

11th conference of the International Sports Engineering Association, ISEA 2016

Ski boot soles based on a glass fiber/rubber composite with improved grip on icy surfaces

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Abstract

A study on the effect of glass fibers/rubber composites on the grip on ice has been conducted in order to develop new materials for ski boot soles with increased grip in winter environments. The study has been conducted analyzing the friction of a composite material and of a ski boot sole containing an insert made of the composite material and comparing the results with those obtained using rubber and a thermoplastic elastomer. The analysis of the morphology of the composite surface, by Scanning Electron Microscopy, shows a homogenous distribution of glass fibers of approximately 10 μm of diameter in the rubber matrix. Moreover, the measure of the contact angle shows that the composite material has a higher water repellency compared to the rubber matrix. The measure of the coefficient of friction indicates a significant effect of the glass fibers on the grip on icy surfaces. The increased grip can be ascribed to the stiffness of the glass fibers that are able to have a mechanical grip on the ice surface and to the increased contact angle and water repellency of the composite that decrease the formation of a water layer below the sole.

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Peer-review under responsibility of the organizing committee of ISEA 2016

Keywords: ski boot; friction; sole; rubber/glass fiber composites.

1. Introduction

Slips and falls are very common when walking with ski boots and they are often the cause of serious injuries. The sole of a ski boot is a very unique system that must have a stiff behavior 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 boots with soles [1] with parts made of materials less hard with respect to the plastic used for the main body of the boot [2], with the aim to improve the anti-slip properties of the soles. In particular, the soles of boots used for ski-touring and freeride skiing 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 behavior of elastomers on wet and icy surfaces. For example, Grönqvist et al [3] have tested 49 types of winter footwear on dry and wet ice, determining the most important parameters for each condition. From their evaluation, material type and hardness as well as cleat design has 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 was 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.

We have previously studied [5] the factors influencing the coefficient of friction (COF) of the materials used for the

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production of soles for ski boots on wet floors and icy surfaces. The results of our study [5] have pointed out that the stiffness and the roughness of the material used for the sole have a fundamental effect on grip performances. In particular, the results obtained show 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 measure of grip 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. The performance ranking of the 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 the soles of ski boots. The comparison of different sole treads indicates that the best results in terms of anti-slip behavior are obtained with the soles that present the wider contact area with floor. However, even the most performing thermoplastic polymer or rubber tested in our previous study (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 possess an efficient 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 fiber composites, finding a significantly increased COF on ice for the materials containing the fibers. 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 fibers that are perpendicular to the base of the sole. According to Treksta™ the purpose of the rigid glass fibers 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 repellency 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 fibers composite. For this reason, we have performed a study in order to assess the performances of this type of composite material and to understand the effect of the fibers in the rubber matrix. Moreover, we have prepared a ski boot sole complying with ISO 5355 norm, containing parts made of the rubber/glass fibers composite and compared its grip performances with those of a standard rubber sole.

2. Materials and Methods

The rubber/glass fiber composite (Material 1) and the rubber material used as matrix for the composite (Material 2) have been kindly provided by Treksta™.

The soles have been produced by over-injection moulding of polyurethane on the rubber and rubber/glass fiber composite and are all complying with ISO 5355 norm. In the present study only the soles for the heel part of the ski boot have been tested since this part is more flat 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 cm² each of Material 1, the rubber/glass fiber 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 1. Soles used in the present study, indicating the zone of the rubber/fiber composite insert position in Sole 3.

The chemical composition of the Soles and Materials surfaces 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 fiber content has been measured by thermo-gravimetric analysis (TGA) using a Perkin Elmer TGA 7 instrument using a scan rate of 20°C min and a air flux of 30 mL/min.

The Shore D hardness of the materials and of Surface 1 has been measured according to ISO 878 at 23°C.

The surface topology of the rubber/glass fiber 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 were taken without any particular specimen preparation. The micrographs were taken with a backscattered electrons detector that permits to distinguish the fibers (white) from the darker plastic substrate. The fibers composition was analysed using an EDS detector (OXFORD INCA 350). The height of the fibers 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 using an Instron 1011 dynamometer attached to the sole or the material with a screw attached to a steel cable connected with the dynamometer. A pulley system was used in order to drag the material or sole horizontally on the testing surface. A weight of 15 kg evenly distributed on the material (surface of the Materials of 145 cm²). The experiments have been repeated 5 times and averaged. The experiments have also been performed on a solid surface that mimics the concrete surface of mountain huts floor (Surface 1). The temperature on the ice surface has been measured using a digital infrared thermometer. The tests have been conducted on ice at -10°C and at -1°C. In the second case 10 mL of water were 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 was cooled in a refrigerator at the set temperature for at least 1 hour before the next test.

3. Results and Discussion

The chemical composition (confirmed by FTIR analysis) and the hardness of the different parts of the soles are reported in Table 1 and 2.

Table 1. Chemical composition and hardness of the Materials used.

Material tested	Chemical composition	Shore D Hardness
Material 1 black part	Rubber/glass fiber	19
Material 1 grey part	Rubber/glass fiber	20
Material 2	Rubber	21

Table 2. Chemical composition and hardness of the Sole tested (Sole 3 has also two inserts made of Material 1).

Sole tested	Chemical composition	Shore D Hardness
Sole 1	TPU	38
Sole 2	Rubber/TPU	33/59
Sole 3	Rubber/TPU	30/59

The FTIR analysis have confirmed that the composition of the dark and grey parts on the composite Material 1 have the same chemical composition (vulcanized polyisoprene rubber) and the different colours are due only to marketing and aesthetic reasons.

The measure of the hardness 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 Figure 1) made of a rigid (59 Shore D) TPU material that is necessary to achieve the correct release of the boot from the binding according to ISO 5355 norm. The comparison of Material 1 with Material 2 shows that the presence of the glass fibers does not have a significant effect on the hardness: Moreover, the data in Table 1 and 2 show that Material 1 and 2 are softer compared to the main rubber material used for Soles 2 and 3.

Measuring by TGA analysis the difference between the weight residue above 800 °C of Materials 1 and 2 it has been possible to determine that the composite Material 1 contains approximately 4 wt% of glass fibers.

The morphology of the composite surface was evaluated by Scanning Electron Microscopy with a backscattered electrons detector that allows an easier imaging of the glass fibers thanks to the presence of silicon atoms (bright contrast), with respect to the purely hydrocarbon plastic matrix (dark contrast) (Figure 2). The SEM analysis with a EDS detector has confirmed that the fibers inserted in the rubber matrix have a purely SiO₂ composition. The SEM micrographs in Figure 2 indicate that the glass fibers have an average diameter of approximately 10 µm with an average distance between fibers of 150 µm. The micrographs also show that part of the fibers are bended on the surface and that some voids, probably due to the pull out of the fibers during the cutting process performed to produce the specimens for analysis, are present. The multifocal analysis has shown that the fibers protrude from the surface of less than 10 µm.

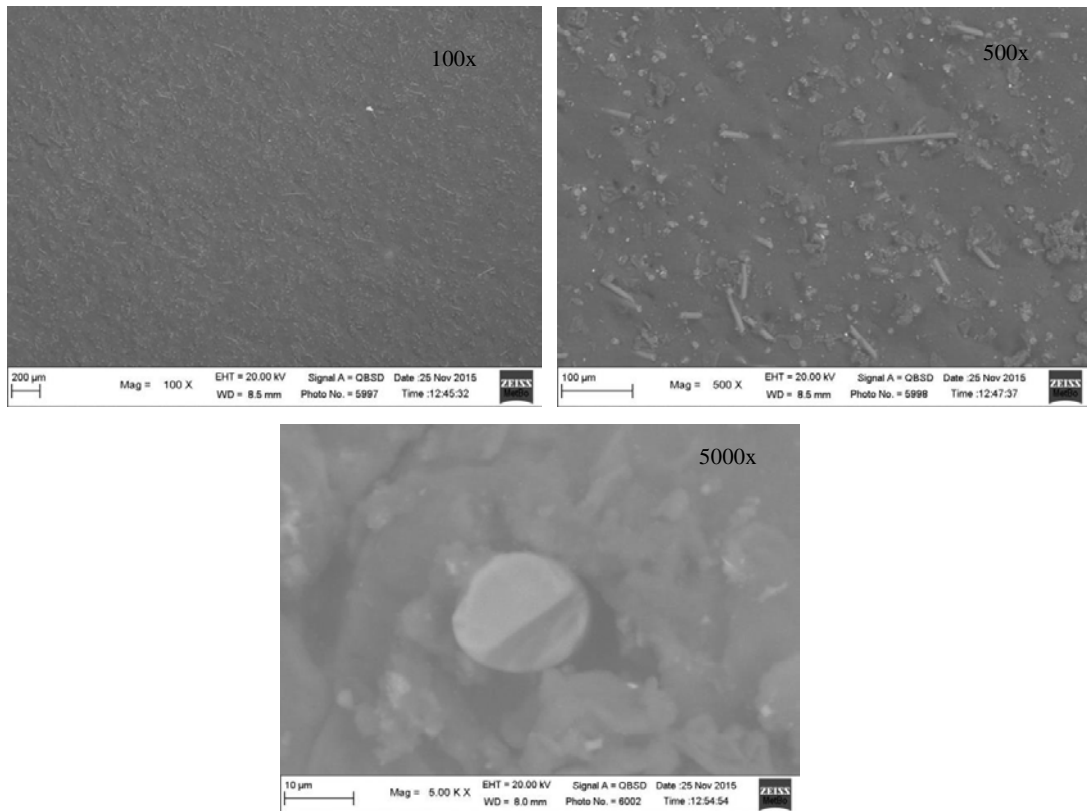


Figure 2. SEM analysis of the surface of the rubber/glass fiber composite (Material 1) at 5000, 500 and 100X magnifications.

The effect of the presence of the glass fibers on the water repellency 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 surface significantly affects the friction of plastic materials on snow and ice. The results of contact angle measurements (Table 3) show that the composite material has a higher contact angle (and therefore more water repellency) compared to the rubber material used for the composite matrix.

Table 3. Water contact angles on the materials used in this study.

Material tested	Contact angle *
Material 1 black part	89 ± 5
Material 1 grey part	87 ± 5
Material 2	68 ± 3

*drop volume 4µL

Wettability is a very important property of materials, especially in applications which directly involve surface contact with liquid or icy water layers, that determine the material behaviour and performances. Wettability is partially due to an intrinsic property of materials depending on their specific surface chemistry, but it can be easily manipulated by tailoring the surface properties, especially by the roughness of the surface. 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]. This is exactly what observed in our study; the polyolefinic nature of the Rubber material induces its mainly dispersive behaviour giving rise to quite hydrophobic surfaces. The insertion of glass fibers 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].

Our previous work [5] has shown that the COF value can be used to rank the grip performances in real conditions on wet

surfaces for different materials used for ski-boots soles. For this reason, we have measured the COF on icy surfaces and on a surface (Surface 1) that can mimic the internal floor of alpine huts where slip and falls can also occur (Figure 3). The tests on Surface 1 (that has a 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.

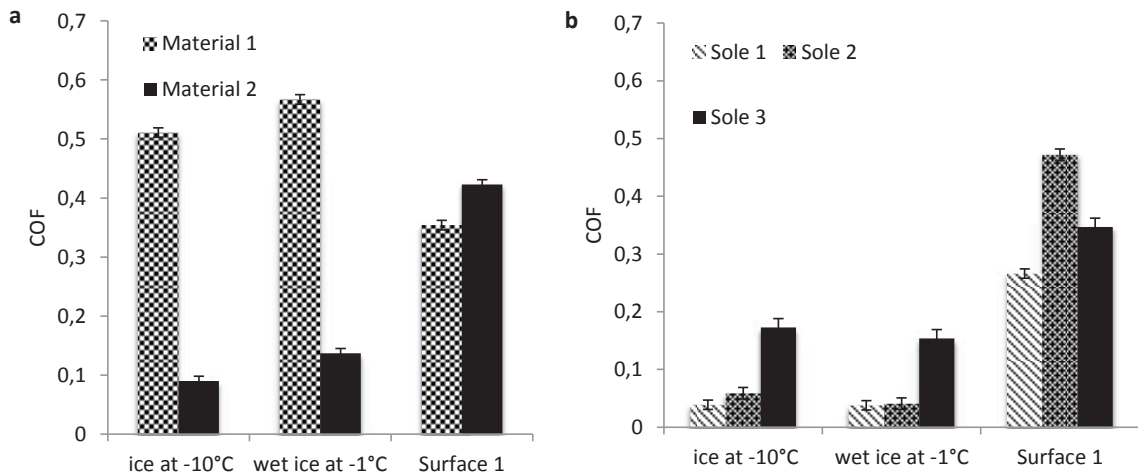


Figure 3. COF of materials (a) and soles (b) on ice and on surface 1.

In our previous studies [5] we did not observe significant differences between 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 (made of the same rubber material without the glass fibers). These results clearly indicate a very positive effect of the glass fibers on the friction on icy surfaces. This increased friction is due to the mechanical grip of the rigid glass fibers on the ice surface. Indeed, glass fibers have an elastic modulus comprised between 60 and 90 GPa [10] while the materials of the rubber matrix that we have used have an elastic modulus below 100 MPa [11] even at low temperatures (-20°C). The results in Figure 3 also show that the COF at -1°C on wet ice of Material 1 (with glass fibers) is significantly higher compared to that measured for Material 2. In addition, 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 the fibers are able to have a contact with the ice surface even if a water layer is formed on the ice surface since they protrude of a few microns from the surface of the rubber. Moreover, the mechanical grip of the fibers 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 governed 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 permit a more efficient water removal below the surface and therefore the glass fibers 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 3 show that the COF on icy surfaces of Sole 3 (that has two inserts containing Material 1, the rubber/glass fibers composite) is at least 3 times higher with respect to that of the sole that does not contain the insert in Material 1 (Sole 2). This result indicates again the positive effect of the fibers on the friction on icy surfaces. The smaller COF value of Sole 1 can be ascribed, according to our previous results [5], to the higher stiffness of the material used for that sole.

The 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 the glass fibers have a negative effect in this case. The reason of this behaviour can be ascribed to the fact that in Material 1 mainly the glass fibers are touching the surface and therefore there are less contact points between the material and the surface. Indeed, we have previously found [5] that the surface roughness has a significant effect on the COF, and in particular that 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 the materials used for the other two soles.

4. Conclusions

The results obtained indicate a significant effect of the glass fibers on the grip on ice. The increased grip on icy surfaces can be ascribed to the stiffness of the glass fibers that are able to have a mechanical grip on the ice surface and to the increased

contact angle and water repellency that decrease the formation of a water layer below the sole. The opposite effect observed on the hard surface can be explained in terms of the higher surface roughness (less contact points) with respect to the other Materials. The data obtained in this study will be used to model, using Finite Element Analysis, the effect of fibers on grip on icy surfaces in order to optimize the type of fiber and distribution necessary to increase the grip. The results of the present study can be also applied to other types of shoes and boots to be used in winter environments.

Acknowledgments

This work was financed by Calzaturificio Dalbello, Asolo, Italy.

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