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

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Abstract

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

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1. Introduction

Winter sports are very popular activities, performed by an estimated 200 million people in the world each year. This number is in constant growth thanks to the increasing development of new terrains together with an advance in materials and technology. Winter sports are generally high-energy outdoor sports and therefore involve inherent risks, resulting in numerous falls and collisions. These impacts produce significant traumatic injuries, with an average of around 1.5/1000 skiers/day (Burtscher et al, 2008).

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The statistic of the distribution of these injuries over the body have discording results depending on the country taken into exam (McBeth et al, 2009). Nevertheless, all the studies agree that the most affected areas are head, shoulders, spine and knees. Due to the high healthcare expenses connected with these injuries, there is a strong interest in prevention. This can be done on different levels, from regulation of ski slope activities (Hildebrandt et al, 2011) to the development of more efficient protective equipment such as helmets (Jung et al, 2011) or back protectors. The usage statistics and specific studies on back protectors are very limited; Michel et al (2010) have conducted an overview of the potential protective effects of back protectors combining an athlete survey with experimental performance tests. Despite the protective expectations of the customers there is no specific performance standard related to snow sports. The industry is currently using motorcycling standards to test impact performances and market their products. The EN 1621-2 standard defines two levels of protection, based on the measurement of the transmitted force through the protector when hit by a falling mass with an energy of 50 J; the highest level of protection being level 2 (Average F_{peak} <9 kN, Max F_{peak} <12 kN) and the lowest being level 1 (Average F_{peak} <18 kN, Max F_{peak} <24 kN). Manufacturers of protective gear for winter sports (i.e. back, hip, elbow or chest protectors) have been focused, in recent years, on the development of new soft shock adsorbing materials. Historically, all the protectors had a “hard-shell” construction consisting of a hard outer shell of thermoplastic material with an inner soft padding foam. In these products the shock attenuation technology, coming from the motorcycling industry, is based on the concept of distributing the force of the impact over a wider area. Recently, the market has seen an increasing number of products based on the new “soft-shell” technology adopting soft polymeric foams. Indeed, the new soft polymeric foams have higher comfort both from an ergonomic (due to the low thickness and softness of the material) and thermal (since the production processes and the material characteristics allow to obtain perforated structures) points of views. These materials present a pseudo dilatant nature (Palmer et al, 2005), reacting like hard and rigid materials when hit by high speed impacts and like viscous materials when hit by low speed impacts. This behaviour enables a high level of protection in case of crash as well as a good flexibility and comfort.

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

2. Materials and Methods

A total of five back protectors have been tested (Fig. 1); all samples are commercially available products in size L, certified for protection level 1 or 2 according to EN 1621-2.

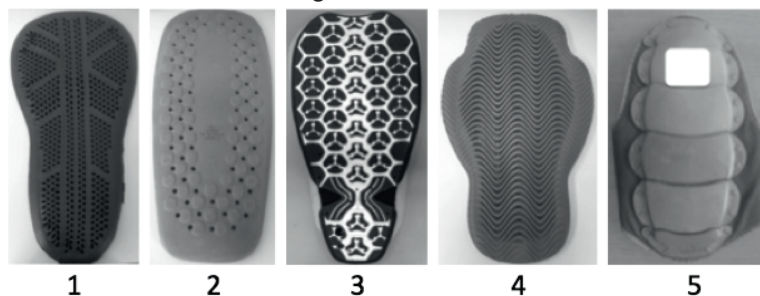


Figure 1. Commercial back protector tested.

The chemical composition has been determined by Fourier transform infrared spectroscopy (FT-IR) with a Perkin Elmer Spectrum One instrument, using an Attenuated Total Reflectance (ATR) detector. Hardness has been measured using a Hildebrand shore A durometer at 23°C according to ISO 868. Dynamic Mechanical Thermal Analysis (DMTA) is a powerful tool used for the characterization of polymeric foams (Rodríguez-Pérez, 2002). DMTA has been performed applying an oscillatory force to the sample and analysing the response as a function of temperature and/or frequency. Due to the visco-elastic nature of the polymers tested, a sinusoidal stress induces a

sinusoidal strain consisting of an in-phase or elastic part (ε'), and an out-of-phase or viscous part (ε''). The ratio between ε'' and ε' is called $\tan\delta$ and gives an indication of the damping behaviour of the material. DMTA tests have been performed with a Rheometrics Dynamic mechanical thermal analyser DMTA 3E model, with a single cantilever bending geometry, using a strain of 0.1%, in a temperature range of -50°C to $+50^{\circ}\text{C}$ (temperature scan speed of $3^{\circ}\text{C}/\text{min}$) on samples of $20 \times 8 \times 4$ mm directly cut from the protector. Three frequencies have been used (1 Hz, 10 Hz and 50 Hz). Impact tests have been performed using an Instron Dynatup 9250 HV instrument with a flat aluminum anvil and a flat circular impact head with a diameter of 4.5 cm. To avoid the influence of the curvature of the protectors the impacts have been performed only on flat sections; a total of two tests per sample have been performed to ensure the consistency of the results. The samples have been tested at 20°C and after being kept at -5°C for 24 hours. The testing time was below 30 seconds, so it can be assumed that the samples maintained their temperature during the tests. A load cell placed in the tup recorded the resistance offered by the specimen to the falling weight during the impact, measuring the load-time curve. The impact velocity has been measured using a sensor that was also used for starting data acquisition. The deflection of the sample has been calculated using the load-time curve and the impact velocity. The energy absorbed by the sample has been derived from the area under the load-deflection curve. This type of tests provides a more complete information set (impact time and force, depth of penetration, etc.) on the material properties compared to the EN 1621-2 norm, which only measures the transmitted force.

3. Results and discussion

Table 1 provides an overview of the selected back protectors showing that significant differences in thickness and hardness are present among the protectors tested.

Table 1. Characteristics of the protectors tested.

Protector	Construction	Protection level (EN 1621-2)	Mass (g)	Density (g/cm^3)	Thickness (mm)	Hardness (Shore A)
1	Soft-shell	2	283	0.15	16	33
2	Soft-shell	2	657	0.35	19	23
3	Soft-shell	1	325	0.22	16	15
4	Soft-shell	2	472	0.35	18	14
5	Hard-shell	2	525	n/a	30	85

The materials have been characterized by FT-IR analysis in order to determine their chemical composition. The comparison with a database of polymeric foams shows that protectors 1, 2 and 3 are made of a blend of polyvinyl acetate, ethylene vinyl acetate (EVA) and nitrile butadiene rubber. Protector 4 is made of a polyurethane blend containing polydimethylsiloxane, while protector 5 is made of a sandwich of a hard polypropylene exterior shell with a foam of polyolefines based elastomers. Furthermore, SEM analysis showed that all the soft-shell protectors have a closed cell structure with a wall thickness and cell dimensions that depend on the density and chemical composition of the foams.

The influence of temperature on the visco-elastic properties for the materials used for ski back protectors has been measured by DMTA analysis. This parameter is of relevant importance since this kind of equipment is subjected to large temperature changes during use and storage. Although DMTA is a low strain technique compared with the high strains during impacts, it permits to highlight the influence of temperature and frequency on the material properties (Mantena et al, 2003). The elastic modulus measured at 1 Hz for the four soft-shell back protectors and the effect of frequencies on protector 1 are reported in Fig. 2. Protector 5 has not been tested since it was not possible to cut a sample suitable for DMTA analysis from the protector. From the DMTA data it is evident that protector 1 has the smallest variation in the temperature range investigated. All the soft-shell materials show an increase of the elastic modulus when increasing the frequency, which is more intense for temperatures above 0°C . The values of the elastic modulus for the different materials at 20°C are reported in Table 2, along with the $\tan\delta$ values. It is clear that the frequency of the applied force has an important effect on the material stiffness. For

example, a 8-fold increase can be observed for protector 4 moving from 1 Hz to 50 Hz. This frequency-sensitive pseudo-dilatant behaviour is responsible for the particular properties of soft foams used for protective equipment. The materials are soft when are not stressed with high speed or frequency and therefore provide a good ergonomic comfort. On the contrary, when a fast stress is applied (e.g. an impact during a fall) the material behaves as a rigid material, distributing the impact over a wider surface. The materials used for soft-shell protectors present high $\tan\delta$ values ranging, at 1 Hz, from 0.32 to 1.2, indicating a strong damping behaviour of the materials. The $\tan\delta$ values decrease by increasing the frequency of the stress. Thermoplastic polyolefines, such as the material used for protector 5, generally have $\tan\delta$ values significantly lower compared to those of the foams used for soft-shell protectors (Karian, 2009).

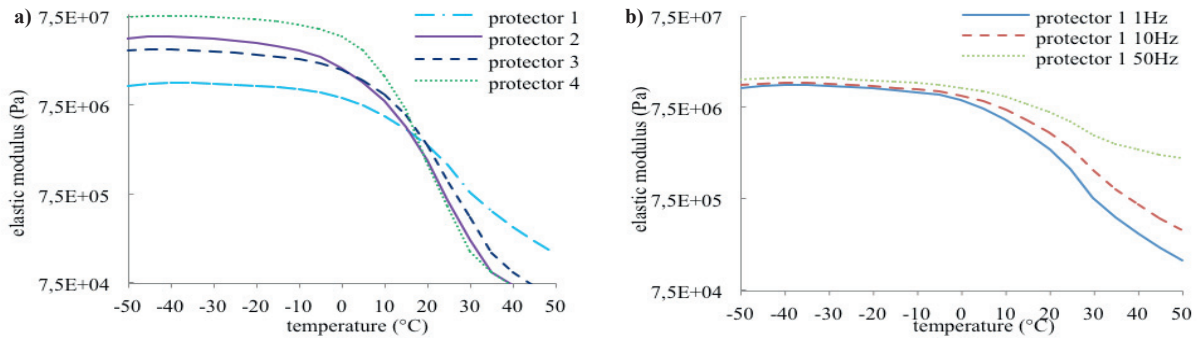


Fig. 2. Elastic modulus measured at 1 Hz (a) and effect of frequency for protector 1 (b).

Table 2. Effect of frequency on elastic modulus and $\tan\delta$ at 20 °C.

Frequency	Protector 1		Protector 2		Protector 3		Protector 4	
	E'	$\tan\delta$	E'	$\tan\delta$	E'	$\tan\delta$	E'	$\tan\delta$
1Hz	2.6×10^6	0.32	1.8×10^6	0.77	2.6×10^6	0.60	1.8×10^6	1.20
10Hz	4.5×10^6	0.28	4.6×10^6	0.58	5.6×10^6	0.46	6.8×10^6	0.78
50Hz	6.4×10^6	0.16	1.0×10^7	0.34	1.8×10^7	0.26	1.5×10^7	0.47

The impact tests have been performed with an impact energy of 50 J; the results of the impact force over time are reported in Fig. 3 at 20°C and -5°C. In general a good shock absorbing material should present a low impact force spread over a longer time, resulting in a reduced energy transfer rate (Newell et al, 2012) and thus to a smaller probability of injury.

The soft-shell protectors present three regions in the impact curve, typical of visco-elastic foams. A first linear elastic region (controlled by cell wall bending and stretching) followed by a plateau of deformation (controlled by non-linear elastic buckling). These two regions are separated by a clear yield point. Finally, there is a densification area where the force increases sharply (controlled by collapse of cell walls) (Ashby, 1983). On the other hand the hard-shell sample behaves as a typical rigid polymer with a high impact force concentrated in a short time (Karian, 2009). The time-to-peak for the hard protector was higher compared to soft-shell protectors due to the curved shape of the rigid external shell, to the void present between the hard part and the soft part and to the larger thickness of the protector. Protector 1 has the lowest peak impact force and longest time-to-peak, therefore being the best shock absorber. From the analysis of the impact force-displacement curves it has been possible to conclude that densification has been reached for values of strain between 0.61 and 0.69, values that are in accordance with those reported in literature for polymeric foams (Verdejo, 2003).

As demonstrated by DMTA analysis soft materials are strongly temperature dependent. For all the soft-shell protectors, the first part of the impact absorption process (hard behaviour) at -5°C (Fig. 3b) is increased with respect to 20°C since the material is more rigid due to the reduced motions of polymer segments at low temperature. The second part of the impact curve after the yielding point is not anymore present since, as measured

by DMTA analysis, the soft materials have a sharp decrease of $\tan\delta$ values below 0°C and therefore have lost most of their viscous behaviour. On the contrary, the hard-shell protector does not present a significant change at low temperature since the mechanism of impact protection is performed by energy dissipation over a wider area, without a viscous absorption of the impact. However, fractures in the outer part have been observed at low temperature for protector 5 and therefore a not efficient multi-impact behaviour is expected. Protector 4 has the largest change in impact behaviour that can be connected with the largest modulus increase showed by DMTA analysis in Fig. 2. The results have shown good consistency, with error bars below 3% for all the parameters taken into account in Figure 3 and Table 3.

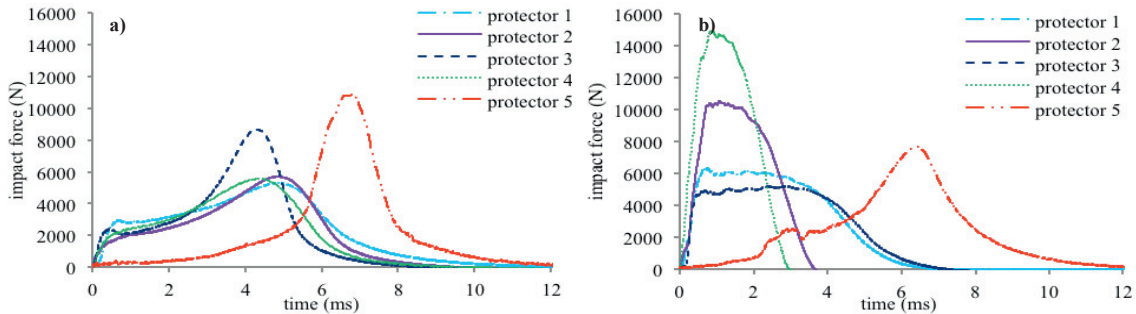


Fig. 3. Impact force as function of impact time at 20°C (a) and -5°C (b).

Table 3. Results of the impact tests at 20°C and -5°C.

Protector	F _{max} (N)		Time-to-peak (ms)		Energy absorbed (J)		Energy absorbed/thickness (J/mm)		Penetration (mm)	
	20°C	-5°C	20°C	-5°C	20°C	-5°C	20°C	-5°C	20°C	-5°C
1	5301	6292	4.8	0.7	45.7	44.0	2.8	2.8	14.6	8.7
2	5728	11196	4.8	1.7	46.2	44.3	2.4	2.3	15.0	7.9
3	8644	5220	4.3	2.9	45.4	45.5	2.8	2.8	13.7	10.9
4	5549	15534	4.3	0.8	46.3	40.7	2.6	2.3	14.2	7.4
5	15537	7644	7.9	6.3	41.2	44.0	1.4	1.5	26.8	21.7

The behaviour of the samples after multiple impacts has been tested by repeating the impact for five times consecutively in the same area of the sample, with a time between impacts of 1 minute. The results are shown in Fig. 4a for a soft-shell protector (protector 2), and in Fig. 4b for the hard-shell one. The other soft-shell protectors presented behaviours similar to that of protector 2. From Fig. 4 it is clear how the hard-shell protector has a sensible increase in the peak impact force after multiple impacts due to the yielding effect that the impacts have on the hard material. Moreover, some damages (permanent compressions and fractures) were present on protector 5 after the first impact and therefore the impact was distributed over a smaller area with a reduced width of the protector (that is responsible of the reduced time-to-peak after the first impact). On the other hand, the soft-shell materials present a negligible increase of the peak impact force. The first impact curve shows a clear elastic region after which a constant slope of plastic deformation takes place. This behaviour is still observed in the following impacts but with a lower yield point. The explanation of this decrease can be connected to the damage that some regions of the structure have received during the first impact, which leads to a softening of the foam structure (Park, 1991); such damage remains in the structure making the foams easier to deform.

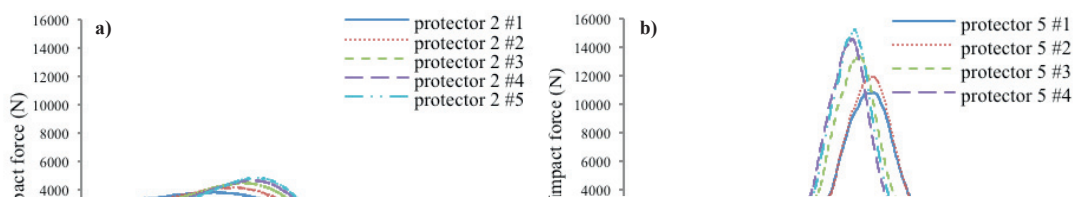


Fig. 4. Multi impact behaviour for soft-shell protector 2 (a) and hard-shell protector 5 (b).

4. Conclusion

The study of the impact and thermo-mechanical properties of materials used for back protectors indicates that the materials used for soft-shell protectors present a shear-sensitive behaviour and are rigid at high speed impacts while are soft for low speed deformations. The hard-shell protector present a longer time-to-peak due to its curved shape, does not change the impact properties at low temperature but does not have a good multi-impact behavior. On the contrary, soft-shell protectors have good multi-impact properties and are more sensible to temperature.

The analysis performed for this paper can be used as a protocol during the design of helmets and body protectors in order to select the best performing materials and geometries.

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