

Review

Materials, Designs and Standards Used in Ski-Boots for Alpine Skiing

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Abstract: This review article reports the recent advances in the study, design and production of ski-boots for alpine skiing. An overview of the different designs and the materials used in ski-boot construction is provided giving particular emphasis to the effect of these parameters on the final performances and on the prevention of injuries. The use of specific materials for ski-boots dedicated to different disciplines (race skiing, mogul skiing, ski-mountaineering *etc.*) has been correlated with the chemical and physical properties of the polymeric materials employed. A review of the scientific literature and the most interesting patents is also presented, correlating the results reported with the performances and industrial production of ski-boots. Suggestions for new studies and the use of advanced materials are also provided. A final section dedicated to the standards involved in ski-boot design completes this review article.

Keywords: ski-boots; alpine skiing; ski-boot materials; ski-boot design; ISO standards

Overview of Contents

This review summarizes the most significant results reported in the scientific and industrial literature (patents) in the field of ski-boots for alpine skiing. A critical analysis of the data has been performed in order to highlight the areas of research and the problems that have not been already

addressed, pointing out new possibilities for research and development in this field. The review has been divided in the following sections:

- *Introduction*: provides a general introduction on the development of ski-boots and on unsolved questions.
- *Ski-boot designs*: the effect of different designs and the evolution during the last century are reported along with a review of the effect of design on injuries and performances.
- *ISO Standards*: the standards involved in the preparation of ski-boots are reported, highlighting the most important features that are needed for ski-boot security.
- *Materials used for structural parts (cuff, shell and tongue)*: this section analyzes the structural materials used for ski-boots, correlating the chemical structure and the visco-elastic properties of the plastic material with ski-boot performances.
- *Buckles*: the materials used for buckles are reviewed.
- *Ski-boot soles*: the different types of soles used in ski-boots are reviewed, with suggestions for new hybrid soles with improved grip and performances.
- *Liners*: the effect of liners on thermal and ergonomic comfort is discussed.
- *Evolution, new trends and conclusions*: in this section the new trends and ideas for further research are discussed, along with a summary of the main results reported in this review.

1. Introduction

Skis have been used for 2500 years to permit the motion of people living in countries where the snow was present for several months a year. The first skis were only plank of woods with laces to link the traditional leather boots used in the Nordic and Alpine regions. At that time skiing was mainly performed in flat areas to help the transportation of loads and for this reason the first recreational activity with skis was cross-country skiing. Alpine skiing was born only afterwards and, therefore, the first equipment used to ski down the steep terrains of the Alps was developed starting from those already used for skiing in flat snow-fields (thin skis, leather boots and heel free bindings). However, the characteristics of those materials were not satisfactory for the needs of alpine skiers. The development of alpine ski equipment has been done, in the beginning, mainly by trial and error, using on-snow tests. However, in the last few decades, the research in the field of plastic materials and the optimization of new software for the design of sport equipment have permitted the development of new materials and designs that have increased the level of performance, security and comfort of ski-boots [1]. These improvements have been driven by the growth of alpine skiing as a recreational sport. The new users request lighter materials, more comfort, increased durability and improved performances. With the increasing number of users, new standards and rules for the production of safer materials have also been developed.

Despite the large market of ski equipment, not many scientific papers have been published on this subject in the past. Moreover, most of the scientific work regarding the development of new materials and designs for ski-boots has been published as patents. However, in the last few years an increasing number of interesting papers have been published on this topic. For this reason, the aim of this review is to report the main results of scientific papers and patents in order to present the “state of the art” in materials and designs used for ski-boots. Some unpublished data will be also reported in order to

complete and clarify the results already described in the literature. Every part of the ski-boot (cuff, shell, liner, buckles, soles *etc.*) has been analyzed in terms of design and materials used; particular emphasis has been given to the combined effect of design and material properties on the final performances and on the prevention of injuries. The materials used for ski-boots dedicated to different skiing disciplines have been correlated with the viscoelastic, chemical and physical properties of the materials used for the different parts of ski-boots. The sectors that lack scientific studies are also analyzed with suggestions for new studies for the development of boots with improved performances. On the basis of the results of published papers and patents and on the evolution of ski-boots, a trend for the development of future ski-boots is also provided. The ISO standards for the construction of ski-boots are also reviewed, highlighting the problems and the lack of international norms dealing with ski-boots.

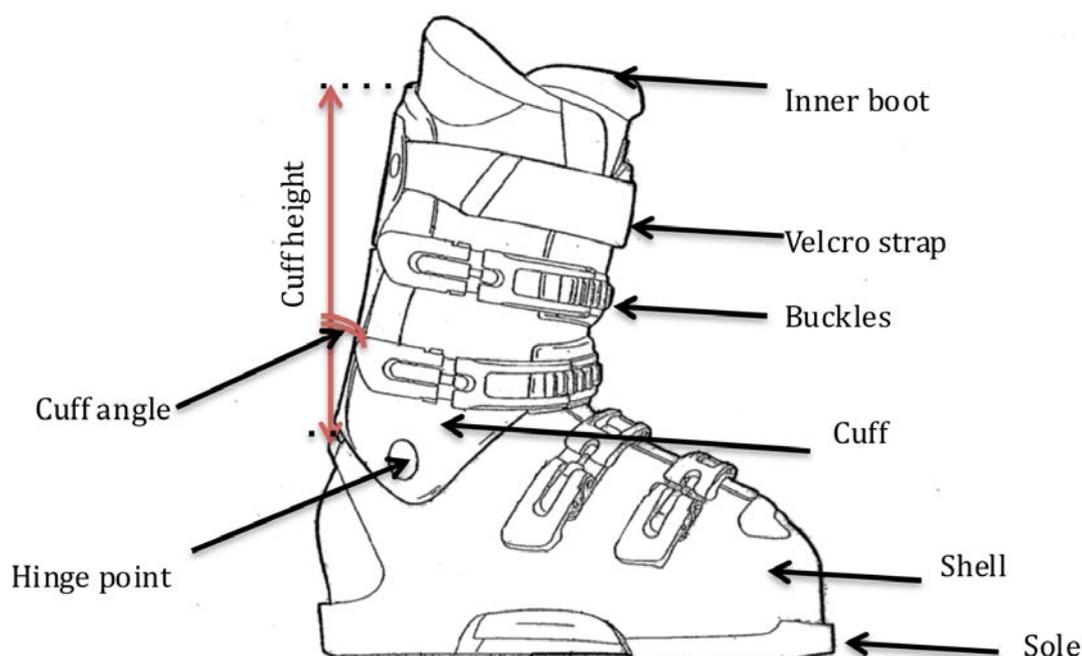
2. Ski-Boot Designs

Ski-boot performances have been significantly improved in recent years using new materials and new designs. In our opinion, in order to deeply understand the reason for these improved properties and to predict new trends, an analysis of the evolution of ski-boot materials and designs in the last century is necessary. Even if the number of ski-lifts and of alpine skiers was dramatically increasing, the ski-boots used in the 1950s 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 permitted a much stronger control of the edges and a more precise and fast skiing [2], new boots were necessary. The first changes were made in order to improve the boot stiffness and to allow a greater control by using stiffer and thicker leathers 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, who inserted elements made of fiberglass reinforced epoxy resin in 1947 [3]. Using the knowledge acquired on reinforced epoxy composites, Lange produced in 1960 the first ski-boot completely made of plastic, using acrylonitrile butadiene styrene (ABS) polymers [4]. 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 [5]. The problems connected with the use of ABS plastic were partially solved in 1965 using Adiprene, a thermoplastic polyurethane manufactured by Dupont. With this new material it was possible to produce ski-boots by injection molding. In the same year, Rosemount introduced to the market the first ski-boots completely made of composite materials, using fiberglass epoxy resin composites, with a shell that was made in two separate parts to permit the insertion of the foot [6]. The mass production of plastic ski-boots started in 1966 with Lange that used an *Overlap* design, made of two parts, the lower part called shell and the upper part called cuff (Figure 2). In the same year production was also started by Nordica in Montebelluna (Treviso, Italy) in collaboration with API Plastic, using a polyurethane made by Bayer for aerospace applications (Desmopan) [7] (Figure 1).

Figure 1. First ski-boot with plastic shell and cuff, molded in Montebelluna, Italy (picture courtesy of API Plastic).



Figure 2. Ski-boot parts for an *Overlap* ski-boot.



In 1972, Hanson introduced the rear entry design that was afterward used by Nordica and Salomon [8,9]. Rear entry ski-boots have gained a large commercial market in the 80s and 90s. However, their production has been decreasing in the following years and rear entry boots are currently used only for youth and rental boots [10]. One of the reasons of this change can be ascribed to the force needed to remove the foot from a rear entry boot that is higher compared to that from an *Overlap* ski-boot and can be a major problem in case of ankle injuries [11]. Another reason can be connected with the difficulty to adapt the shape of the front part of the shell of the ski-boot to the foot shape and therefore have a precise control of the skis. The last important innovation in ski-boot design was made by Eric Giese, a former NASA engineer, in 1979. Taking inspiration from the joint of

spacesuits, he designed a ski-boot that was made of an additional tongue, which was controlling the flex of the boot [12]. This construction was named *Flexon* design and now is also known as *3-pieces* design or *Cabrio* Design. In the last few years, several new models have been introduced to the market; however, the main construction designs have always been related to the *Overlap*, the *3-pieces* designs or to a combination of these two designs.

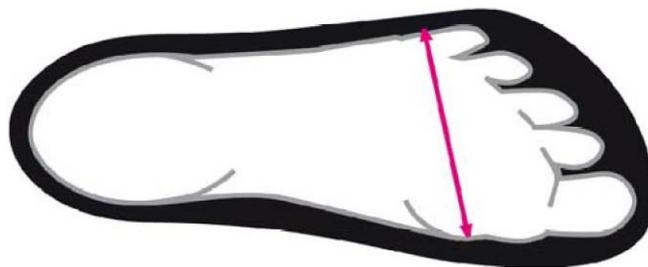
Nowadays, ski-boots are composed of several parts assembled using screws and bolts. A standard ski-boot with *Overlap* construction is composed of the parts reported in Figure 2. Other parts such as the footboard (a plastic or rubber part between the shell and the sole of the inner boot) and the tongue can be also present in the ski-boot. Every part of the ski-boot is made of a different material and the parts are assembled by means of metallic or plastic connectors. The choice of the right material and design is made in order to have:

- Efficient transmission of loads from the skier to the ski edge to control the ski.
- Quick connection of the boot with the binding and safety release of the boot in case of fall.
- Absorption of shocks.
- Protection of the foot and of the ankle from injuries due to overloads during falls.
- Good comfort with uniform foot pressure and temperature/humidity optimal conditions.

The design of ski-boots is of fundamental importance in order to combine good skiing performances with comfort. The functional parameters to be taken into account when designing a ski-boot are:

- Plastic width in the different parts of cuff and shell.
- Shell *Last* (maximum width of the inner part of the shell) (Figure 3).
- Geometry of the sole.
- Cuff height and angle (Figure 2).
- Hinge point between shell and cuff (Figure 2).

Figure 3. Shell *Last* that measures the internal width of the larger part of a ski-boot.

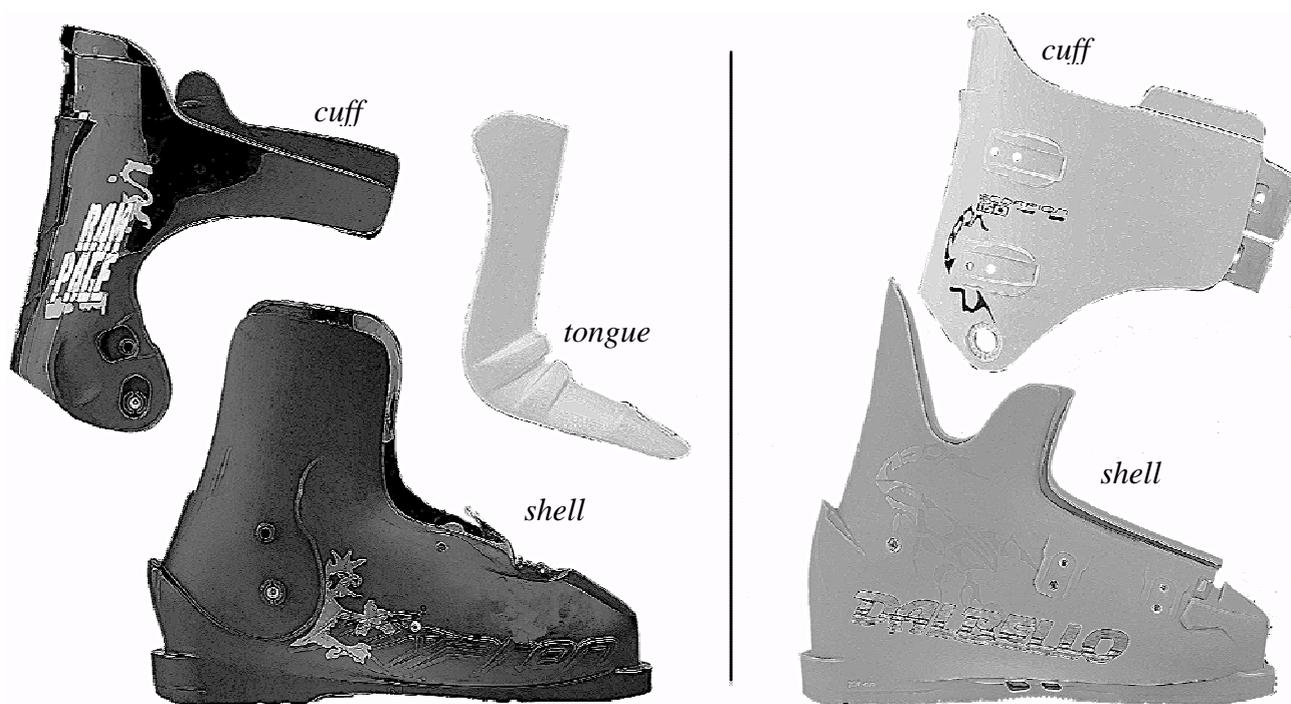


The internal form of the shell and of the cuff must be shaped to follow the anatomical shape of the foot. However, since foot shapes are different from person to person, a shell shape that can fit all feet does not exist. Therefore, all ski-boot producers prepare boots with different shapes and *Lasts* depending on their consumer target. For example, a 95 mm *Last* (measured for a size 26.5 Mondopoint) is generally used for racing while larger *Lasts* (up to 105 mm) are used for more comfortable and less precise boots. The shell can be modified by grinding the plastic in the points of pressure or by combined heat and pressure (boot-fitting). The possibility to modify the form of shell

and cuff by heat and/or pressure is not possible with all types of plastic materials and will be described in detail in Section 4.

As previously reported, the two main ski-boot designs that are present nowadays in the market are the two-pieces *Overlap* construction and the three-pieces *Cabrio* construction developed by Eric Giese [12] (Figure 4).

Figure 4. Disassembled *Cabrio* designed (left) and *Overlap* designed (right) ski-boots.



The analysis of the commercial products present on the market shows that the most common design is the *Overlap* that is composed of a lower part (shell) connected by metallic screws to the upper part (cuff). The forward flex of the boot is controlled by the bending of the upper-back part of the shell (spine) and by compression of the lower front part of the cuff on the shell. This second interaction can provide the undesired enlargement of the instep of the shell if the boot is not properly designed. This design provides the best fit in the front part of the shell since the two parts of the shell overlap, and therefore the tightening of the buckles decreases the internal volume providing a tight and precise fit. Moreover, this construction provides a fast power transmission from the skier to the ski edge. For these reasons *Overlap* design is the only one currently used in World Cup racing ski-boots. The *Overlap* construction can sometimes give rise to problems in entry and exit of the foot from the boot in cold weather conditions, especially if stiff plastics are used.

Cabrio design is less used with respect to *Overlap* design, even if for some producers (Dalbello and Full Tilt, as reported on their websites) and for some skiing disciplines (freestyle and mogul skiing) is the preferred design. *Cabrio* design does not use friction to resist the flex. Instead, it uses a separate piece of plastic (the tongue) that acts as a spring [12]. This has two advantages: first of all the application of force is progressive, and second the boot returns to its original position when the force is released. In order to ensure that the flexing force remains under control even with extreme bending, the plastic is formed into the same bellows-like shape used in spacesuits. The result is a smoother flex that

starts off soft and progressively stiffens [12]. When tightened, the mid buckle pulls the foot rearward, which helps keep the ankle in the rear pocket of the boot [12]. The progressivity of the flex makes this type of ski-boots very efficient in adsorbing shocks during landings or skiing in moguls, and this is the reason it is the design of choice for freestyle and off-piste disciplines. Moreover, the possibility to move the tongue permits an easier entry and exit of the foot from the shell with respect to the *Overlap* construction. The main drawback of this design is related to the difficulty to adapt the shell shape to the skier's foot closing the buckles. This has a negative effect on the control of the edges with the front part of the boot and for this reason this type of boots is not used anymore in World Cup races. However, the use of thermo-formable liners (Section 7) permits the use of shells with a narrower *Last*, without compromising the comfort and allowing a more precise edge control. Moreover, since the flex of *Cabrio* designed boots is mainly governed by the tongue, the flex stiffness of the boot can be easily modified by changing the tongue with one made of a plastic with different stiffness. On the contrary, it is more difficult to change the flex of an *Overlap* designed boot since it requires the use of different materials for the cuff and/or the shell. In the last few years a combination of the two designs has been developed, with a tongue and front part with *Overlap* construction. This new design combines the precise fit and edge control of *Overlap* construction with the flex progressivity of the *Cabrio* design.

Several design parameters are fundamental in order to improve performances and reduce stresses and injuries. For example, as widely reported in the literature [13–19], the angles of tibia and foot with respect to the base of the boot and the pressure of the foot on the base of the ski-boot are responsible for ski injuries. Some researchers have studied the correlation between ski-boot design and load at the knee joint [20,21]. The results reported show that more than 30% of knee injuries are caused by excessive ligament strain [20,21]. Also, ankle and foot injuries (approximately 7%) are due to skiing dynamics and skiing posture [20,21]. It is also reported in the literature [19] that the injury mechanism for anterior cruciate ligament (ACL) rupture involves the valgus movement combined with external rotation. According to other authors [15], ACL rupture can occur when the skier tries to stand up after or during a fall. The injury mechanism involves the combined valgus movement with deep flexion, which causes internal rotation and anterior displacement of the tibia. In all cases, it is clear that moving from the physiological varus-valgus angle (Figure 5) of 170° increases the tangential forces on the tibial plateau, thus decreasing knee stability. Since many skiers have valgus or varus leg alignments, proper skiing posture can be achieved by machine milling the boot sole or moving the position of the cuff with respect to the shell using a canting system positioned in the hinge point between cuff and shell, until a good posture is obtained. A different approach has been developed by Corazza *et al.* [22] that have studied the forces that causes the medial collateral ligament injury (Figure 6) using a boot-board that can measure the forces acting during the turning phase. The loads applied during the turning phase (Table 1) have been measured using a boot-board instrumented with four pressure sensors. From the data obtained from the boot-board, a special finite element model (FEM) was developed in order to design a ski-boot able to decrease the stresses responsible for knee injuries.

Figure 5. Varus-valgus angle and related medial collateral ligament injury (a). The force transferred from the femur to the tibia can be decomposed as shown in (b) in normal and tangential forces. In (c) F_1 and F_2 are forces normal to tibial plateau, t_1 and t_2 tangential forces. An increase of 10° of varus-valgus angle respect to normal physiology increases tibial plateau tangential force by a factor of 2 (from reference [22]).

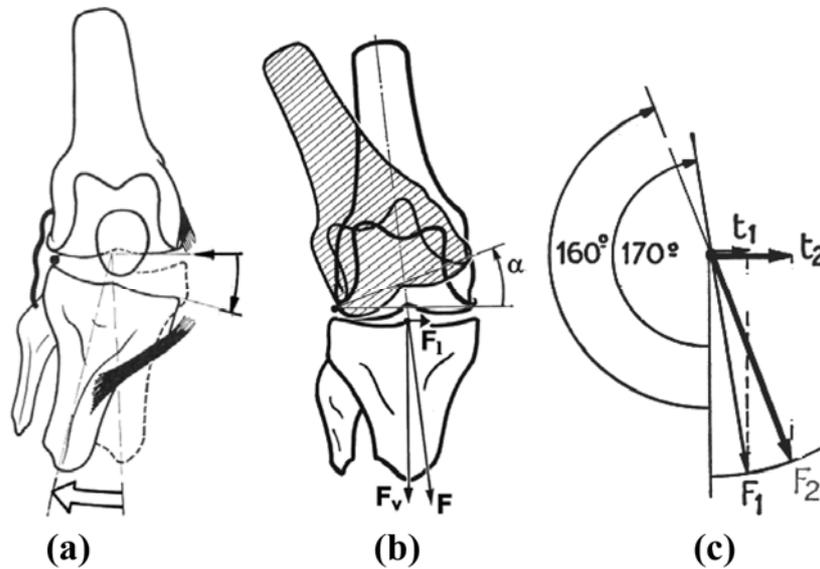


Figure 6. Forces acting on the skier during turning phase (a). F_{GROUND} (ground reaction) acts eccentrically respect to the skier axis generating M_{GR} moment that deforms the lower part of the ski-boot (b). M_{GR} moment acting on the ski-boot sole causes sole and sole joint deformation resulting in drift angle β that reduces the real value of the ski inclination on the ground (from reference [22]).

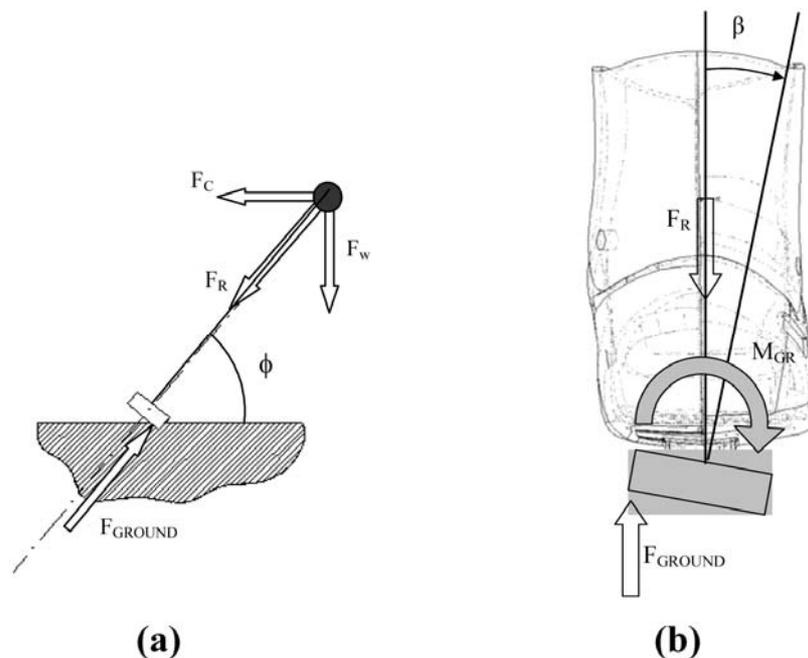


Table 1. Loads applied during the turning phase [22].

Position of the force or moment	Mean acting loads during turning phase
Anterior left	235 N
Anterior right	2 N
Posterior left	755 N
Posterior Right	137 N
Moment exerted along medio-lateral axe	-41.5 Nm
Moment exerted along antero-posterior axe	19.1 Nm
Resultant Force	1129 N

On the basis of these results, the authors have developed an innovative ski-boot in which the angle between the leg and the ski was not modified by changing the angle between the cuff and the shell, but by changing the angle between the lower part (sole) and the shell, which were connected with screws. Petrone *et al.* [23] have used an instrumented boot-board (Figure 7) which was also able to stiffen the ski-boot by connecting the boot-board to the boot shell. The method was also implemented using a Motion Capture technique in order to measure the boot deflection patterns under cyclic loadings. A set of 46 semispherical markers (6 mm diameter) was placed on the boot surface to define a reticular mesh of control nodes (Figure 8). In this way, the authors have been able to record the torsional (Figure 9) and bending moments applied on the ski-boot. They have found that the Rear Restraint Torsional Stiffness Kt^{RR} (Figure 9) presents a 20% increase when the boot-board was connected (ON position) to the shell with respect to the non-connected position (OFF). The peak values of the torque transmitted by the boot-board (Figure 10) are found in correspondence of the edge transition from external to internal turn. The torsion moment showed minimum values in correspondence with the maximum roll values, therefore suggesting that the boot-board stiffening effect is not requested when the ski is in full carving conditions.

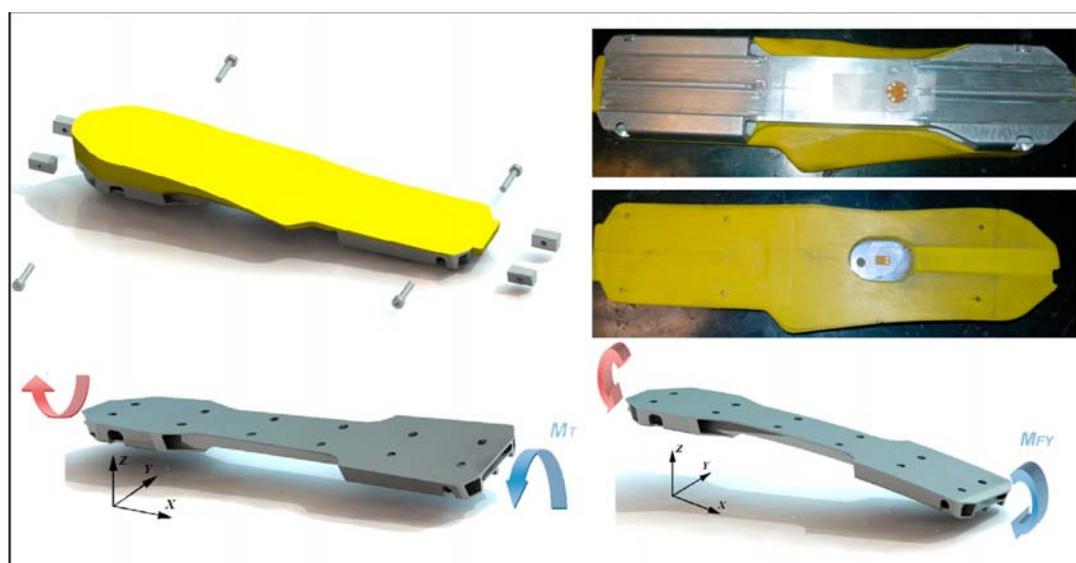
Figure 7. Instrumented boot-board (from reference [23]).

Figure 8. Analysis of ski-boot movements using a Motion Capture technique (from reference [23]).

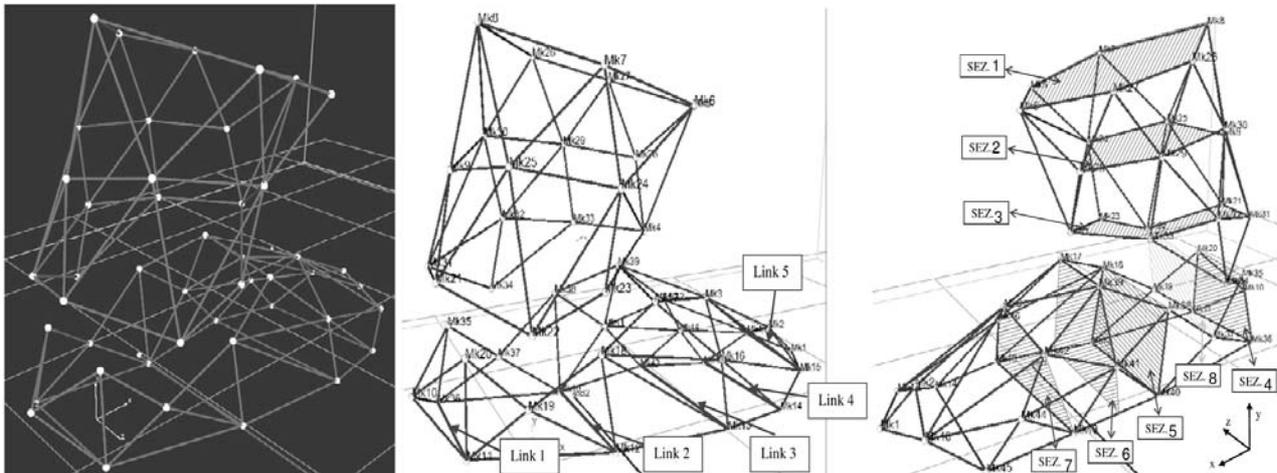


Figure 9. Torsional stiffness of ski-boot (from reference [23]) with the boot board connected (ON) and non-connected (OF), presence of a dummy foot (ND when no foot was inside the boot or DF when present) and with clips open (OP) or closed (CL).

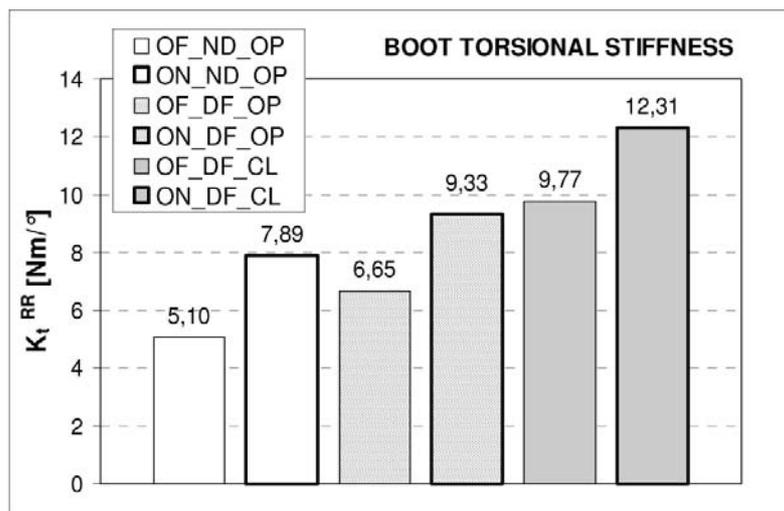
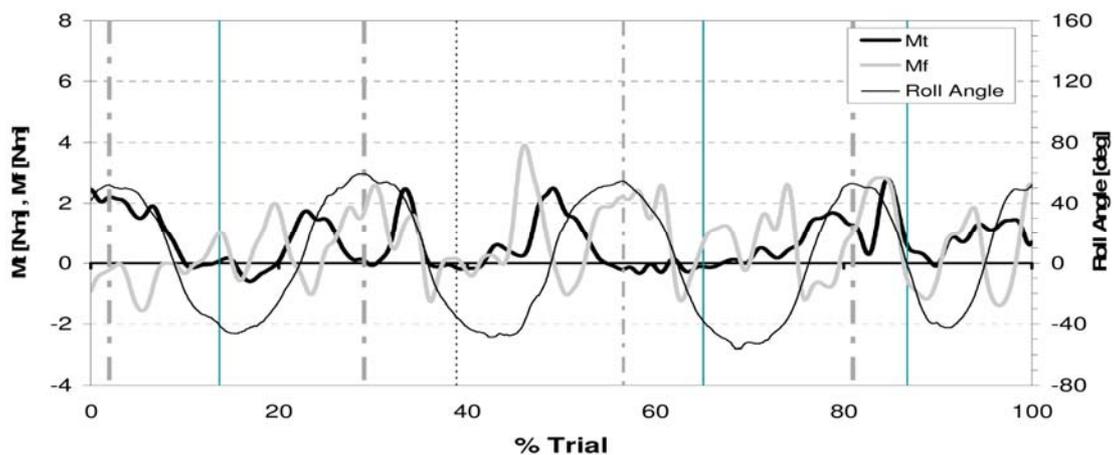


Figure 10. Torsional (M_t) and bending moments (M_f) during on-snow slalom tests in OFF state (From reference [23]).



Instrumented boot-boards and pressure devices have been extensively used for the determination of the loads that are present during skiing [24–28] with the aim to understand the causes of injuries, and design more efficient and safe ski-boots. For example, Schaff *et al.* [29] have studied the effect of foot pressure patterns in ski-boots with different designs and dimensions. They have found that the geometry over the dorsum of the foot (instep) has an important influence on the comfort and on the performances since a poorly adapted boot can increase the forefoot load during flexion. They have also found [29] that rear entry boots allow a higher force transmission compared to conventional *Overlap* boots, since present higher pressure values along the tibia near the boot top. Kuipers *et al.* [30–32] have studied the effect of a modified ski-boot to prevent injuries in mogul skiing. The idea at the base of the study was to avoid the boot induced anterior drawer (BIAD) effect responsible of ACL injuries that could be caused by stiff ski-boots. A ski-boot with an increased forward lean flex was prepared in order to obtain a reduced BIAD. The smoother flex was obtained by cutting parts of the cuff and of the shell close to the instep. A mobile high-speed camera was used to monitor the skiing movements. The force needed to bend the boot was lower compared to that of a traditional ski-boot but the skier did not felt any problem apart a slight decrease in speed control and balance. On the contrary, shock absorption and forward flex were increased. The analysis of the forces applied on the knee-joint pointed out a decreased force using the modified ski-boot with respect to the un-modified ski-boot and for this reason the authors claimed that the modified ski-boot should prevent ACL injuries. These results suggest that boots with *Cabrio* design should be less dangerous for ACL injuries with respect to boots with *Overlap* design due to their more progressive flex. Indeed, this type of construction is generally used in skiing disciplines, such as mogul skiing and off-piste skiing, in which a rough and uneven snow surface is skied. However, other authors report that one of the main causes of leg injuries is the excessive forward movement of the leg. For example, Hauser and Asang [33], studying the influence that ski-boots have on tibial shaft injuries, have found that the relative lack of stiffness and support of the boot shaft allows the tibia to flex forward in dorsiflexion to the point where biomechanical failure occurs. They proposed that the boot shaft should not allow the ankle to reach the “locked position” of the ankle joint (approximately 45°) in dorsiflexion, unless by a forward bending moment which corresponds to the minimum fracture moment of the average diameter bone (200 Nm). Karpf *et al.* [34] have shown, by means of a simplified two-dimensional plastic model of the tibia, that concentrated loads on the distal shaft of the tibia will result in stress patterns identical to those expected for boot-top fractures. They further reported that the use of a higher boot shaft design, that distributes the load in a broad pattern, results in lower stress loadings on the tibial shaft. Other authors [35] have studied the effect of the height and of the stiffness of the ski-boot on injuries. In particular, Lyle *et al.* [36] reported the optimal ski-boot stiffness for the prevention of boot-top fractures. Using a computer model they have concluded that an optimal design should permit application of the force near the knee, as far up the lower leg as possible. They also reported that the force must be distributed over a larger width as possible, in order to avoid the crushing of the bone and injuries to the soft tissue. They also suggest that a stiffer flex should be used in order to obtain greater control since a higher shaft minimizes the maximum bending moment. The optimal height of the boot is a controversial topic since other authors claim that high ski-boots are more dangerous for knee injuries and boot-top fractures [37].

Senner [38] has developed, together with Lange Ski-Boots, a flexible rear spoiler able to decrease ACL injuries. The rear spoiler flexes only when the backward moment exceeds a certain threshold value, yielding of only a few degrees. The results of his studies indicate that a flexible rear spoiler permits a reduction in tension forces on the ACL and the yielding may also produce positive effects on muscles. The data obtained by Senner have been used by Van den Bogert [39] to build a computational model to study the effect of ski-boot design on knee ligament injuries. The effect of the lateral inclination was also studied by Senner *et al.* [40] concluding that canting settings are able to reduce the misalignment but only by about 10%. Increased ski-boot canting settings would therefore be desirable. Knee kinematic studies have also shown [40] that rotational misalignment could not be linked to any significant increase in injury risk.

Ski-boot manufacturers generally sell ski-boots with a Flex-Index value that describes the flexural stiffness of the boot. The Flex-Index was first introduced by Salomon and is generally used by all the producers [10]. However, no information on the test method and on the type of test bench is provided by ski-boot manufacturers. Moreover, the testing temperature (that has a consistent effect on boot stiffness) is not reported by any producer when providing a Flex-Index value. A method for the determination of the force needed to flex a ski-boot has been reported by Reichel *et al.* [41] using a test bench. A prosthesis (Figure 11) has been manufactured with a specially designed ankle joint. The displacement has been measured by a path measurement sensor while the applied force has been measured by a load cell (Figure 12). A hysteresis curve has been obtained flexing forward and backward the ski-boot (Figure 13). The boot has been fixed with angles of 0° and 20° with respect to the applied force. The results obtained point out that the anatomically designed prosthesis is able to perform measurements with higher reproducibility and with the possibility to apply forces in all directions, while with a standard uniaxial-hinged prosthesis this is not possible.

Figure 11. Prosthesis for ski-boot test bench (from reference [41]).



Figure 12. Ski-boot test bench (from reference [41]).

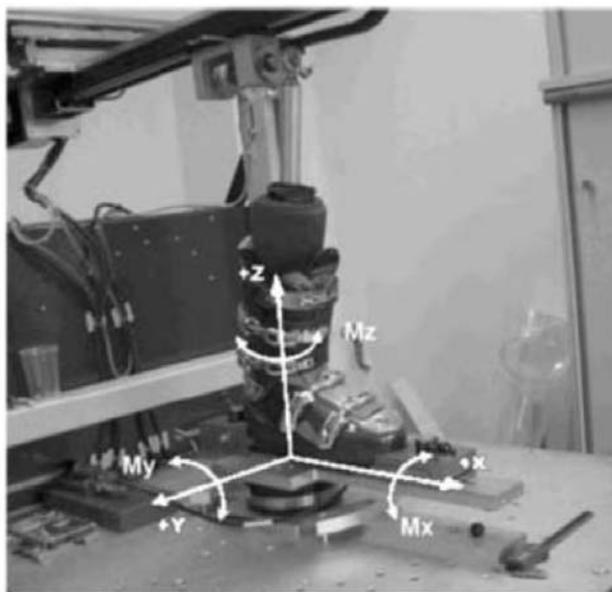
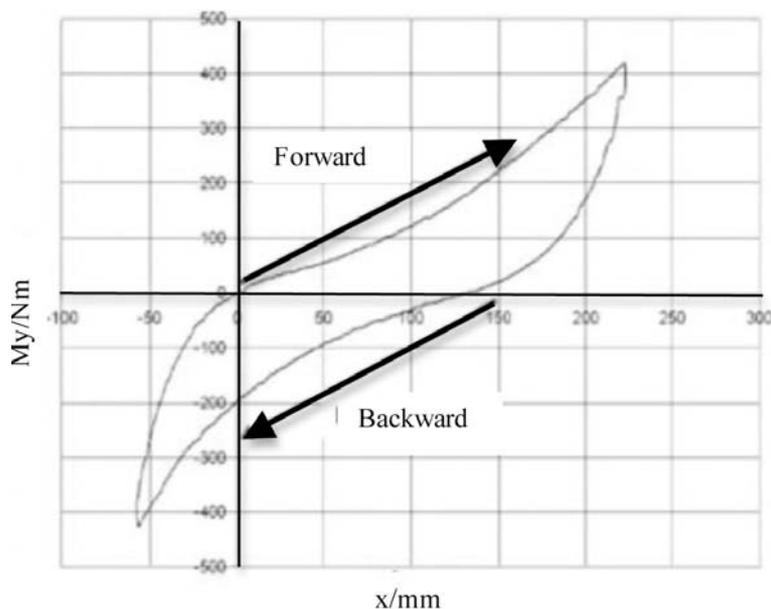


Figure 13. Force-displacement curves obtained with a ski-boot test bench (from reference [41]).



Other studies have been conducted for the preparation of test benches and lower leg prosthesis in order to define a test method and an apparatus for the measure of hysteresis flex curves [42–44]. However, Bonjour *et al.* [45] report that several problems still need to be solved for the development of a standardized test method for the measure of ski-boot stiffness. In particular, in their opinion, only the stiffness of the boot/leg pair is measurable and different results will be obtained with different legs and therefore different prosthesis. Nordica ski-boot manufacturer has presented a method to determine the progressivity of the flex using a test bench able to measure the force-displacement curves. However, no details on the method have been reported in their press-release [46]. In our opinion, the lack of a standardized method for the determination of the flex is a major issue in the

correct choice of the ski-boot and in the comparison of the properties of ski-boots made by different manufacturers. A method that compares the stiffness of ski-boots at different temperatures is therefore fundamental not only for scientists working on ski-boot development but also for consumers. Another shortcoming in the test procedures for ski-boots is the absence of a method for the measure of the rebound speed of the boot after it has been flexed during the turning action. Indeed, the return speed has an important effect on the ski-boots performances. In particular, if the elastic rebound is too slow, the cuff may not be back in time in the neutral position for the following turn or to adsorb an obstacle. On the contrary, if the return speed is too fast it can transmit a backward force to the skier, thus compromising its balance. The return speed is governed by ski-boot design and type of plastic, as will be described in Section 4. Therefore, a standardized method for the determination of the rebound speed is also needed for the development of more efficient ski-boots.

3. ISO Standards

As reported above, no standard test exists for the determination of the flexural stiffness and of the elastic rebound of ski-boots. The only two ISO standards for the design of ski-boots define the area of the ski-boot in contact with the binding. This is due to the fact that the efficient behavior of the binding in releasing the boot during a fall is significantly affected by the geometry and rigidity of the ski-boot part in contact with the binding. Therefore, in order to ensure the proper binding release function, alpine ski-boots must be realized observing limits and prescriptions in terms of dimensions and design of the boot interface. The ISO norms are:

- ISO 5355 (Alpine ski boots—Requirements and test methods) [47].
- ISO 9593 (Touring ski boots for adults—Interface with touring ski bindings—Requirements and test methods) [48].

The ski-boot/binding interface is also ruled by ASTM F944-97 that reports the standard specification for properties of adult alpine ski-boots. ISO 9593 requires a minimum percentage of the area in contact with the bearing surface of the binding of 25% in the toe and of 40% in the heel. In terms of materials used, both standards require that the hardness of the material at the binding interface (toe and heel) must be not less than 50 Shore D (measured at 23 °C). Moreover, the coefficient of dynamic friction at the toe and heel binding interfaces between the boot material and a low friction element of poly(tetrafluoro ethylene) (PTFE, Teflon) must be <0.1. When a material different from TPU is used in the heel part of the boot, there must be at least one longitudinal low friction area to act as a bearing surface for the ski-brake.

Other requirements requested by the ISO standards are the difference in sole length of two ski-boots in a pair (2 mm maximum) and perpendicularity of the sidewalls and toe (1 mm for ISO 5355 and 2 mm for ISO 9593). The mounting point for positioning the binding on the ski must be indicated by a line on each side of the lower surface of the boot; the line must be clearly visible and permanent, not less than 10 mm in length. Ski-boots producers are pushing for the development of new norms that take into account different types of bindings, such as, for example, the binding system for ski-mountaineering developed by Dynafit.

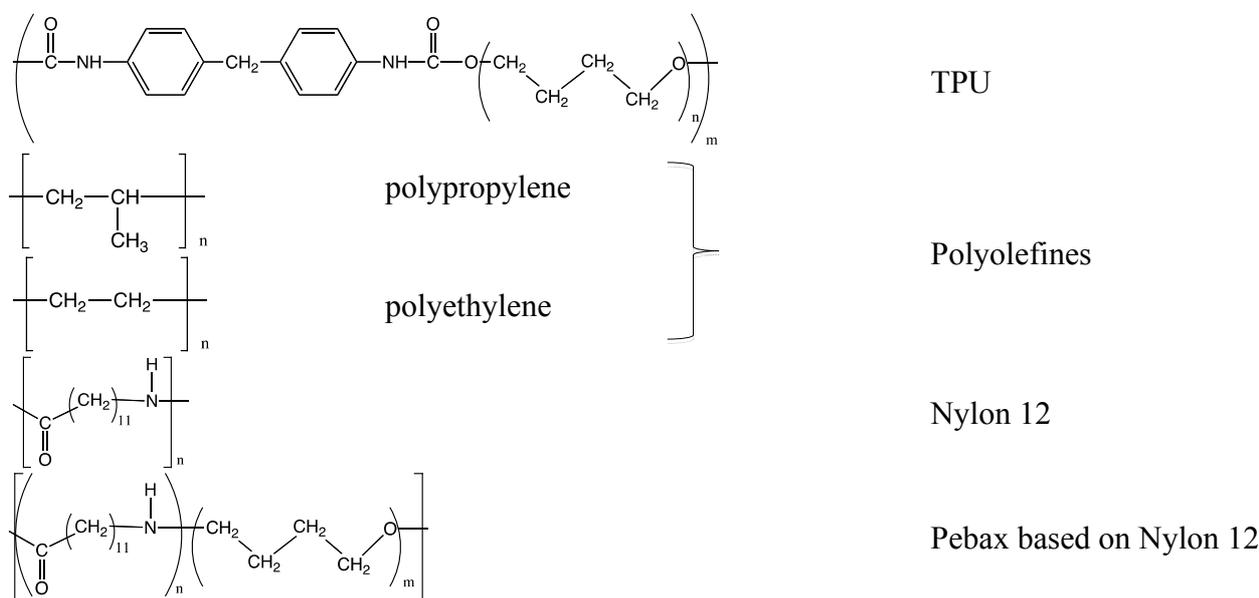
4. Materials Used for Structural Parts

Several materials are used for the construction of ski-boots [49]. Even if in some cases the choice of the material is made on economic and aesthetic bases, nevertheless, all the materials should comply with several important features:

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

Additional important parameters in the choice of the appropriate materials are the density, the transparency and the dye-ability. For these reasons, the “ideal” plastic to be used for ski-boots should be lightweight, have the optimal visco-elastic properties, be resistant to impacts and degradation and maintain the same optimal properties in the widest range of temperatures. There is no single material that completely fulfills all the characteristics reported above and that is clearly superior to the others in every aspect. In several cases, different materials are used for the shell, the cuff and, if present, for the tongue. The optimal type of material must be chosen accordingly to the type of skiing discipline (racing, freestyle, recreational, moguls *etc.*) and of the skier (weight, physical characteristics, skiing technique *etc.*). Generally, the choice of the proper material is performed with a trial and error procedure using on-snow tests with professional skiers. However, in the last few years, test benches for the measure of the flexural behavior, FEM computer aided simulation and dynamical mechanical thermal analysis (DMTA) have been used for the determination of the optimal material for the different part of the ski-boot as will be discussed in the following. According to ski-boots producers [50], the main classes of materials used for ski-boots are thermoplastic polyurethanes (TPU), polyolefin copolymers, polyamide (Nylon) and polyamide-polyether block copolymers (Pebax) (Figure 14).

Figure 14. Polymers used for the production of ski-boot shell and cuff.



A statistical analysis of the plastics used for the models present in the catalogue of one of the largest ski-boots producers (Salomon [50]) indicates that polyurethanes and polyolefines are the most used materials. In particular, 74% of the male models are made of polyurethanes, 11% of polyolefines, 11% of both polyurethanes and polyolefines and the remaining 4% of Pebax. These results have been confirmed by the analysis performed with a Fourier Transform Infrared (FTIR) instrument (Perkin Elmer Spectrum One), equipped with an Attenuated Total Reflectance (ATR) detector (that permits to directly measure the chemical composition of the plastics of the ski-boot) of the models commercialized by a major ski-boot producer (Calzaturificio Dalbello). In particular, the peaks at 1699 and 1727 cm^{-1} were used to identify the polyurethane based materials (Figure 15), the peaks at 1456 and 1439 cm^{-1} were used to identify polyolefin based materials (Figure 16), the peaks at 1635 and 1552 cm^{-1} were used to identify polyamide based materials (Figure 17).

Figure 15. FITR analysis of a polyurethane based material.

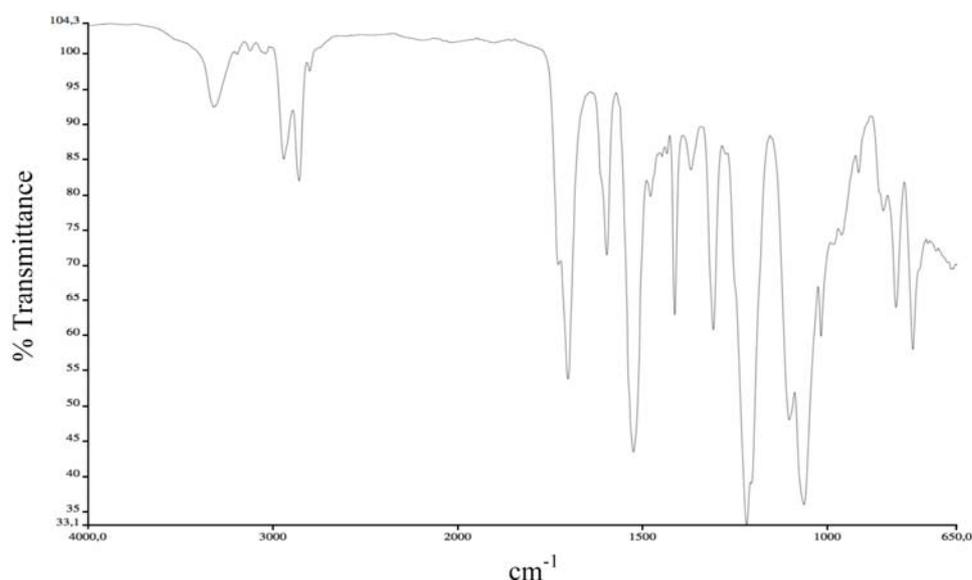


Figure 16. FITR analysis of a polyolefin based material.

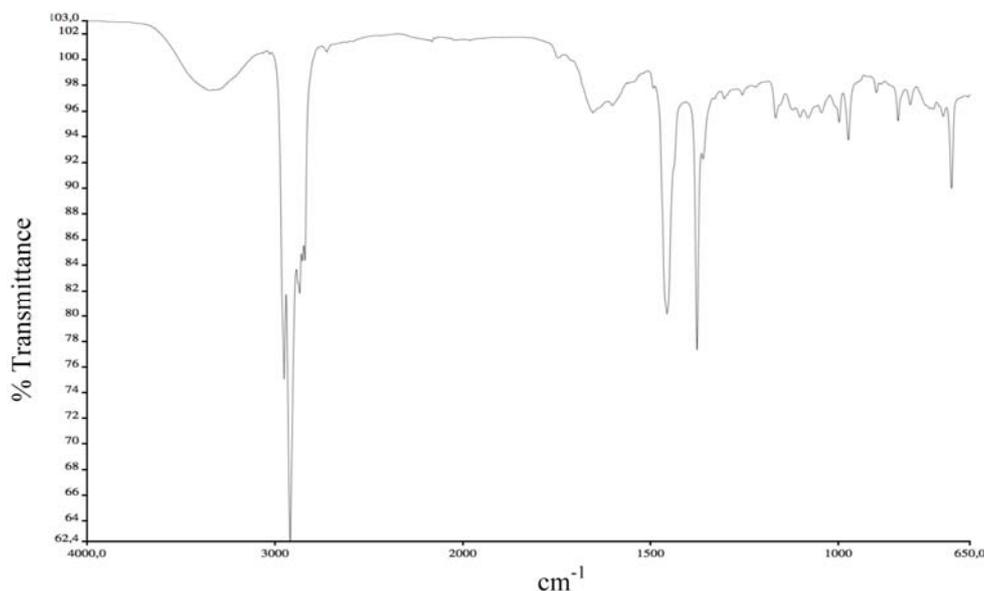
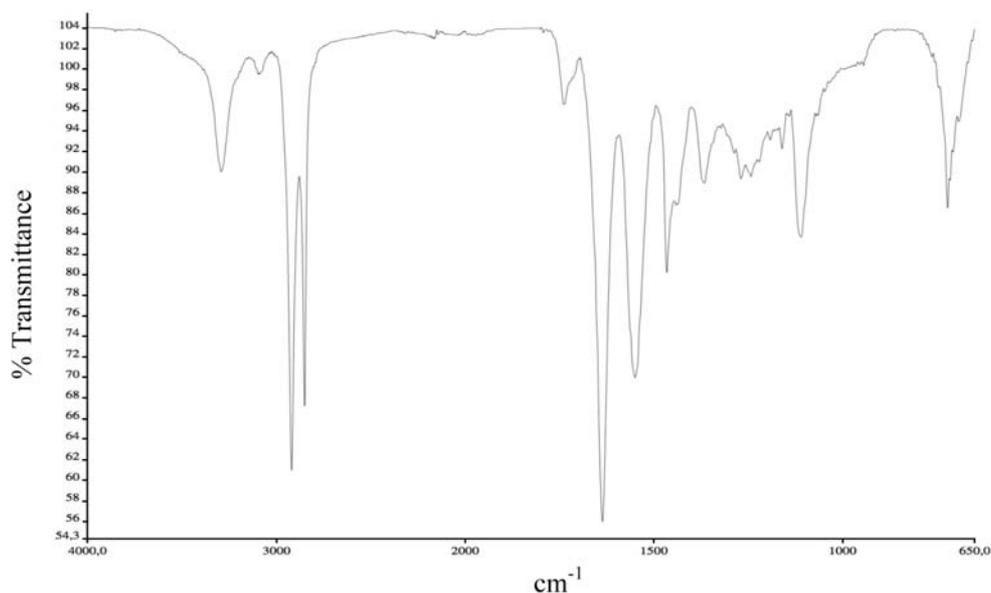


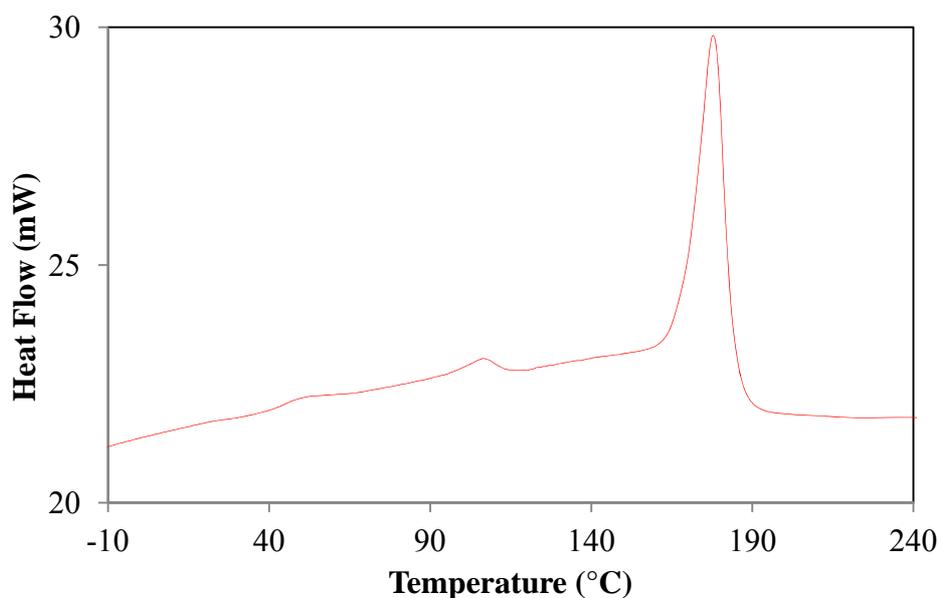
Figure 17. FTIR analysis of a polyamide based material.

FTIR results on Dalbello ski-boots indicates that 72% of male ski-boots models are made of polyurethanes, 25% of polyolefines and the remaining 3% of Pebax. For both producers (Dalbello and Salomon) the models made of Pebax are commercialized as ski-mountaineering boots and are provided with a ski-walk mechanism and a rubber sole. A larger number of models made in polyolefines are used for women and junior ski-boots. In particular, the women models made completely or partially in polyolefines are 57% for Salomon [50] and 52% for Dalbello while for junior ski-boots the percentage is even larger (82% for Salomon [50] and 88% for Dalbello). The reason for these differences among male, female and junior models is connected with the viscoelastic and physical properties of the plastics (as will be explained in the following) and in some cases with the price of the plastic materials. Indeed, polyolefines (that are commodity plastics and cheaper than TPU) are used for less expensive models.

TPUs can have different chemical compositions of both the urethane block and of the soft block. FTIR analysis has shown that the two most used soft blocks are polyether (e.g., poly(butylene glycol) and poly(ethylene glycol)) and polyester. In some cases, ski-boot producers refer in their catalogues to TPUs made with different soft blocks, simply (and erroneously) as polyethers and polyesters. Methylene diphenyl diisocyanate (MDI) is the most used monomer for the preparation of the aromatic urethane block. The presence of blocks derived from MDI has been confirmed by FTIR analysis due to the presence of a peak at 1595 cm⁻¹. Polyethylene and polypropylene are the two most used polyolefines and are often used in blend with synthetic rubbers such as SBR (styrene-butadiene block copolymers) and SEBS (styrene-ethylene-butadiene-styrene block copolymers). The presence of styrene based units has been confirmed by FTIR due to the presence of signals at 1643 and 698 cm⁻¹ ascribable to styrene groups. The most used polyamide is Nylon 12, since it presents the best fatigue properties, lower density and lower water absorption with respect to the most common polyamides, such as Nylon 6 and Nylon 6.6. Pebax is a block copolymer of Nylon 12 with an ether soft block. The chemical structure of the polyamide have been confirmed by differential scanning calorimetry analysis (DSC) analysis since the material presented a melting temperature of 175 °C, that is typical of

polyamide 12 (Figure 18). 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 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 [51].

Figure 18. DSC analysis of a polyamide based material used for ski-boots.



The first property of the plastic to be taken into account when designing a ski-boot is the low temperature impact resistance (Table 2). Petrone *et al.* [52,53] have studied the effect of the impact of a ski-boot against different obstacles. Kinematic data have been collected by means of a stereo-photogrammetric system. The peak values of impact loads have been measured using load cells and accelerometers, against different types of obstacles and kick directions. The highest values of kicking velocity and impact force have been obtained with toe kicks. Impact tests using a drop tower have also been performed. The drop tower tests showed that an energy higher than 43.5 J for shell only and of 214.7 J with a dummy foot inserted are necessary to break the ski-boot at -20 °C. The impact resistance of plastic materials is measured using Charpy (ISO 179) and Izod (ASTM D256) methods with notched samples (since the breaking of the plastic is normally started by the presence of cut and imperfections on the surface). The choice of Charpy or Izod methods is performed randomly by plastic producers and a direct conversion of the values obtained with one method to the other, by a conversion factor, is not possible. The impact resistance of the classes of materials used for ski-boots can be strongly decreased by UV degradation or hydrolysis, since the degradation produces a decrease of the molecular weight of the polymer backbone. Below a certain threshold molecular weight the materials become brittle at low temperature. For this reason, UV and hydrolysis stabilizers are added to the materials used for ski-boots. Old models without stabilizers suffered from unexpected brittle failures. However, up until now no data have been reported in the literature regarding the effect of aging on impact resistance of ski-boots.

Table 2. Properties of the most used thermoplastic materials for ski-boots shell and cuff [54–57].

<i>Material</i>	<i>Elastic modulus at 23 °C [Mpa]</i>	<i>Elastic modulus at 0 °C [MPa]</i>	<i>Elastic modulus at –20 °C [MPa]</i>	<i>Hardness Shore D</i>	<i>Impact Resistance</i>	<i>Density [g/cm³]</i>	<i>Melting Temp [°C]</i>	<i>HDT [°C]</i>
TPU	200	490	970	60	Charpy 16 kJ/m ²	1.18	230	62
Polyolefin	270	387	857	52	Izod 105 J/m	0.89	140	75
Nylon 12	450	846	1113	64	Charpy 8 kJ/m ²	1.01	178	115
Pebax	390	741	1000	69	Charpy no break	1.01	172	97

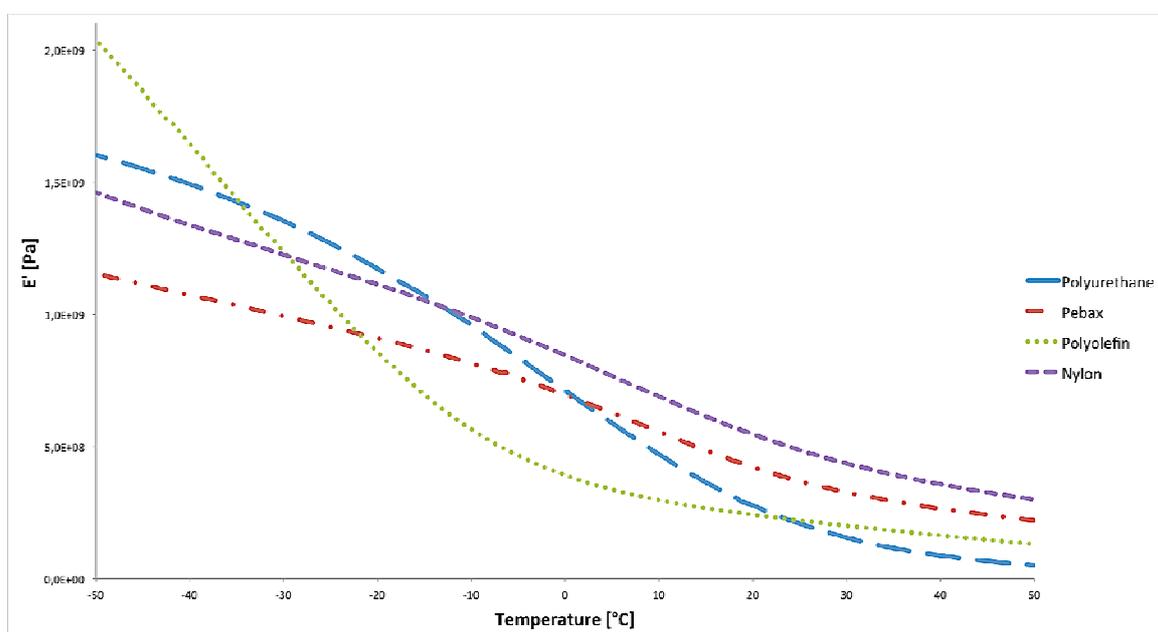
Tensile modulus measured according to ISO 178; Hardness shore D measured according to ISO 878; Impact resistance measured at –30 °C with notch according to ISO 179 (Charpy) and ASTM D 256 (Izod); Melting temperature measured by Differential scanning calorimetry (DSC); HDT: heat distortion temperature at 0.45 Mpa according to ISO 75.

The second important parameter to be taken into account is the elastic modulus measured by ISO 178 (for flexural modulus) and ISO 527 (for tensile modulus). The test specimens should be conditioned according to ISO 291 since it is well known that the elastic modulus depends on the conditioning (relative humidity and temperature) of the plastic materials. The standard conditioning temperature is 23 °C at 50% relative humidity. The materials commonly used in ski-boots have elastic modulus at 23 °C comprised between 100 and 500 MPa, even if in certain parts of the boot (for example, the back section of the cuff) more rigid plastics can be sometimes used. An indirect measure of the modulus can be performed by Shore D hardness measurements. This technique provides a quick and easy indication of the stiffness of the plastic directly on the ski-boot and for this reason is widely used by ski-boot manufacturers. The analysis of the hardness of materials used by a ski-boot manufacturer (Calzaturificio Dalbello) shows that the hardness is always between 62 (for race boots) and 52 (for rental and junior models) Shore D, measured at 23 °C. The elastic modulus to be used depends on the thickness of the shell and cuff and on the desired flex and comfort of the boot. However, it is not only important to take into account the elastic modulus at room temperature but it is probably most important to consider the modulus increase when the temperature is lowered. As previously discussed, the flex stiffness of a ski-boot depends on the geometry (thickness of the plastic and design) and on the stiffness of the plastic used. Since the sport of skiing is performed at temperatures that are not constant and can be as low as –40 °C, it is clear the need for a material that does not change too much its stiffness in order to have a ski-boot with a more uniform behavior in different skiing conditions. All plastic materials become stiffer as temperatures decrease due to the reduced mobility of the polymer chains. However, the increase in stiffness depends on the chemical structure of the repeating unit of the polymeric materials. Moreover, inside a class of materials, different crystallinities and molecular weights can produce different behaviors. The data reported in Table 2 show how polyamide based materials (Nylon and Pebax) suffer of less stiffening with respect

to polyurethanes and to polyolefines (that suffer of the most consistent stiffening among the materials used in ski-boots).

Recently, dynamical mechanical thermal analysis (DMTA) has been used as a tool for measuring increases in stiffness of plastic materials used for sport equipment and also to study the effect of degradation on elastic modulus [58–60]. This analysis is performed applying an oscillating force to the material that can simulate the effect of the cyclic forces applied by the skier on the ski-boot during the skiing action. Several important data can be obtained from this analysis. In particular, from the component in phase with the applied force it is possible to measure the elastic modulus E' (elastic component) while using the component not in phase it is possible to measure the loss modulus E'' (viscous component) [61]. The elastic and loss modulus (measured at 1 Hz frequency) dependence over temperature for the four most used plastic materials are reported in Figures 19 and 20 [59].

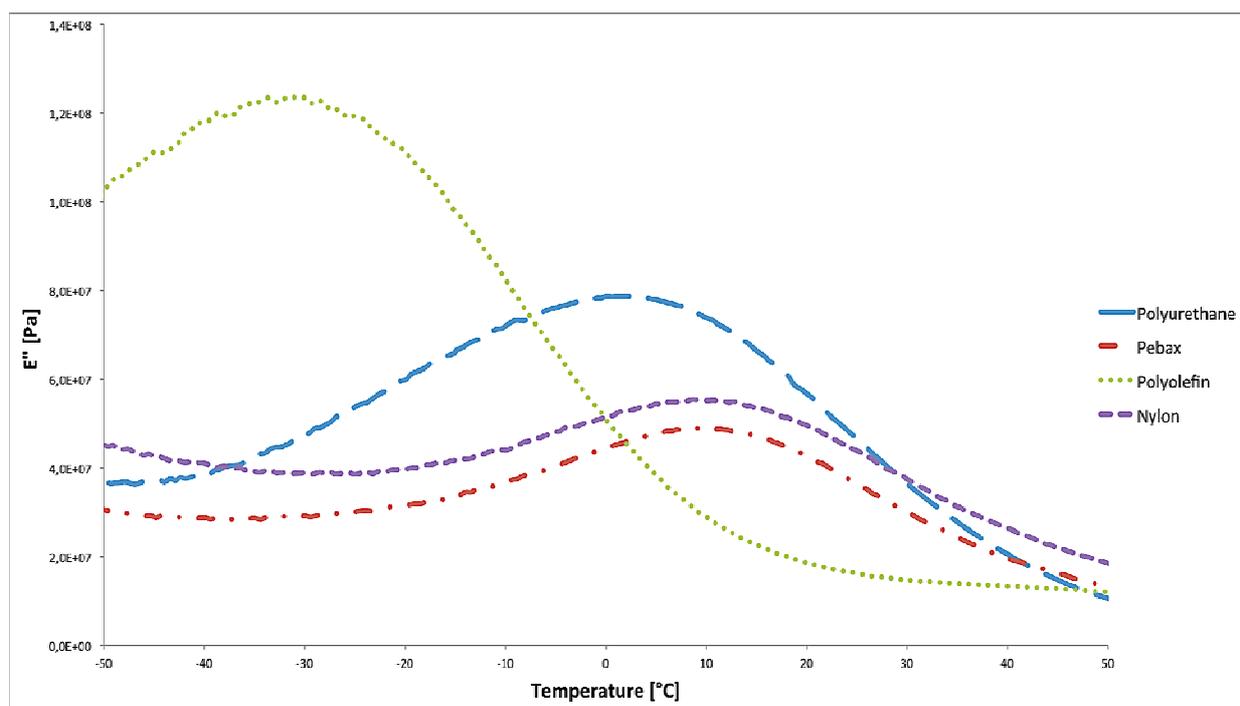
Figure 19. Storage modulus of plastic used for ski-boots shell and cuff, measured at 1 Hz.



The ratio between E' and E'' is called $\tan\delta$ and gives an indication of the damping behavior of the material. The higher E'' and $\tan\delta$, the less elastic is the material and the longer the time needed to return to the initial position after the flex of the ski-boot during a skiing turn (viscous behavior). For this reason, materials such as polyamides, with low E'' and $\tan\delta$ values, are used for the tongue of *Cabrio* design, since a more damping material would not have the spring-like behavior necessary to return the boot to the initial position after the bending of the tongue that gives the turning impulse to the ski [62]. On the contrary, materials with higher E'' and $\tan\delta$ are able to dampen more efficiently the shocks that are applied to the ski-boot during skiing on a rough surface, thus allowing a more relaxed skiing. For the same reason a racing ski-boot cannot be made of Pebax or Nylon since the vibration generated at high speed are not damped by the material. Moreover, the elastic rebound could be too fast, thus compromising the balance of the skier. For this reason, all racing boots are made of TPU (generally with polyether soft segments) that has good damping and an optimal rebound speed. The DMTA results in Figures 19 and 20 provide a better understanding in the choice of materials for cuff and shell made by ski-boots producers. For example, high level ski-boots (commercialized with

Flex-Index higher than 110) are made of TPU that has the best visco-elastic behavior while polyolefines are generally used for recreational and junior boots, which need more damping. Moreover, as will be reported in the following, polyolefines have a lower scratch resistance with respect to TPU and also for this reason are generally not used for high-performance and expensive ski-boots.

Figure 20. Loss modulus of plastic used for ski-boots shell and cuff, measured at 1 Hz.



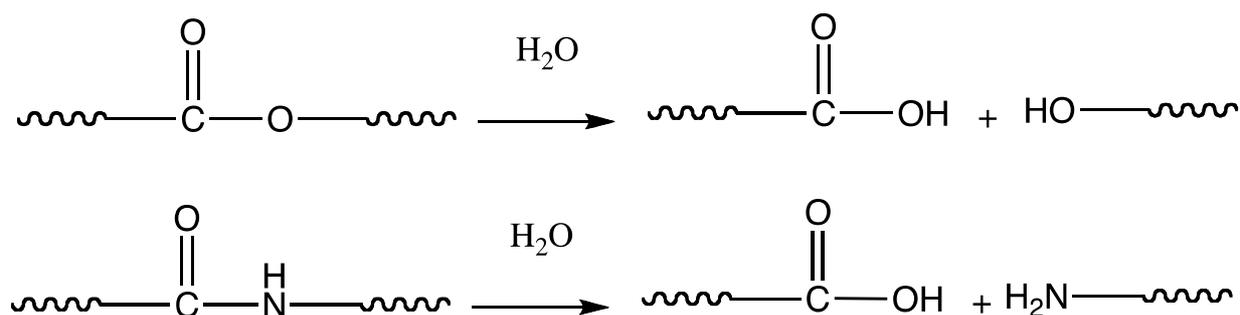
DMTA analysis has been used for the determination of the damping of skis [60]. This study has shown that the behavior of the ski is strongly influenced by the polymeric top-sheet of the ski. In particular, materials that showed a strong damping at 0 °C, as measured by DMTA analysis, provide the best skiing behavior. The effect of different frequencies has also been analyzed and a finite element analysis has been conducted with good correlation between experimental results and DMTA data [60]. On the contrary, a specific study on the damping effect of plastic on ski-boots has never been reported in the literature and correlated with DMTA data.

Another important characteristic to be taken into account when designing a ski-boot is the density of the plastic since the final weight of ski-boots strongly depends on the plastic weight. This is more important when the ski-boot is also used for up-hill walking or climbing, as for example in ski-mountaineering. The lightest plastics are polyolefines followed by Pebax and Nylon while polyurethanes present the higher density (Table 2). A 17% decrease in weight for Pebax and Nylon boots can be expected with respect to TPU boots. The statistical analysis of the ski-mountaineering models present on the catalogue of a major ski-boot producer specialized in ski-mountaineering (S.C.A.R.P.A. [63]) indicates that 67% are made of Pebax or Nylon, 26% of TPU and 7% of a mixture of Pebax and carbon fiber composites. The use of Nylon (that is stiffer than Pebax) permits to produce ski-boots with thinner shells and cuffs and therefore with reduced weight. For the same reason carbon fiber composites are used for ski-boots used in ski-mountaineering races [63].

UV stability is one of the main problems of thermoplastic materials. UV degradation can produce both discoloration of the final product (with problems mainly related to aesthetics) and cleavage of the polymer backbone (that can cause a molecular weight decrease with the consequent drop of thermo-mechanical properties and low temperature impact resistance) [64]. UV degradation is mainly due to the formation of radicals caused by the homolytic cleavage of sigma carbon-carbon bonds. This degradation can be enhanced by the presence of pigments [64]. For example TiO_2 (that is widely used as white pigment) is well known to catalyze the UV degradation of plastics [64]. For this reason, UV stabilizers are generally added by plastic producers. In particular, hindered amine light stabilizers (HALS or HAS) or UV adsorbers (e.g., oxanilides and benzotriazoles) are generally used [64]. Phenolic antioxidants are generally added to the material as stabilizers for thermo-oxidative degradation (mainly generated during the injection molding process).

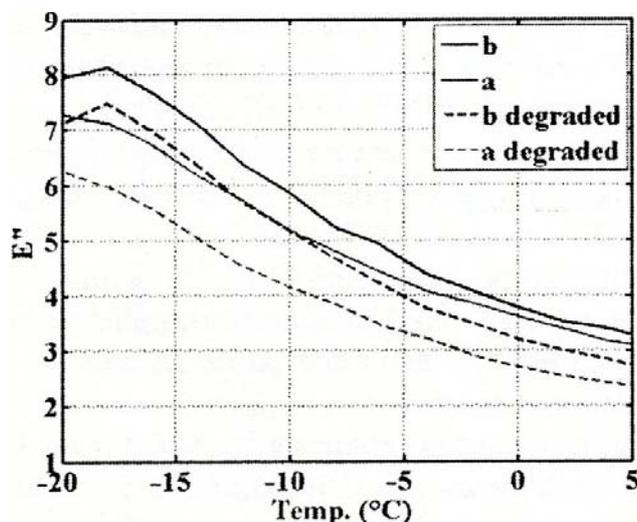
Hydrolytic stability is also a major issue for some plastics. Hydrolysis is a reaction between water and polar groups such as esters, urethanes and amides (Figure 21) [65]. Hydrolysis causes the cleavage of the polymer backbone and the consequent molecular weight decrease. Since polyolefines do not contain polar groups that can be hydrolyzed, normally do not suffer of this problem [65]. For the same reason ether based polyurethanes suffer from less hydrolysis with respect to ester based polyurethanes. Hydrolysis is accelerated by temperature and, of course, by humidity. Soaking the boot in hot water for boot-fitting purposes should be avoided. The effect of degradation on plastics used for ski-boots has been reported from Parisotto *et al.* [58] by means of DMTA analysis of two Pebax samples before and after degradation in hot steam. The results obtained (Figure 22) show a decreased modulus after degradation that can be ascribed to the decreased molecular weight due to hydrolysis and/or to water absorption. On the basis of these data it is clear the importance to store ski-boots in a dry ambient, especially if they are made of TPU, Pebax or Nylon.

Figure 21. Hydrolysis of ester and amide functional groups.



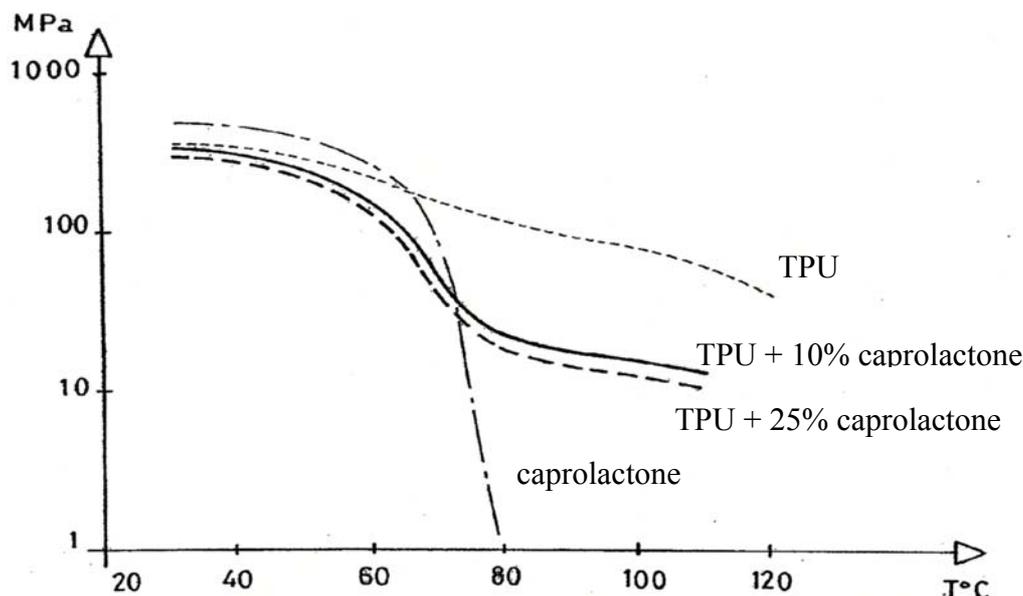
The scratch and abrasion resistances of materials are also important, not only for the aesthetics, but also for the correct release of the binding. Softer plastics generally have less scratch and abrasion resistance and for this reason, according to ISO 5355, materials with shore D hardness higher than 50 must be used for the parts in contact with the binding. However, different classes of materials also present consistently different scratch resistances. In particular, polyolefines are more prone to scratch, while polyurethanes present the best scratch resistance [66]. The scratch and abrasion resistance can be measured according to ISO standard 4649.

Figure 22. DMTA analysis of two Pebax samples before and after degradation in hot steam water (From reference [58]).



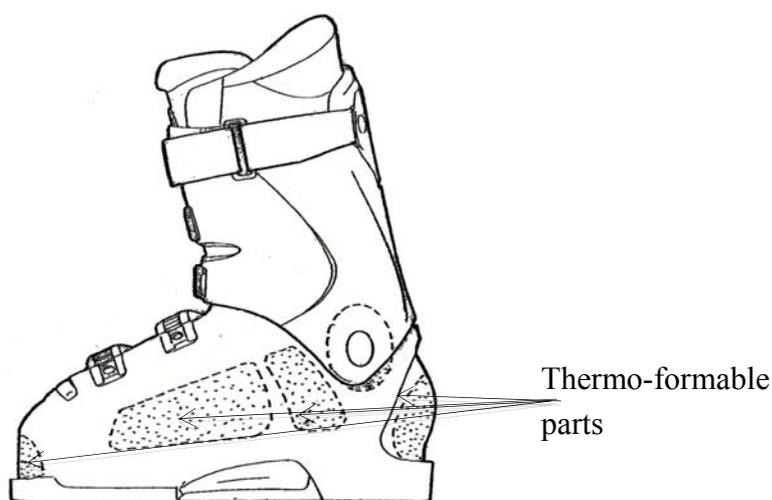
The polymeric materials used for ski-boots belong to the class of thermoplastic polymers, which means that the material can be melted and reformed since it does not have permanent cross-links as in the case of thermoset materials. For this reason, the shell and cuff of ski-boots can be completely recycled. Nevertheless, it should be taken into account that some properties can be slightly decreased during recycling due to thermally induced degradation reactions that occur during recycling. The thermoplastic character of the polymers used for ski-boots can be used to adapt the shape of the boot to the skier foot. Indeed, every foot has a different shape and pressure points can be present when a foot is inserted in a ski-boot that is not anatomically compatible with the foot. For this reason, in the recent years, ski-boot producers have developed new methods for the modification of the shape of the inner and outer part of the ski-boot. If the temperature of the shell and cuff is maintained between the melting temperature and the heat distortion temperature (HDT, the temperature at which the material can be deflected under a load of 0.45 MPa) the plastic can be deformed using pressure. If the boot is then cooled to room temperature, the deformation can be permanently maintained. This process allows adapting the shape of the boot to the shape of the skier's foot, providing more precision in skiing and more comfort. However, the gap between the softening point and the melting point can vary depending on the type of plastics and in some case, as for example for polyolefines, can be narrow (see Table 2) and it can be difficult to soften the material without causing its melting or even its degradation. Polyurethanes are the materials that have the largest processing window (Table 2) but at temperatures below 80 °C strong forces could be necessary to deform the plastic. In order to prevent burning on the skier's foot, 80 °C is the maximum temperature that can be used if the thermo-modification is made with the foot of the skier inside the boot. For this reason, new polymeric systems have been patented in order to obtain materials with an optimized softening temperature. Salomon has patented [67] the use of a blend of polycaprolactone with polyurethane in order to decrease the softening temperature of polyurethanes. The DMTA curves in Figure 23 show that the polymer blends present a decreased softening point without significantly affecting the stiffness below 40 °C.

Figure 23. DMTA analysis of plastic for thermo-formable shell and cuff (adapted from US Pat Appl 20080000109).



The materials with this softening behavior at 80 °C can then bi-injected in the zone where generally a point of pressure is present on the skier's foot (Figure 24). We have measured the amount of enlargement of the shell dimensions after thermo-formation using a Salomon Quest Max-100 size 27.5 Mondopoint. After heating at 100 °C for 15 min in a convection oven, a wooden foot prosthesis corresponding to a foot of size 28.5 was inserted. After cooling in water the prosthesis was extracted from the boot. An enlargement of 4.0 mm in the position in which the *Last* is measured (Figure 3) was observed. The boot partially returned to the initial size (2.1 mm enlargement were still present) after 30 days at 25 °C. This return can be ascribed to the well-known shape-memory effect of thermoplastic polyurethanes [68].

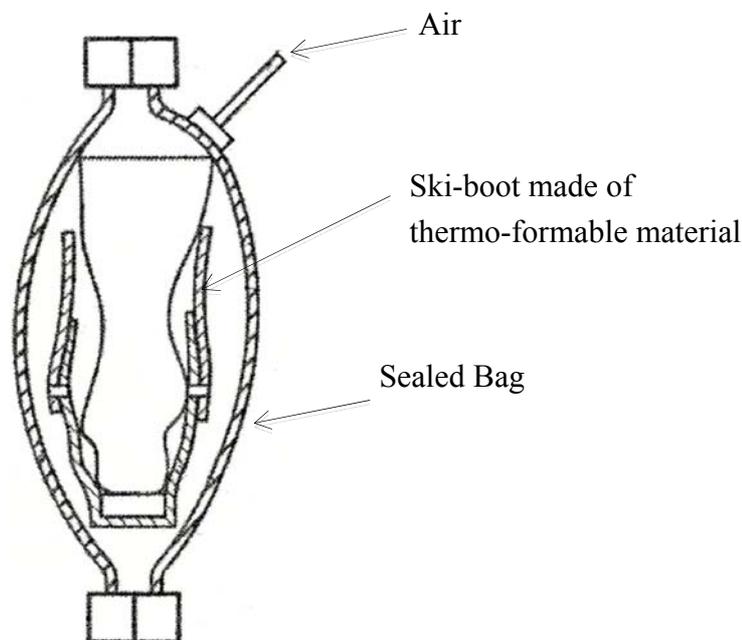
Figure 24. Ski-boot shell with thermo-formable parts.



More recently, Fischer has patented [69] a blend of Nylon with a ionomer (polymer containing ionic groups) composed of a copolymer of ethylene and methacrylic acid (EMAA) to obtain a material

very soft at 80 °C that could be shaped around a skier's feet applying an external pressure with a dedicated apparatus (Figure 25) that involves a sealed bag to produce a pressure on the ski-boot after heating.

Figure 25. Apparatus for thermoforming ski-boot shell and cuff (adapted from US patent Appl 2010236101 [69]).



The difference between this method and the method previously reported by Salomon lies in the fact that in this case the shell is adapted by external pressure on the skier's foot while in the method patented by Salomon it is the foot pressure that enlarges the shell. One of the problems of this method is related to the very low elastic modulus at 80 °C needed to adapt the shell on the shape of the foot. Therefore, during the thermoforming process, the part ruled by ISO standards can suffer deformations that can be dangerous for the safe release of the boot from the binding during a fall. A study of the deformation that occurs on the sole of the boot during the thermoforming process should give important information on this point. Moreover, both methods apply the heat on the entire boot, even in the part where thermo-formation is not needed. Therefore, a method that selectively provides heat only in the points where thermo-formation is needed should be developed.

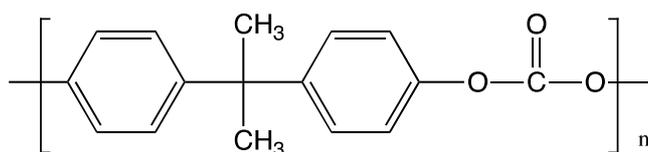
Plastic materials for cuff, shell and tongue are molded into form by the injection molding process. The process consists in melting the material and pumping it under pressure in metallic molds [70]. Cuff and/or shell can be made of two or more materials by the use of bi-injection processes in which a first part is injected in a mold and after molding the plastic part is placed in a second mold where the second material is injected. The multi-injection is made in order to have the harder material in the part where more torsional rigidity is needed to transmit forces to the ski, while the softer material is injected in the parts where more comfort is needed. The coloration of the ski-boot can be made during the injection molding process using *Masters* (polymer mixtures containing a high level of dyes) that can be easily blended with the polymer during the injection process. The direct addition of dyes into the polymer does not permit a homogeneous dispersion of the color [70]. The dyes can have an effect on the visco-elastic properties of the plastics and therefore on the final performances of ski-boots. This

is due to the nucleating effect of pigments that alters the crystallinity of the material and to the plasticizing effect of the plastic used to prepare the *Master*. For this reason, ski-boots made of the same material but with different colors can have different performances.

5. Buckles

The first buckles for ski-boots have been patented by Hans Martin of Henke Speedfit in 1967 [5]. The buckles provide an easier and more efficient closure of shell and cuff. The number of buckles on a single boot depends on the geometry and on the end use of the boot. High performance boots with *Overlap* design usually have four buckles (two on the shell and two on the cuff) while boots with *Cabrio* design present three buckles. In this design the central buckle is connected to the shell and not to the cuff. In this way the pressure over the tongue (to keep the heel in the rear pocket of the boot) does not change when the boot is flexed. On the contrary, if the buckle is attached to the cuff, the pressure of the closure changes during the movement of the cuff that occurs during the skiing action [62]. Micrometric adjustment of the levers is used for a more precise fit. Buckles are generally made of metallic materials (e.g., titanium or aluminum containing alloys for reduced weight). The only plastic material suitable for the construction of buckles is bisphenol A polycarbonate (Figure 26) that is a material that combines good mechanical properties up to 100 °C with outstanding low temperature impact resistance due to its ability to adsorb energy since it presents a γ -transition well below the glass transition temperature ($T_{\gamma} = -105$ °C) [71]. However, the main drawback of the use of polycarbonate lies in its scarce resistance to solvents that can impart partial crystallization and dramatically decrease the impact resistance.

Figure 26. Chemical structure of bisphenol A polycarbonate.



The upper part of the cuff is generally closed with a Velcro strap to provide more power transmission. An elastic band closed with a metallic clip (called *Booster* strap) can also be used to provide a more efficient elastic return to the neutral position after flexing the boot during the application of the force to the ski. Even if buckles are of fundamental importance for the precise fit of the ski-boot, for the foot hold during skiing and can have a significant effect on flex stiffness, no scientific studies have ever addressed this topic.

6. Ski-Boot Soles

As previously reported, two norms exist for ski-boots soles. One concerns ski-mountaineering and one traditional alpine skiing. The soles for each activity are different since a more precise energy transfer between the ski and the binding is necessary in alpine skiing while more grip on snow, rocks and ice is needed for ski-mountaineering. Therefore, in traditional alpine skiing, the sole of the ski-boot is rigid and made of the same material of the shell. The thickness and hardness of the sole are

regulated by the ISO standards previously reported in Section 3. The ski-boots used in alpine ski racing are regulated by the International Federation of Skiing (FIS) and must have a maximum distance between the boot sole and the base of the heel of 45 mm. Plastic plates are often added below the shell to obtain the desired height. The rigid materials generally used in ski-boots do not have a good grip on ice and wet surfaces and therefore rubber soles are used for ski-mountaineering boots. The material used for this type of boots is generally made of vulcanized natural or synthetic rubber that offers more wear resistance with respect to thermoplastic elastomers. The drawback of the use of a soft rubber material is the lack in power transfer between the skier and the ski since the sole tends to bend when a load is applied, leading to a less precise control of the skis. For this reason Plake *et al.* [72] have patented a system that presents four rigid cylindrical pins in the sole in the point where the sole is in contact with the binding, allowing an efficient transfer of the forces from the skier to the binding for a more precise control of the skis (Figure 27 left).

Figure 27. ISO-touring boot-sole (left) and hybrid sole with rubber parts and ISO-alpine norm (right).



Some producers have provided the possibility to change the heel and the toe parts of the sole in order to have boots that can have the properties desired for the type of application needed. The soles of this type are generally attached to the shell using metal screws. The soles used for ski-mountaineering also present a rockered shape (heel and toe are higher than the central part of the boot) that helps the walk with a rigid sole. In the last few years a new type of hybrid sole (Figure 27 right), that presents a rigid part that fulfills the norm of alpine ski-boots and a soft part that provides grip on ice, has been developed.

7. Liners

Liners (also called inner boots) are made to provide thermal insulation, cushioning and comfort. The inner boots are generally formed of several parts glued or sewed. The upper front part is open to allow the entrance of the foot and can be closed by means of laces. A tongue of a more rigid material is generally present, since this part is the one that transfers the force of the skier to the shell and to the

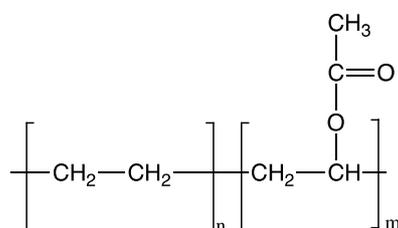
ski. In some cases the tongue is not present and the inner boot has an overlap construction. This construction permits a more efficient wrapping of the tibia for improved comfort, but provides a less effective energy transfer with respect to the tongue construction (Figure 28). The upper part of the inner boot is generally more rigid since part of it is outside the plastic cuff. The softer parts of the inner boot are made of foamed materials that provide insulation and cushioning. Salomon has been the first brand to patent [73] a boot liner that utilizes thermo-forming materials to provide a better fit.

Figure 28. Liners with overlap construction (**left**) and with tongue construction (**right**).



Different foamed materials with open and closed cell morphologies can be used. The most used material is ethylene vinyl acetate (EVA) (Figure 29) partially cross-linked. EVA has also the ability to be fitted by heating and formed on the shape of the skier's foot (thermo-formable liner) since it has a softening point of 90 °C (that can slightly change depending on the density and cross-linking) allowing changes in the shape of the foam and retaining these changes after cooling [74]. The thermo-formability is due to the presence of semi-crystalline regions (which act as physical cross-links) that are completely melted at around 90–95 °C, as measured by DSC analysis (Figure 30). When the temperature is lowered back to 25 °C, the crystalline region is re-formed and therefore the new shape is retained.

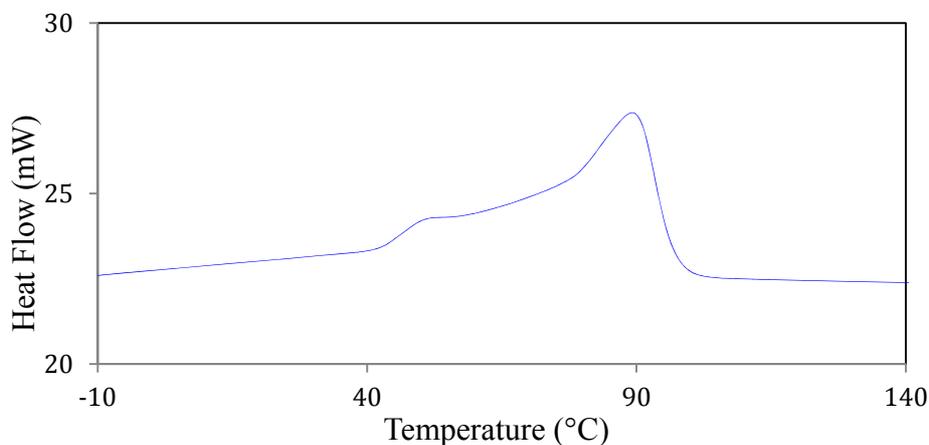
Figure 29. Ethylene vinyl acetate chemical formula.



The properties of the different types of EVA are related to their density (that depends on the EVA/expansion-gas ratio) and to the type of expansion gas used. Azodicarbonamide is used as blowing agent but is considered toxic in some countries [74]. Depending on the morphology of the cells (open/closed and dimensions) the material can be thermo-formed with different efficiency and can maintain the dimensional stability after use (compression set). Closed cell materials offer the best

properties of compression set and thermo-formability [74]. Materials with different densities are used in the different parts of the boot, and often a sandwich of materials is used.

Figure 30. Differential Scanning Calorimetry analysis (first heating scan) of thermo-formable EVA used for ski-boot liners.



The thermal insulation properties of ski-boot liners have been reported by Fauland *et al.* [75]. The thermal resistance of the plain material was found to range from 0.235–0.289 m²K/W. The authors also reported that insulation properties strongly decrease with humidity. When a laminated material was used, no moisture evaporation occurred, causing a rapid increase in relative humidity inside the liner. Moreover, the foamed material presented a very poor water absorption and overnight drying does not occur due to the barrier properties of the closed cell material. The increased moisture level can also be responsible after a few days of microbial growth. The study [75] also points out that the most exposed part of the foot to frostbite is the toe part and care must be taken in order to provide a good insulation of this part. The authors have also compared different materials in order to find the textile fabric able to remove more efficiently the moisture; wool has proved to be more efficient with respect to synthetic fabrics, such as polyamide and polypropylene. Another advantage of wool is that it adsorbs a fair amount of moisture without imparting a sensation of dampness and provides significant insulation also when it is wet, due to the heat released during sorption of water in the wool [75].

Recently, Moncalero *et al.* [76] have presented a study on the effect of different materials on the thermal insulation of ski-boot liners using wireless sensors that measure temperature and humidity inside the liner in outdoor conditions. The results obtained show that closed cell EVA liners have a higher thermal insulation with respect to open cell materials. However, the higher insulation is also combined with a lower permeability to moisture and therefore a higher humidity was measured inside the closed cell EVA foams. EVA liners offer the best thermal insulation for both male and female genders and the difference with other liners increases as the ambient temperature decreases. The ski-boots temperature seems to be not affected by the alternations of uphill/downhill phases and by wind speed. In general, higher temperatures have been recorded for men testers with respect to those recorded for women. The efficiency of thermal insulation can also be measured using infrared thermography methods [77].

8. Evolution, New Trends and Conclusions

The evolution of ski-boots in the last few years has been quite fast, in particular in the use of new materials and designs. This evolution has been required by the change of ski shapes and materials. For example, with the new *Rocker* design of skis (skis with tip and/or tail that start rising closer to the binding with respect to the point of maximum width of the sidecut) a more centered stance is needed since the unbalance of the skier's weight forward or backward is easier due to the rockered shape of the ski base. The use of instrumented boot-boards that measure the foot pressure on the ski-boot base, combined with high-speed camera analysis, should help in the design and in the test of ski-boots with improved balance.

The evolution of ski-boots suggests that the design will be differentiated depending on the skiing discipline and on the type of skier. Preliminary results [59] suggest that *Cabrio* designed ski-boots have a more progressive flex with respect to *Overlap* designed ones and therefore are more efficient for skiing disciplines, such as mogul skiing and off-piste skiing, that needs a good absorption of the roughness of the snow surface and a progressive flex. However, more studies are needed to confirm this point. In particular, tests for the measure of flex at different bending angles, with the test bench reported in the literature by Reichel *et al.* [41], should be performed. These tests should be combined with on-snow tests with sensors able to measure the cuff-shell movement during the act of skiing. This type of tests will significantly help the design of ski-boots with more progressive flex. Also, the measure of the rebound speed should be studied in detail, since the overall behavior of ski-boots is ruled by the combination of forward flex and elastic backward rebound. The analysis of the flex combined with the use of computer simulation will also help to choose the optimal plastic width of shell and cuff in order to minimize the weight and optimize the flexural and rebound behavior. The flexural tests should also lead to the determination of a standard method for the measurement of the Flex-Index that, so far, has no scientific background and is performed with different protocols and apparatus by ski-boot manufacturers. The development of a standard Flex-Index method will help not only the research and development scientists but also the ski-boot users in the choice of the most appropriate model. The lateral stiffness of ski-boots should also be studied, since it has a significant influence in skiing performances. Moreover, since both designs currently used present several drawbacks, the aim of R&D departments should be the development of ski-boots that solve those problems. For example, the development of hybrid systems, that have the progressive flex of *Cabrio* design combined with the precise fit of *Overlap*, should be deeply investigated. A simple method able to modify the flexural behavior of ski-boots should also be developed. Indeed, the flex is affected by plastic stiffness that is sensible to temperature changes and different flex stiffnesses are needed for different skiing disciplines (e.g., harder for racing, softer for freestyle, moguls and off-piste skiing). So far, this flex modification is possible by changing the tongue of the *Cabrio* designed boots, while it is not possible for *Overlap* ski-boots unless part of the material of the shell is cut [30]. A system able to easily adapt the flex to the external conditions (temperature, type of snow, skiing discipline *etc.*) should have a great impact on the ski-boot market.

The analysis of ski-boots commercialized in the last few years indicates that a larger number of ski-boots with ski-walk mechanism are present on the market with respect to the past (for Calzaturificio Dalbello [62] 38% with respect to 15% of 10 years ago). This feature has not only been

applied to ski-mountaineering boots but also to boots used by recreational skiers since it helps to walk on flat and rigid surfaces (e.g., parking lots). The use of new ski-boot soles that combines the rigidity of a traditional alpine skiing sole (with ISO alpine norm 5355) with the grip of a rubber sole is also increasing [63]. Several ski-boots have now the possibility to interchange different soles that comply with the two ISO standards [63]. The durability of the sole should also be studied in detail since the soft parts that provide the improved grip are more prone to wear. The study of the torsional stiffness should also be performed since the presence of soft parts can have a negative effect on lateral stiffness and therefore on the ski-edge hold on hard or iced snow.

The increased performances of ski-boots are not only due to the different designs but also to the continuous progress of the materials used for their construction. This progress is mainly attributed to three factors: lightness, performance and comfort. The use of lighter materials is fundamental in skiing disciplines that combine downhill skiing with climbing (ski-mountaineering) and in freestyle disciplines. However, lightness can be also an important factor for recreational skiers. The simplest way to reduce weight is to reduce plastic thickness. However, ski-boots with thin plastics suffer from easier breaking at low temperature and provide less thermal insulation. Therefore, a more appropriate way to decrease weight is to use materials with lower density and/or with an increased modulus/weight ratio. However, the use of very stiff materials (e.g., carbon fiber or Kevlar/polymer composites) can provide a less progressive flex and an elastic rebound that is too fast. Therefore, a proper design aided by computer simulation with the use of the multi-injection technology must be used. In this way, the stiff materials can be selectively positioned where hard and thin parts are needed, while more viscous materials can be positioned in the parts that control the flex (e.g., the tongue in *Cabrio* design or the back and the instep parts of the shell of *Overlap* design).

The choice of the materials should also be performed taking into account the stiffness increase at low temperatures. Indeed, materials that are less sensible to temperature stiffening permit skiing with the same technique and with the same effort in different climatic conditions. The effect of temperature on plastic stiffness can be studied by DMTA analysis that, as reported in Section 4, can also provide important information on the viscous behavior (analyzing E'' and $\tan\delta$) of the boot and therefore on the dynamic (elastic rebound) behavior of the boot. DMTA analysis should also help in the choice of new materials with viscous behavior, able to dampen vibrations and adsorb shocks especially in freestyle, off-piste and mogul skiing disciplines.

In the last years, a few ski-boots producers [50,63] have developed ski-boots with shell and cuff that can be adapted to the foot shape in order to have a precise control of the ski without pressure points on the foot. The use of materials, such as the ionomer blend developed by Fischer [69], which significantly softens at 80 °C without degradation, helps to adapt the shape of the boot to the skier's foot. However, it is important that the new materials retain the same visco-elastic behavior (flex and rebound) of a standard ski-boots. Moreover, the new materials should be analyzed to assess their durability. In general, more studies on the durability of all plastic materials used for ski-boots are necessary, since the low temperature impact resistance of ski-boots (that is responsible for brittle fractures) is significantly affected by the molecular weight decrease due to degradation reactions.

The Kyoto protocol and the increased attention of consumers to environmental issues are pushing the use of materials obtained from renewable resources and with a reduced carbon footprint. Examples of this search for environmentally friendly materials are already present on the market (e.g., Pebax

Rnw made from castor oil [51]) but are confined to expensive boots [63]. Researchers should develop the same approach also on plastic materials used in larger quantities, such as polyolefines and TPUs. Every year, the chemical industry is introducing to the market new materials based on renewable resources, but so far most of them do not fulfill the strict requirements needed for the production of ski-boots with high standards of safety and performance.

The analysis of the ISO standards shows that new norms are needed to standardize the tests for the measurement of the flexural stiffness and to take into account the evolution of ski-boots in recent years.

The analysis of the data reported by ski boot producers [62,63] also suggests that the use of thermo-formable liners will increase. This increase is driven by the request of high performance ski-boots with improved comfort. A detailed study of the effect of foam characteristics (cell dimensions, wall thickness and type of crosslinking) on the thermo-forming behavior is therefore needed. In particular, new studies should describe a method for the determination of the thermo-forming behavior, for example, using compression-set tests at different temperatures. It has been reported that the use of thermo-formable liners made of closed cell EVA produces a higher thermal insulation [76]. However, preliminary results [76] show that the higher thermal insulation is also combined with increased moisture content inside the liner. More studies on the moisture management and on the thermal insulation of ski-boots liners are therefore necessary, along with the development of new foamed materials.

As a general conclusion, the materials and designs used for ski-boots have achieved fast development in last decade. More scientific studies are needed to fully understand the capability of the new materials and take full advantage of their potential. The use of advanced analytical methods and the development of a standard procedure for the determination of the visco-elastic behavior of ski-boots, both in laboratory and on the snow, are of fundamental importance to further improve the performances and comfort of ski-boots.

Conflicts of Interest

The authors declare no conflict of interest.

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