Emilia Irzmańska, Agnieszka Brochocka

Influence of the Physical and Chemical Properties of Composite Insoles on the Microclimate in Protective Footwear

Central Institute for Labour Protection

National Research Institute (CIOP-PIB),
ul. Wierzbowa 48, 90-133 Łódź, Poland
E-mail: emirz@ciop.lodz.pl

Abstract

The objective of the paper was to evaluate the influence of the physical and chemical properties of composite insoles on the microclimate in protective footwear under conditions of hard physical work. The study used the sorption kinetics of composite insoles using artificial sweat with acidic and alkaline pH, the porosity of the composite structure, and measurement of the microclimate inside the footwear in a test involving human subjects under laboratory conditions on a treadmill. The results revealed that sorption kinetics largely depend on sweat pH – sorption is slower at alkaline pH (less effective moisture transport across the insole) than at acidic pH (more effective moisture transport). Strong correlations were found between the sorption parameters of the composite insole at alkaline pH and the porosity parameters of its structure. The microclimate measurements showed optimum temperature and humidity levels inside the footwear, which remained within the thresholds of comfort of use defined in the literature. It was found that composite insoles containing a polycarbonate melt-blown nonwoven may be recommended in particular for non-permeable protective footwear in conditions of very intensive physical work, which is accompanied by a shift in pH from acidic to alkaline.

Key words: *insoles, protective footwear, sweat sorption, sweat pH, porosity, footwear microclimate, comfort of use.*

Introduction

The basic function of protective footwear is the protection of the lower extremities against workplace hazards [1, 2]. It has been shown that while the materials used in such footwear do protect the feet efficiently, they deteriorate the ergonomic [3] and hygienic [4, 5] properties of the footwear considerably. Depending on the existing hazards, protective footwear may be constructed of "hermetic" materials, with protective elements constituting an additional burden on the feet. The materials and protectors used in such footwear hamper the distribution of heat and sweat which are produced in considerable amounts during physical exercise. Currently available insoles for protective footwear used in conditions of hard physical work are hygroscopic products that retain large amounts of moisture in their structure, which results in deteriorated hygienic properties [4]. High temperature and excessive humidity inside footwear lead to the decomposition of organic substances present in sweat. This, in turn, promotes the growth of pathogenic bacteria and fungi, adversely affecting the hygienic properties and safety of these products and reducing the period of time over which they may be used [5]. Insoles are typically designed as systems of adhesively bonded materials, which decrease their elasticity and comfort of The sole of the foot contains approximately 140,000 sweat glands, as compared to approximately 60,000 on the dorsal surface [6]. Therefore insoles may be the key structural element in ensuring an appropriate microclimate around the foot in footwear. It has been shown that the higher density of sweat glands on the plantar surface of the foot leads to excessive dampness of footwear materials in the toe, sole, and heel regions [7]. Insoles come in direct contact with the plantar surface of the foot and research has revealed that they absorb as much as 85 - 90% of the sweat generated by the feet. Therefore they should be designed to efficiently support the transport of moisture (sweat).

If insoles are made of a polymer or textile material buffering moisture, then effective liquid moisture transport is hampered and sweat accumulates in other footwear textiles (that is, in the lining, sole, socks, and liner) [4, 8, 9]. It has been found that the more moisture is removed from the immediate vicinity of the feet, the better the microclimate in the footwear becomes [10].

It should be stressed that the process of moisture (sweat) removal from protective footwear is complicated due to the special design of footwear, and it may be very difficult, as is the case of all-rubber boots. It is argued that sweat in liquid form accumulates in footwear soles, which leads to their gradual saturation,

especially if the upper is impermeable. Under these circumstances, an important role is played by support textiles (liner, sole, socks, lining etc.), which may facilitate the drainage of moisture along the fibres to a level above the shoe upper, where it may evaporate as a result of ventilation occurring during movement [11]. In this case, of importance is the influence of the structure of a textile product on its ability to sorb and desorb liquids in terms of such parameters as the chemical composition of the fibre, the fibre macrostructure, and the textile structure and weave [12].

While performing intensive physical work under difficult conditions (in mining, steel works, fire fighting etc.), sweat pH turns from acidic to alkaline. Therefore it was hypothesised that sweat pH influences the efficiency of sweat transport across composite insoles and thus affects the comfort of use of protective footwear. The objective of the study was to evaluate the influence of the physical and chemical properties of insoles on the microclimate inside protective footwear under simulated conditions of hard physical work. Composite insoles were subjected to physical and chemical measurements of porosity and sweat sorption (at acidic and alkaline pH), and the laboratory results were verified in a functional experiment involving human subjects (measurements of the microclimate in protective footwear).

Experimental

Materials

The authors of the present study had previously conducted research concerning the design and production of composite insoles for protective footwear, and their experiments are described at length in paper [13]. Based on their previous results for protective parameters (mechanical and hygienic – in accordance with the standards applicable to protective footwear) and microbiological parameters (based on the criteria currently used for casual footwear), which were reported in the above-mentioned work, two types of insoles were selected for further study. The insoles differ in terms of the chemical composition of fibres used in the middle layer (polycarbonate or polyamide).

The composite insoles designed comprise three layers:

- Top layer: woven fabric with an elementary warp satin weave 4/1(3). One side of the fabric is dominated by a warp overlap consisting of hydrophobic fibres (pneumatically linked textured yarn made of DTY (draw textured yarn) polyester fibres with a linear density of 220/48×2 dtex, white, manufactured by ELANA S.A, Toruń, Poland, under the trade name of TORLEN®), while the other has a weft overlap consisting of hydrophilic fibres (man-made lyocell cellulose fibres - open-end yarn with a linear density of 25 tex, manufactured by LINZ TEXTIL® GMBH, Linz, Austria, under the trade name of TEN-CEL®, white, in a crude form);
- Middle layer: a bioactive nonwoven fabric produced using melt-blown technology from commercially available polymers:
 - LEXAN Resin polycarbonate (General Electric Plastics, USA) for composite insole variant 1,

Table 1. Characteristics of the insoles for protective footwear studied.

No.	Type of insole	Component, blend ratio, %	Structure, type of fabric, blend ratio, %	Thickness, mm [76]	Weight, g/m ²
1	Composite insole designed (variant 1)	PES/LY/PC/PP = 10/20/60/10	Three-layer textile composite consisting of: ■ woven fabric made of PES/LY = 10/20, ■ melt-blown nonwoven made of PC = 60, ■ stiffening nonwoven made of PP = 10. The layers were spot-welded using ultrasound.	5.60	450
2	Composite insole designed (variant 2)	PES/LY/PA/PP = 10/20/60/10	Three-layer textile composite consisting of: woven fabric made of PES/LY = 10/20, melt-blown nonwoven made of PA = 60, stiffening nonwoven made of PP = 10. The layers were spot-welded using ultrasound.	5.80	450

- AQUAMID 6 polyamide (Auqafil Engineering Plastics, Italy) for composite insole variant 2; containing a biocidal substance (magnesium monoperphthalate);
- Bottom layer: a nonwoven consisting of polypropylene fibres (FILTEX S.A., Poland), used as a substitute for gasket felt.

Characteristics of the composites studied are given in *Table 1*, while physical and chemical properties of the melt-blown nonwovens used in the composite insoles, which were meant for use in protective footwear, are presented in *Table 2*.

Methodology

Evaluation of porosity

The porosity of the composite insoles was examined using a capillary porosimeter (PMIAPP, USA) [14]. We determined the mean sizes of the largest and smallest pore fractions, which in turn made it possible to determine the internal voids that form capillaries with varying diameters participating in the process of liquid absorption and distribution in the material. The analysis involved the following parameters:

- substitute diameter of the largest pores (bubble point), μm;
- substitute diameter of the largest pores, μm;

average size of the main fraction pores, μm.

Evaluation of sorption

The kinetics of the sorption of the composite insoles was studied using a sorption meter (SORP-3, Poland) [15]. This apparatus was used to analyse the kinetics of the phenomenon, providing information about the wettability of the surface as well as the time and maximum rate of the sorption process. Based on the sorption curve determined, the following parameters were calculated:

- Maximum sorption, S_{max} the amount of liquid absorbed per unit of area of the sample in μ l/cm²;
- Mean sorption rate, V_{30-70} the sorption rate calculated as the increase in sorption in time over the section of the sorption curve between the points corresponding to 30% and 70% of S_{max} in μ l/cm²s;
- Maximum sorption rate, V_{max} sorption rate at the extreme of the sorption curve in μ l/cm²s;
- Total sorption time, t_{max} time from the moment when the sample made contact with the wet surface to the end of the sorption process in s.

The sorption test was modified in two ways by the authors of the study presented. Due to the fact that the composites studied are to be used in protective

Table 2. Physical and chemical characteristics of the melt-blown nonwovens used in the composite insoles designed for protective footwear; *) The absorption of cold water by the melt-blown nonwovens studied was measured according to Standard PN-EN ISO 62:2008 "Plastics — Determination of water absorption". **) The water content of the melt-blown nonwoven samples studied was determined by coulometric titration using a Karl Fischer DL 39 coulometer from Mettler Toledo. During the Karl Fischer analysis, water contained in the nonwoven samples was released from the polymers in an oven at 110°C in an atmosphere of high purity nitrogen.***) The nonwoven samples studied were analysed by Fourier transform infrared spectrometry (FTIR). IR spectrophotometric spectra were acquired by means of Genesis Series FTIRTM apparatus from Unicam, using the following parameters: measurement range: 4000–500-1, resolution 4.0, and the number of scans done while acquiring a background spectrum: 16. The preparation examined, in the form of KBr tablets containing sample material at a concentration of 1 mg per 300 mg of KBr, was subjected to spectrometric analysis.

No.	Type of insole	Average fibre diameter, nm	Wetting angle, degree [66]	Water absorption, w/w % *)	Water content, w/w % **)	Vibration bands for FTIR spectra (W-3748 for PA W-3750 nonwoven; W-3750 for PC nonwoven), cm -1 Vibrations of –OH groups ***)
1	polycarbonate fibers	3.006	60	644	5.75	3437
2	polyamide fibers	3.177	70	847	7.70	3000 – 3500

footwear, the measurements were made under a load of 5 kPa. Additionally acidic synthetic sweat and alkaline synthetic sweat were used to simulate the process of sweat production during gradually intensifying physical exercise, which causes a shift in sweat pH. The synthetic sweat solutions were prepared in accordance with the procedure described in the standard concerning textile colour fastness to perspiration [16].

Evaluation of microclimate inside footwear with insoles

A functional study of footwear was conducted on ten active male firefighters aged 25 to 30 (28 \pm 1.5). The subjects underwent a medical examination which ruled out cardiovascular diseases, metabolic diseases, diseases of the locomotor system, and dermatological lesions on the skin of the lower extremities (the study protocol was approved by the Commission of Scientific Research Ethics at CIOP-PIB, decision No. 52/2009). The insoles were placed in certified impermeable protective firefighter boots. The boots were equipped with special protective elements, that is, steel toecaps designed to withstand an impact of up to 200 J and steel insoles fitted in the soles to provide puncture protection. Prior to the functional study, the footwear, insoles, and standard socks (CO/PA = 60:40) were conditioned for 24 h in a standard air atmosphere at 23 ± 2 °C and relative humidity of $50 \pm 5\%$.

The methodology for measuring the temperature and humidity inside footwear was described at length in our previous paper [4]. The microclimate was measured with two T/RH sensors (temperature with ± 0.3 °C accuracy; humidity with 1.5% accuracy). One integrated temperature and humidity sensor (ElproHotbox SE, Germany) was placed inside the boots between the sock and insole, medially, under the longitudinal arch of the foot. Another sensor measuring the temperature (Elpro, Switzerland) was placed in the central area of the dorsal region of the foot, where the surface of the skin comes in contact with the footwear outer most intensively. Measurements were conducted in a continuous online mode, with readings made every 3 minutes. Physical exercise was implemented using a treadmill (VIASYS HealthcareTM, Germany) with an adjustable belt speed. The tests were carried out in a laboratory at constant climate conditions: air temperature of 23 ± 2 °C, relative humidity of $50 \pm 5\%$, and air movement of 0.10 m/s.

The experimental procedure for the footwear microclimate testing consisted of the following three phases:

- Phase I warm-up on a treadmill at a speed of 7 km/h for 10 min,
- Phase II exercise on a treadmill at a speed of 5 km/h for 60 min,
- Phase III rest in a seated position for 30 min.

Statistical analysis

Sorption properties of the textile materials measured under different conditions (acidic and alkaline pH) were analysed for statistical differences. Also relationships between the sorption properties and porosity of the textile composites tested were examined.

A 95% confidence interval (± 2 SD) was adopted. The Kolmogorov-Smirnov test showed that all the variables analysed in the study were distributed normally. To identify statistical differences in terms of the pH of the solution's influence on the process of sorption, we conducted repeated mixed analysess of variance (ANOVA). Pairwise comparisons of means were carried out using post-hoc tests with Bonferroni correction for multiple comparisons. The level of significance adopted was 0.05 (for the maximum sorption rate) and 0.001 (for the maximum sorption and mean sorption rate, and the total sorption time). If the p value is less than the p threshold adopted, then the given factor (acidic/alkaline pH) has a significant influence on sweat sorption parameters.

The presence of a correlation between the parameters studied (porosity and sorption) was examined using Pearson's r. Statistical analysis was also conducted for measurements of the microclimate in the footwear with a view to identifying differences in temperature and humidity in the region between the foot and insole for two types of insoles over three phases of footwear use. The statistical significance of the parameters was evaluated using such statistical coefficients as the mean, standard deviation, and coefficients of variation. Analysis was conducted by means of SPSS Statistics 17.0 software.

Results and discussion

Analysis of porosity and sorption

The composite insoles developed represent a multi-layer material system including both hydrophilic and hydrophobic fibres that is conducive to sorption, but also involves absorption, surface wetting, and capillary transport through pores (voids). The three materials used for the composite, differing in terms of their morphological structures (a woven fabric, melt-blown nonwoven, and stiffening nonwoven), spot-welded by means of ultrasound, provide a gradient of density. This kind of insole structure ensures varied porosity with a prevalence of the smallest-diameter pores. It should be stressed that the middle layer exhibits the greatest variation in porosity, consisting of a melt-blown nonwoven characterised by considerable interfibre porosity, which is confirmed by 3D images of the composite (Figure 1).

The technology of ultrasound bonding was used to spot-weld three layers of different chemical composition and structure. This made it possible to avoid lamination, in which layers are attached by adhesive substances. Instead a spatial structure enabling easy transport of heat and moisture was created. This technology was developed by Irzmańska et al. and described at length in [13]. The upper layer of the insole (a woven fabric with a satin weave) quickly absorbs liquid (sweat) due to its thicker and stiffer fibres, which lead to larger pores located near the place of sweat secretion. These are synthetic PES fibres, which continue to be stiff after wetting. Effective distribution of the liquid occurs in the second layer, which is composed of thinner, nanometric melt-blown fibres, forming smaller pores in the spaces between them. The use of thin and smooth hydrophilic fibres (polycarbonate, PC or polyamide, PA, Figure 2) results in increased capillary pressure, which causes the liquid to flow further away to the third layer. The third layer, which comes in contact with the footwear, is made of hydrophobic fibres with limited absorptive capacity, whose task is to drain the sweat away along the support textiles, such as socks, to a level above the boot upper, where it evaporates as a result of ventilation occurring during movement. Similar conclusions were formulated by Kuklane et al. and Holmer et al. [17, 18].

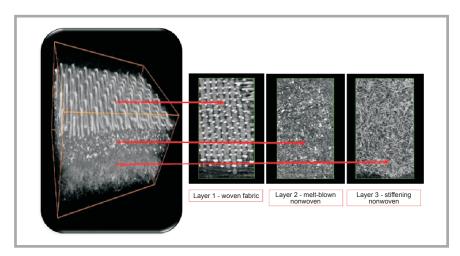
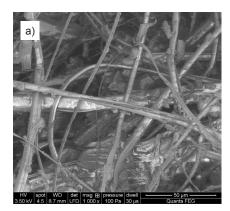


Figure 1. 3D cross-section through the structure of the composite insole designed for protective footwear.



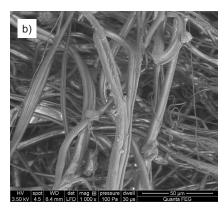


Figure 2. SEM image of a cross-section through the middle layer of a composite insole consisting of melt-blown nonwoven made of: a) polycarbonate (PC) and b) polyamide (PA) fibres.

According to Morton et al. [20], sweat particles may be attached to fibres mechanically or by physical and chemical processes. The mechanical attachment of sweat particles may be caused by surface attraction (adhesion) or accumulation inside microcapillary voids, crevices or fractures (porosity) as a result of capillary forces. This kind of sorption plays a major role in the case of fibres and products characterised by a highly non-uniform macroscopic structure. In turn, sweat particles attached to fibres by physical and chemical processes are bound by absorption.

In the present study, the insoles designed held sweat both effectively by physical/chemical and mechanical processes. From the point of view of the process of liquid (sweat) transport, the key element in the insole structure is the melt-blown nonwoven, made of two types of hydrophilic polymers: polycarbonate (PC) or polyamide (PA). According to Silverstein et al., as compared to other polymers, polyamides are characterised by high

water absorption. Even though in theory polyamide fibres are considered hydrophobic, it has been found that one can modify their water sorption properties by the addition of low molecular weight molecules of hydrophobic nature which limit the availability of the polymer to water molecules [19]. According to Morton et al., the hydrophilic properties of polyamides depend on the structure of the macromolecules, that is, the content of -OH groups [20]. The polyamide and polycarbonate macromolecules used in this study are characterised by polarity, which means that they readily absorb water (Table 2). Both the polycarbonate and polyamide fibres used in meltblown nonwoven are characterised by high wettability, which suggests that they have hydrophilic properties. This is additionally confirmed by the wetting angle $(\Theta < 90^{\circ})$ and moisture content obtained (*Table 2*).

In the study presented, sweat was also held in the insole structure mechanically as a result of adhesion and liquid accumulation inside microcapillary voids, crevices and fractures due to capillary forces. Sorption effectiveness is then largely determined by the capillary tension, which is responsible for moisture retention and its distribution between voids in the material. In turn, capillary tension levels depend on the type of liquid and environment. According to Larry Kenney [21], the pH of a liquid affects the capillary tension, which is increased by acidic pH and decreased by alkaline pH. During exertion, when the body secretes sweat more intensively, the pH of sweat gradually shifts from acidic to alkaline, which has been observed during strenuous sports exercise. In the present study, it was assumed that a similar phenomenon occurs during hard physical work, e.g., among steelworkers, miners and firefighters. It is a physiological fact that human sweat is characterised by low surface tension (pH 4-6.8) and contains inorganic components (e.g., chorine, sodium, potassium, and phosphorus ions) as well as organic ones (e.g., urea, creatinine, ammonia, uric acid, and glucose) [21]. Acidic sweat contains primarily inorganic components and, especially, "strong electrolytes" (N+ and K+), which increase the surface tension of the liquid due to the strong affinity of these ions to polar water molecules. Thus one could expect that during physical exercise alkaline sweat containing predominantly organic compounds, which decrease the surface tension, will not be as readily transported by textiles. The influence of sweat pH on the efficiency of capillary transport in protective products has not been studied to date or documented with appropriate scientific evidence.

In the study presented, we sought to confirm the physical phenomena above. Generally it was found that the insoles studied exhibited very good sorption properties (Table 3). Our tests also confirmed a characteristic feature of the sorption process, that is, very high intensity at the initial stage, followed by much lower intensity up to the state of saturation. Furthermore we observed that the sorption rate of the composite insoles was incremental due to structural differences between the layers, which is shown in the 3D image of the composite insole (Figure 1). Our experiments showed that the chemical composition of the liquid (sweat pH) is a statistically significant factor influencing the effectiveness of sorption by composite insoles (Table 4). We also found that the chemical composition of the liquid

had a significant influence on the kinetics of sorption by composite insoles - alkaline pH improved sorption effectiveness in terms of increasing the amount of liquid absorbed, thus also increasing the maximum sorption time, while acidic pH improved sorption effectiveness in terms of the maximum and mean absorption rates. The above findings were observed to strongly depend on the type of fibres used in the textiles, which was also reported by Patnaik et al. [23], Petrulyte et al. [24], Bogusławska-Bączek et al. [26], Hes et al. [27], and Mangat et al. [28]. Analysis of differences in the pH taking into consideration the material variants showed the insoles containing polycarbonate fibres (variant 1) to have the best sorption properties at alkaline pH and those containing polyamide fibres (variant 2) to have the best sorption properties at acidic pH. Both insole variants contained the same satin weave woven fabric from Lyocell and polyester fibres.

Even though alkaline pH theoretically decreases the surface tension of the fibres, which should imply inferior capillary transport, the presence of very thin hydrophilic polycarbonate fibres and a great number of small pores significantly improves the sorption effectiveness of the composite material. In turn, the polyamide variant more effectively absorbs and transports liquids with acidic pH, which theoretically increases the surface tension of the fibres, thus improving capillary transport. Different pH values of the liquid have different wetting effects on the fibre surface, increasing or decreasing the ability of the fibres to adhesively bind water [22 - 24]. Thus it was found that at alkaline pH, the exceptionally efficient liquid transport is due to the structure of the melt-blown nonwoven, which consists of an extremely high number of nanometric filaments, which was also reported by Dutkiewicz, who examined nonwovens for hygienic applications [29]. The very high capillary tension generated between them is responsible for retaining moisture in the nonwoven layer. Therefore the driving force for efficient liquid (sweat) transport in the melt-blown nonwoven is surface tension, that is, the attraction between droplets of body fluid (sweat) and the surface of fibres, as well as the configuration of a large number of voids (pores) in the insole structure, which was discussed in detail by, e.g., Dutkiewicz [29] and Woodcock [30]. The presence of smaller pores, entailing greater surface tension, leads to more efficient capillary transport in insoles (Table 3).

Table 3. Descriptive statistics of sorption parameters at alkaline and acidic pH for composite insoles with the middle layer consisting of melt-blown nonwoven made of polycarbonate fibres (variant 1) or polyamide fibres (variant 2).

Sorption at	Parameter	Composite insole variant, Mean/SD				
Corption at	1 didilicter	1 2 341.4/20.6 347.5/1 17.5/3.8 26.8/0 9.9/1.6 24.4/0 52.2/5.2 63.7/7 310.00/13.76 361.10/1 15.99/3.47 25.67/1 10.04/0.98 23.47/1	2			
	Sorption (S _{max})	341.4/20.6	347.5/13.6			
ا ام مانامه ال	Maximum sorption rate (V _{max})	17.5/3.8	26.8/0.9			
alkaline pH	Mean sorption rate (V 30-70%)	9.9/1.6	24.4/0.9			
	Maximum time (t _{max})	52.2/5.2	63.7/7.8			
	Sorption (S _{max})	310.00/13.76	361.10/10.26			
:-:	Maximum sorption rate (V _{max})	15.99/3.47	25.67/1.76			
acidic pH	Mean sorption rate (V _{30-70%})	10.04/0.98	23.47/1.90			
	Maximum time (t _{max})	44.40/4.38	48.38/5.09			

Table 4. ANOVA for differences between insole variants in respect of sorption parameters and post-hoc comparisons based on estimated marginal means.

Sorption parameters	ANOVA statistics				Composite	Post hoc comparison	
	F	df		Р	insole variant		
Sorption	11.57		33	< 0.001	1	alkaline pH > acidic pH	
(S _{max})					2	alkaline pH < acidic pH	
Maximum sorption rate	5.64				1	alkaline pH > acidic pH	
(V _{max})					2		
Mean sorption rate	2.99	3		< 0.05	1	not significant	
(V _{30-70%})					2		
Maximum time	15.44			< 0.001	1	alkaline pH > acidic pH	
(t _{max})	15.44	.44			2	not significant	

Table 5. Pearson's correlations between sorption parameters at alkaline and acidic pH and porosity parameters for composite insoles.

Variant	Parameter	So	rption a	at alkaline	рН	Sorption at acidic pH			
variant	Parameter	Smax	V _{max}	V _{30-70%}	t _{max}	Smax	V _{max}	V _{30-70%}	t _{max}
	Substitute diameter of the largest pores	-	-	-	-	0.37	0.46	0.44	-0.49
1	Size of the smallest pores of the main fraction	0.86	0.90	0.92	-0.92	-0.46	0.43	-0.35	-0.36
	Size of the largest pores of the main fraction	0.32	0.42	0.58	-0.58	-	-	-	-
	Mean flow pore size	0.34	0.48	0.45	-0.53	-	-	-	-
	Substitute diameter of the largest pores	0.32	-0.33	-0.37	0.47	0.56	0.40	0.56	-0.49
2	Size of the smallest pores of the main fraction	0.49	-0.43	-0.49	0.32	0.92	-0.92	-0.85	0.97
	Size of the largest pores of the main fraction	0.31	-0.34	-0.34	0.42	0.93	-0.92	-0.91	0.88
	Mean flow pore size	-	-	-	-	-	-	-	-

This is confirmed by the correlations between sorption and porosity parameters obtained (*Table 5*). The sorption parameters for insoles containing polycarbonate fibres (variant 1) are strongly related to the pore size at alkaline pH – the greater the size of the smallest pores, the higher the sorption (S_{max}), maximum sorption rate (V_{max}), and mean sorption rate ($V_{30-70\%}$) are, and the lower the maximum sorption time (t_{max}) is. In turn, the sorption parameters for the insole containing polyamide fibres (variant 2) are strongly related to the pore size at acidic

pH (a different type of correlation). In this case, the greater the size of the smallest and largest pores is, the higher the sorption, the longer the maximum sorption time (t_{max}), the lower the maximum sorption rate (V_{max}), and the lower mean sorption rate are ($V_{30-70\%}$).

Analysis of the microclimate in footwear

In order to confirm the conclusions following from the physical and chemical examination of the insoles, we conducted

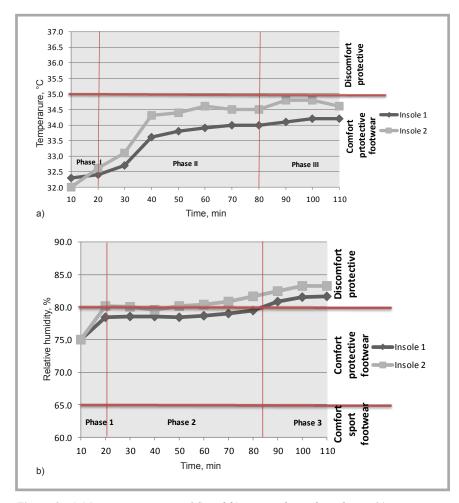


Figure 3. a) Mean temperature in °C and b) mean relative humidity in % in protective footwear with composite and commercial insoles. Insole 1—composite insole designed containing a PC melt-blown nonwoven, insole 2—composite insole designed containing a PA melt-blown nonwoven.

a functional study involving human subjects.

According to Gran [6], insoles store moisture in the form of liquid sweat, as they absorb most of the moisture present in the footwear. A study by Ogden [11] showed that insoles absorb as much as 85-90% of the sweat produced by the feet. Thus one could argue that the more moisture is removed from the immediate surroundings of the feet, the better the microclimate inside the footwear will be. However, the use of unhygienic polymeric insoles with adhesively bonded layers may completely block the sorption properties. In such a case, moisture (sweat) would accumulate in other parts of the footwear and in the socks, promoting the growth of pathogenic bacteria and fungi, which may adversely affect the hygienic properties and safety of protective products and reduce the duration of their use, which was discussed by Irzmańska et al. [13]. According to the literature, optimum conditions for the foot consist of a temperature not exceeding 35 °C and relative humidity of 65 - 80% in protective footwear and a temperature not higher than 34 °C and relative humidity of 60 - 65% in sports footwear [4, 2, 17, 18].

The functional tests confirmed the very good sorption properties of the composite insoles designed. The average recorded temperature shows that the composite insoles enabled the optimum temperature in the footwear during each of the three phases of footwear use (Figure 3.a). In phase I, the two insoles exhibited very similar parameters - the temperature for insole 1 (containing PC melt-blown nonwoven) was about 1% lower than that for insole 2 (containing PA melt-blown nonwoven). During phase II, the difference between the insoles increased to 5%. In phase III, the temperature difference slightly decreased and remained stable at 1.5%. It should be emphasised that the temperature inside the footwear did not exceed 35 °C during exercise, which translates into comfort of use according to the literature data, and the internal temperature remained within the comfort threshold throughout the entire footwear testing cycle, suggesting that the insole materials do not exhibit a buffer action, that is, they do not release the heat stored in the subject resting phase.

Just as in the case of temperature, the mean recorded humidity levels also indicate that the composite insoles studied ensure optimum humidity in the footwear during each of the three phases of footwear use (*Figure 3.b*). A slight and gradual increase in mean humidity was observed for the composite insoles between the three phases. Humidity levels rose by about 3% in phase II, and by about 3% in the rest phase, as compared to phase I. The humidity levels recorded in the footwear with the insoles tested did not exceed 80%, which implies comfort of use of the protective footwear.

The results of microclimate measurements inside the footwear prove that the composite insoles used in the protective footwear lead to optimum temperature and humidity levels in the metatarsal region during simulated physical exercise. They ensure good ventilation and rapid absorption of sweat from the skin, as well as its desorption, which is indicated by the temperature and humidity parameters remaining at nearly constant levels in the rest phase (phase III). The composite insole containing a polycarbonate melt-blown nonwoven and fabric made of Lyocell and polyester fibres exhibited optimum properties, as confirmed by the results of physical and chemical studies – during exercise involving intensive sweat production; when sweat pH becomes alkaline, efficient transport is supported by the structure of composites containing a melt-blown nonwoven made of polycarbonate fibres, efficiently transporting liquids (sweat) at alkaline pH.

Conclusions

- Multilayer composite insoles consisting of both hydrophobic and hydrophilic fibres improve liquid sorption due to absorption, surface wetting, and capillary transport through voids (pores).
- The non-uniform macroscopic structure of the composite insoles influences their sorption kinetics: the composite consisting of a polycarbonate melt-blown nonwoven and fabric

- made of Lyocell and polyester fibres (with very small pores) efficiently transports sweat at alkaline pH, while the composite containing a polyamide melt-blown nonwoven and fabric made of Lyocell and polyester fibres (large pores) efficiently transports sweat at acidic pH.
- Sorption kinetics largely depends on the pH of the liquid (sweat): at alkaline pH the sorption time is longer (moisture transport through the medium is less efficient), while at acidic pH the sorption rate is much higher (moisture transport through the medium is more efficient). Also the fibre type has an impact on sorption kinetics:
 - composites containing a meltblown nonwoven made of polycarbonate fibres efficiently transport liquids (sweat) at alkaline pH;
 - composites containing a meltblown nonwoven made of polyamide fibres efficiently transport liquids (sweat) at acidic pH.
- The composite insoles used in impermeable protective footwear lead to a more beneficial microclimate than that afforded by commercial insoles, meaning lower temperature and humidity levels in the metatarsal region during physical exercise.
- The type of insole recommended for impermeable protective footwear worn during hard physical work (in the mining industry, steel industry, mountain rescue services, and fire services) is the composite insole containing a melt-blown nonwoven made of polycarbonate fibres, as it improves the disposal of alkaline sweat, which is characteristic of intensive physical exercise.
- The results concerning the physical and chemical properties of materials and the microclimate inside footwear prove that during the process of designing and selecting insole materials for protective footwear to be used under conditions of hard physical work, the key criterion is evaluation of their sorption qualities and porosity at acidic and alkaline pH.

Acknowledgements

The study was carried out within the framework of Research Grant no. N N404 068240 (contract no. 0682/B/P01/2011/40) financed by the National Science Centre (Poland) in the years 2011–2013.

Editorial note

Sorption tests were conducted at the Textile Research Institute in Łódź, Poland; porosimetric measurements were made at the University of Bielsko-Biala, Poland; PC and PA melt-blown nonwovens were examined by the FTIR method as well as tested for moisture content and water absorption at the Institute of Biopolymers and Chemical Fibres in Łódź, Poland.

References

- Akbar-Khanzadeh F, Bisesi MS, Rivas RD. Comfort of personal protective equipment. Applied Ergonomics 1995; 26. 3: 195-198.
- Kuklane K, Geng Q, Holmér I. Thermal effects of steel toe caps in footgear. International Journal of Industrial Ergonomics 1999; 23, 5-6: 431-438.
- Garner JC, Wade C, Garten R, Harish Chander, Edmund Acevedo, The influence of firefighter boot type on balance. International Journal of Industrial Ergonomics 2013; 43: 77-81.
- Irzmańska E, Dutkiewicz J, Irzmański R. New approach to assessing comfort of use of protective footwear with a textile liner and its impact on foot physiology. Textile Research Journal 2014; 84, 7: 728–738.
- Irzmańska E. Footwear use at workplace and recommendations for the improvement of its functionality and hygiene. AUTEX Research Journal 2014; 14, 2. DOI: 10.2478/aut-2014-0005.
- Gran G. Investigation on shoe climate and foot comfort. J. Soc. Leath Trades. Chem. 1957; 43, 2: 182-19721.
- Hole LG. Sweat disposal from footwear and health and hygiene of foot skin. *Journal of the Society of Cosmetic Chemists* 1973; 24: 43-63.
- Bertaux E, Derler S, Rossi RM, Zeng X, Koehl L, Ventenat V. Textile, physiological, and sensorial parameters in sock comfort. *Textile Research Journal* 2010; 80, 17: 1803-1810.
- Gulbiniene A, Jankauskaite V, Kondratas A. Investigation of the Water Vapour Transfer Properties of Textile Laminates for Footwear Linings. Fibres & Textiles in Eastern Europe 2011; 19, 3, 86: 78-8.
- Heus R, Schols E. Water vapour transport as a determinant of comfort in evaluating shoes. *Elsevier Ergonomics Book* Series 2005; 3: 445-448.
- Ogden JM. Footwear insole with a moisture absorbent inner layer. United States Patent 5727336, 1998.
- Fohr JP, Couton D, Treguier G. Dynamic heat and water transfer through layered fabrics. *Textile Research Journal* 2002; 72.1: 1-12.
- Irzmańska E, Brochocka A, Majchrzycka K. Textile Composite Materials with Bioactive Melt-Blown Nonwovens for Protective Footwear. Fibres & Textiles in

- Eastern Europe 2012; 20, 6A, 95: 119-
- Grzybowska-Pietras J, Malkiewicz J. Influence of technologic parameters on filtration characteristics of nonwoven fabrics obtained by padding. Fibres & Textiles in Eastern Europe 2007; 15, 5-6, 64-65: 82-85.
- Frydrych I, Goetzendorf-Grabowska B, Prośniak P. Anti-sweat garment inserts (in Polish). Przegląd Włókienniczy – WOS 2003; 9: 9-15.
- PN-EN ISO 105-E04:2011. Textiles Tests for colour fastness. Part E04: Colour fastness to perspiration.
- Kuklane K, Holmer J. Effect of sweating on insulation of footwear. *International Journal of Occupational Safety and Ergonomics* 1998; 4, 2: 123-136.
- Nigel AS, Taylor JN, Caldwell IB. Mekjavic, The sweating foot: local differences in sweat secretion during exercise – induced hyperthermia, Aviation. Space and Environmental Medicine 2006; 77, 10.
- Silverstein R, Bassler G. Spectrometric Identification of Organic Compounds. Wiley, New York, 1963.
- 20. Morton DH, Harley JWS. *Physical properties of textile fibres*. New York, 1993.
- Kenney WL, Wilmore J, Costill D. Physiology of sport and exercise web study guide. 5th edition online study guide. Web Resource ISBN-13: 9781450423458.
- 22. Good RJ. Contact angle, wetting and adhesion a critical review. *Journal of Adhesion Science and Technology* 1992; 6: 1269-1302.
- Patnaik A, et al. Wetting and wicking in fibrous materials. *Textile Progress* 2006; 38.1: 1-105.
- 24. Petrulyte S, Baltakyte R. Liquid Sorption and Transport in Woven Structures. FI-BRES & TEXTILES in Eastern Europe 2009; ; 17, 2, 73: 39-45.
- Adomaviciene M, Schwarz A, Stanys S. Influence of Liquid Nature on Wetting Behaviour of an Inclined Fibre. FIBRES & TEXTILES in Eastern Europe 2007; 15, 5-6: 64-65.
- Bogusławska-Bączek M, Hes L. Effective Water Vapour Permeability of Wet Wool Fabric and Blended Fabrics. FIBRES & TEXTILES in Eastern Europe 2013; 1, 97: 67-71.
- Hes L, Loghin, C. Heat, Moisture and Air Transfer Properties of Selected Woven Fabrics in Wet State. *Journal of Fiber Bio*engineering & Informatics 2008: 968-976.
- Mangat MM, Militký J, Hes L. Thermal Resistance of Cotton Denim Fabric under various Moisture Conditions. *Journal* of Fibres and Textiles 2012; 1: 36-47.
- Dutkiewicz JK. Nonwoven Structures for Absorption of Body Fluids. Brussels: EDANA 2003, ISBN 2-930159-46-4.
- 30. Woodcock AM. Moisture transfer in textile system. *Textile Research Journal* 1966; 36: 855-856.
- Received 20.08.2013 Reviewed 22.04.2014