot sensations have appeared to be very similar between the three models and this prove that ePTFE membranes can perform well in terms of breathability and comfort. As for the feet temperature, sensations of slightly cold for Boot 2 and slightly warm for Boot 1 and Boot 3, especially during physical activity, have been observed; this in accordance with what has been shown for the sensation of slightly warm feeling associated to Boot 1.

It has also been possible to highlight different behavior in term of heat retention among the three boots.

After the insertion of the preheated material (4’), Boot 2 immediately showed a greater heat dissipation (front / internal side/ external side).

In the internal inside, Boot 1 and Boot 2 have had similar behavior. On the contrary, in the external side, although the T_{Max} are very similar to each other, Boot 3 showed a wide dispersion area, larger than the one of Boot 1.

None significant heat loss has been observed in back part of the shoe, where the behavior is about equivalent.

With regard to the sole region of the boot, the behavior is similar for the 3 samples, showing minor dispersion. On the contrary to what happens in other parts of the boot, Boot 2 has had the lowest sole temperature. This behavior, which will be reversed during the test, can be attributed to the strong dispersion in the upper area.

After 17' it is possible to consider that the system is evenly heated. In this phase, Boot 1 has shown the biggest heat retention in the front, internal side and external side of the boot. Boot 2 has shown the major thermal losses among those tested and in the heel region has been recorded the highest temperatures, followed by Boot 1 and Boot 3.

In the sole area, Boot 1 has been the one with the highest insulating behavior: indeed, a difference of 2 °C has been recorded on the average temperature with respect to other soles and a difference of 2,5 °C and 1 °C, with respect to the average and the maximum temperature.

After 25’, the good thermal inertia of the preheated material in this phase of the test, guarantees homogeneous and continuous heat.

There have been no significant changes in temperature in the front part and internal side. On the contrary, heat dispersion for Boot 2 and Boot 3 has increased in the external side.

The sole area has confirmed the trend already detected after 17': it is clear that Boot 1 has a bigger thermal insulation than the other two soles, for which there have been a significant increase in temperature in the “ball of the foot” area.

Overall it is reasonable to assert that Boot 1 offers less heat loss, followed by Boot 3 and Boot 2; this in accordance to what has been found in the sensors output and in the subjective comfort perception.

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8 Conclusions

This thesis not only contains some relevant scientific data but also tries to gather all the knowledge acquired developing a new holistic approach to the design of outdoor functional gear and clothing. Following a growing market and its continuous request of innovation and novelties it has been possible to answer to specific demands coming from some of the leading outdoors companies.
Starting from a detailed analysis of how back protectors for snow sports perform in achieving thermal and ergonomic comfort, it has been possible to set the standard for the testing in simulated conditions obtaining consistent and reliable results. In this case, to add value and consistency to final results, the output coming from sensors have been verified to be in accordance with the subjective comfort perception of each volunteer.
The third validation method has been the use of thermo graphic imaging, obtaining a clear evidence of heat distribution pattern of each back protector tested.
At the same time specific tests have been performed to validate the impact properties of the same back protectors, which results are reported in other literature.
The use of innovative materials such as polymeric foam with low density and a shear-sensitive behavior, coupled with perforated structure, showed major differences for both temperature and tester microclimate, delivering better perspiration and thermal insulation. The above-mentioned foamed back protectors has demonstrated to increase also the ergonomic comfort due to its non-rigid structure which allow better freedom of movement.

The work has continued with the investigation on fundamental aspects of ski boot design to achieve the best performance in terms of mechanical properties, thermal and ergonomic comfort. Since skiing take place in some of the harsher environmental conditions, the thermal comfort achievement become of crucial relevance, not only to ensure proper skiing performance but also to guarantee the skiers safety in avoiding pain and frostbite. Also the plastic outer shell of ski boot contributes to the final result in terms of comfort and therefore performance. For these reasons all ski boots components have been specifically investigated to find innovative materials to be applied with more proficiency in the industrial production.

Three different ski boot liners, made of different materials, have been tested to evaluate their insulating behaviour and their moisture management capability. Tests have been conducted in climatic chamber and than repeated in real skiing conditions.

Evidences have shown better thermal insulation for liner made of closed cell EVA, on the contrary the presence of cracks and porosities in the cell walls allows a larger air movement inside the liner, this implies that moisture is able fill up these spaces decreasing insulation. The chemical composition of the outer part of the upper (PE and PVC) appeared to not have a significant effect on thermal insulation.

Again, infrared thermography has demonstrated to be a useful tool to investigate both heat losses from the liner and feet temperature.

In conclusion, EVA closed cell material has resulted as the best technological solution to ensure decent overall thermal comfort in colder environment, offering the highest level of protection in cold environment even if this solution may lead to slight overheating in warmer skiing conditions.

The second main ski boot part is the plastic outer shell. Even if liners made of EVA closed cell can be tailored via thermo-formation, in some cases this process could not be enough to provide the absence of pain and its negative consequences. It has been demonstrated that boot internal volume can influence dramatically the blood circulation and thus the overall comfort. It has been observed major feet temperature decrease compared to correct volume configuration, causing pain and side effects in the achievement of proper thermal comfort. These are the reasons that led companies starting to think to thermo-formable ski boot shell to avoid pressure points, pain and blood circulation alterations, causing ergonomic and thermal discomfort.

A comparison between different plastic materials in the thermoforming process in terms of deformation and memory effect has been reported. Evidences have shown that boots made of the material with lower modulus at 80°C is the one that can achieve the largest deformation after the thermo-formation process. In fact, this represents the highest temperature with which operate avoiding burns on the feet. Moreover, it has been also demonstrated that thermo-formation process in terms of initial deformation and memory effect is strongly influenced by the thermoplastic material used, the heating time, and the

cooling procedure. The evaluation of the mechanical behaviour of ski boots after thermo-formation process has shown no changes in the ski boot performances.
Moreover, results of this work have appeared useful to contradict some of the common routine in boot fitting (e.g. preferring rapid ice cooling after thermo-formation instead of ambient cooling).
The third ski boot component that has been investigated is the sole. This component is crucial in the achievement of grip performance and in avoiding slips and falls when walking over icy and wet surfaces. Again, mechanical properties of outdoors gear not only give their contribution for pure performance but also become necessary to maintain high-level safety standards.
Even if previous works have investigated the friction behaviour of ski boot soles for alpine skiing, showing that the dynamic coefficient of friction depends on the roughness and on the crystalline structure of the materials, no real improvement in traction on the ice has been demonstrated until the introduction of sole inserts made of composite materials with rubber and glass fibres. The increased grip on icy surfaces can be ascribed to glass fibres stiffness, which is able to generate a mechanical grip on ice surface; moreover, the increased contact angle and water repellence contribute to decrease the formation of a water layer below the sole. Evidences coming from this work find their applications over a wide range of winter products.

Finally, hiking and mountain boots do not make exception in the outdoor industry when the achievement of performances, comfort and safety is pursued. Since one of the most relevant targets in footwear design is the protection from physical trauma and environmental extremes, comfort properties have to be taken into account. In this work has been possible to simulate winter walking activity in a climatic chamber under controlled environmental conditions. The use of wireless miniaturized temperature and relative humidity sensors, coupled with the investigation of the comfort subjective perception of each tester, provided clear information on how the footwear perform with regard to thermal comfort and breathability. Nowadays, although waterproof boots built using ePTFE membranes are able to offer the right balance between insulation and breathability, it has been possible to highlight slightly different behaviors. Also in this case, accordance between sensors data and subjective perception has been found.
Further investigations have involved the evaluation of the heat retention capability of all the boots tested, outlining a detailed picture of the heat losses in all the parts of each boot.

Results have been compared with those previously obtained, showing excellent matching with what has been found in the sensors output and in the subjective comfort perception.

Finally, the last result that it is hoped to have achieved, is to have contributed to the understanding of the delicate mechanisms that rules the interactions of materials, human body and environment, by making available material science, chemistry and the engineering approach to the scientific community and to some future oriented companies.

The passion for the outdoors in a rapidly changing world climate, suggests paying close attention to the human health with respect to sudden climate change events and extreme environmental condition exposure. It follows that this is a very actual work and its results could become crucial in the design of functional equipment.

9 List of publications

9.1 Internationals Journals

– ***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)

– ***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)

– ***Effect of Compression on Thermal Comfort of Ski Boots*** (Martino Colonna, Matteo Moncalero, Claudio Gioia, Federico De Bon, Elisabetta Farella, Davide Giovanelli, Lorenzo Borotlan) - Procedia Engineering Volume 112, 2015, Pages 134–139 (2015)

– ***Thermo-formable Materials for Ski Boots for Improved Comfort and Performance*** (Martino Colonna, Matteo Moncalero, Marco Nicotra, Claudio Gioia, Federico De Bon, Elisabetta Farella, Davide Giovanelli) - Procedia Engineering Volume 112, 2015, 128–133 (2015)

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- **Ski Boot Soles Based on a Glass Fiber/Rubber Composite with Improved Grip on Icy Surfaces** - *Martino Colonna, Federico De Bon, Fabrizio Tarterini, Matteo Moncalero, Grazia Totaro, Claudio Gioia, Paola Fabbri* - Procedia Engineering 147:372-377 · (2016)

- **Thermo-physiological comfort of soft-shell back protectors under controlled environmental conditions** – *Ada Ferri, Francesca Dotti, Matteo Moncalero, Martino Colonna* - Applied Ergonomics 56:144-152 (2016)

- **Effect of material elastic properties and surface roughness on grip performances of ski boot soles** - Matteo Moncalero, Stefano Signetti, Barbara Mazzanti, Pietro Bruzzi, Nicola M. Pugno, Martino Colonna - accepted from International Journal of Industrial Ergonomics

- **Thermo-formation process of plastic shells for winter sport boots for improved comfort and performance** - *Martino Colonna, Nicola Pazi, Matteo Moncalero, Claudio Gioia, Federico De Bon, Davide Giovanelli, Elisabetta Farella* – Accepted from Sports Engineering

- **Effect of the Environment on the Sport Performance: Computer Supported Training - A Case Study for Cycling Sports**, *Alessandro Pezzoli, Elena Cristofori, Matteo Moncalero, Jacopo Padoan* - Chapter in Communications in Computer and Information Science 464:1-16 · (2015)

- **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

9.2 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.

9.3 Conferences

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10 Work experiences and collaboration

10.1 Work experience

Research activities have been proficiently performed in cooperation with Calzaturificio Dal Bello (Via Frattalunga, 12, 31011 Asolo TV) for ski boots and with Marker Germany GmbH (Penzberg, Germany) for protective equipment.
Extensive research activity is currently carried on with Tasci S.r.l. (Via Trento, 138 Zanè VC), with regard of footwear and clothing under the *Montura* brand.
Full-time employed in Tasci S.r.l. as Product R&D and Area Brand Manager.

10.2 Collaborations

- DISAT, Politecnico di Torino, Department of Applied Science and Technology in the person of Prof. Ada Ferri and Ing. Francesca Dotti
- DIATI, Politecnico di Torino, C.so Duca degli Abruzzi 24, Torino, Italy in the person of Dr. Ing. Alessandro Pezzoli
- DICAM, University of Bologna, Via Terracini 28, 40131 Bologna, Italy in the person of Prof Maurizio Fiorini
- Dipartimento di Ingegneria Industriale – Metallurgia, Viale Risorgimento 4 , 40136 Bologna, Italy in the person of Dr. Fabrizio Tarterini

10.3 Awards

ISPO 2014 gold award for the MAP technology developed with Marker Germany GmbH.

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