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Influence of the Structure of Footwear Upper and Lining Materials on Their Electrical Properties

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Abstract
Protective footwear for occupational use conducts static electricity through the upper, linings, insole and outsole into the ground. Footwear must be made from appropriate material to reduce the possibility of electrocution and other electricity-related incidents. In this study the influence of footwear materials for the upper and lining components' structure on their electrical properties was investigated. For investigations leather and various textile laminates were chosen. The thickness of leather coating, composition of textile laminates, the upper-lining system, and relative humidity of the environment on electrical resistivity changes were evaluated. Leather shows antistatic properties at standard humidity, but its electrical conductivity greatly increases at high humidity due to the presence of polar groups in the leather structure. Textile lining laminates composed of natural and synthetic fibres are insulators, but their systems with leather at high humidity show resistivity values close to antistatic materials. Leather acrylic coating decreases the electrical conductivity of materials.

Key words: *leather, textile lining, electrical properties, material structure, environmental humidity.*

Introduction

The main function of protective footwear for occupational use is protection from the risks posed by workplace hazards. Employees' productivity and satisfaction with the workplace can increase greatly when they work with the reassurance of protection against injury. While working with and around electricity, special attention must be paid to footwear that may reduce the possibility of electrocution or other electricity-related incidents [1]. Depending on the contact resistance, footwear can be defined as conductive, antistatic and electrically insulating. Footwear is antistatic if the contact resistivity measured is in the range of $10^5\,\Omega < R < 10^9\,\Omega$. It is considered to be conductive if contact resistivity values fall below this value, while a higher value means the footwear is electrically insulating (***Figure 1***).

Clothing, seating materials and environmental conditions accumulate electrostatic charge in the human body. The discharge can cause sparks and irritating sensations, but antistatic footwear can reduce this effect. The need to dissipate the accumulated electrostatic charge becomes vital in highly flammable and explosive environments, because discharge can lead to explosions as well as risk to human life and the environment. In this case conductive footwear should be used to minimise electrostatic charges in the shortest possible time. Static dissipating footwear works in the same way as conductive, but such footwear is used in less dangerous environments [2].

The electrical properties of footwear mainly depend on insole and outsole materials. Actually footwear conducts static electricity into the ground not only through the insole and outsole but also through the upper and lining material. Such components are produced from materials of a different nature, i.e., leather, textile, plastics, rubber, etc. The material's nature and thickness greatly influence not only hygienic and thermal properties but electrical properties as well [3].

Breathability, moisture absorbency, customisation and durability make leather one of the best components for the upper material of protective footwear [4]. Leather is a fibrous natural polymer whose electrical conductivity depends on the tanning, retanning and fatliquoring materials applied during leather processing [5-7]. Tanning and retanning materials (ammonium salts, chrome powder, dicyandiamide resin, etc.) have a large number of polar groups which combine with active groups in collagen fibres showing certain electrical conductivity. Cationic and anionic fatliquoring agents may also increase the electrical conductivity of leather. On the other hand, fatliquoring agents, such as paraffines and hydrophobic emulsifiers, which lubricate leather fibres, may isolate polar groups and weaken conductivity properties. Hence, during the processing of leather, cations Ca^{2+}, Cr^{3+}, NH_2^+, Na^+, H^+, etc., and anions Cl^-, COO^-, SO_4^{2-}, OH^-, etc., are introduced [8]. Generally cations combine with the acid groups of leather, while anions combine with the alkaline groups. These interactions are unstable and free ions can be easily generated under the effect of water molecules, which imparts electrical conductivity to leather.

The surface of leather is frequently coated with film of various polymers, such as casein, nitrocellulose, polyurethane, acrylic and other resin and polymer compositions, to modify the surface appearance and hide defects, as well as to im-

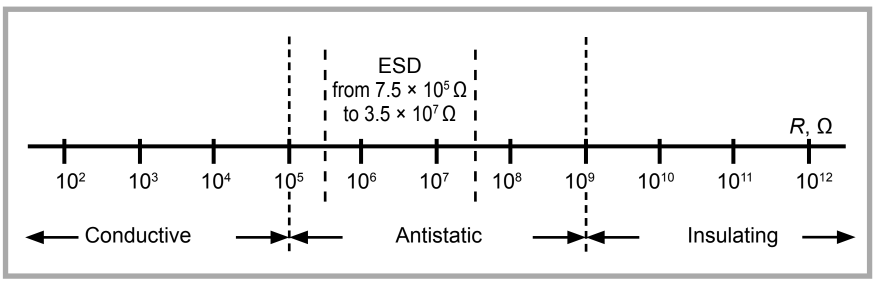


Figure 1. *Scale for the contact resistivity of protective footwear.*

prove physical properties (resistance to water, solvents, abrasion, etc.) [9]. Leather finishing with respect to coating formation not only decreases water vapour permeability and increases waterproofness but may change electrical properties as well. The electrical conductivity of leather often decreases because coating polymers with high insulating properties are used. However, the incorporation of some organic additives into the polymeric composition [10] or the application of advanced leather manufacturing technologies [11] increases the conductivity of leather significantly. On the other hand, leather can change the electrical properties of other materials. For example, the electrical conductivity of natural rubber composites increases by two orders of magnitude when leather waste is mixed in, creating the possibility to use these composites as an antistatic [12].

An optimum microclimate inside footwear can be ensured by using appropriate textile materials for the lining and/or other components, i.e., insoles and inserts [13, 14]. Especially the hygienic properties and comfortability of protective footwear are improved by using laminates made from textile fabrics and nonwovens with desirable hydrophilic and hydrophobic characteristics [15, 16]. Textile fabrics are basically assemblies of fibres that are made of linear long chain polymers and have a large length to diameter ratio. The electrical conductivity of most of these polymers is so low that they are considered as insulators. The specific resistivity of textile materials increases with an increase in the synthetic fibre amount, because many synthetic fibres used for textile fabrics are insulating materials with a resistivity in order of 10^{15} Ω [17, 18]. Textile materials are known for their ability to accumulate electrical charge, therefore it is important to understand how to minimise the detrimental influence of static electricity.

The electrical resistance of materials can change due to the flexing, contamination and moisture absorption from outside or inside sources. It is suggested that in a warm environment the foot may sweat about 30 g/h, and in some cases even up to 50 g/h [19]. Therefore the situation can change drastically when air between leather fibrils and textile fibres is replaced by moisture. Leather water uptake mainly depends on the fibril packing density and chemical materials used during leather manufacturing processes. Water absorbed into the material could contribute free charge carriers or influence the carrier trapping characteristics of the material, or both. As a result, the resistivity of the material decreases with increasing moisture content. Thus the resistivity of insulating, antistatic and static dissipative footwear greatly depends on the relative humidity of the environment [20].

It is necessary to select suitable materials in order to avoid injury from electrical hazards, because footwear may become a source of discomfort or even danger, if it is made of an inappropriate material or used in an incorrect way. There is a variety of different standardised measurement procedures under laboratory conditions for determination of footwear electrical properties. All these methods measure the protection level of the sole system against electrical hazards, but there are no standards to assess the influence of footwear upper materials on preventing static charge build-up and the ability to dissipate one. The goal of this study was to investigate the influence of footwear materials for the upper and lining components' structure on their electrical properties. The electrical resistivity was evaluated in dependence on the thickness of the leather coating, the composition of the upper and lining system, and the relative humidity of the environment.

Experimental

Materials

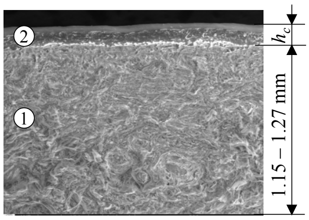
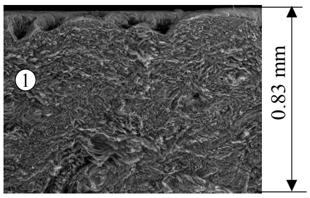
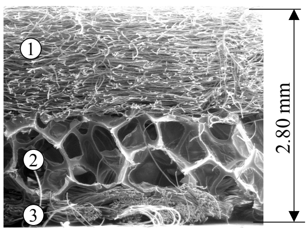
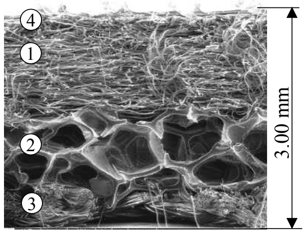
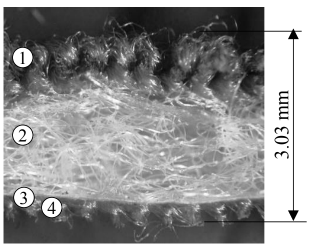
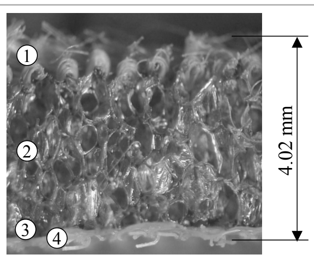
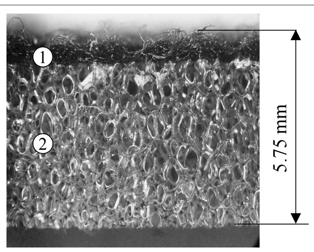
For the investigations, local salted cattle hide was used as raw material for upper and lining leather production. The hides were tanned according to conventional chrome tanning technology in JSC 'Odos gaminiai ir Ko' [5]. After tanning, the leather was coloured with a penetrating aniline dye and full grain crust leather of 1.5 ± 0.05 mm thickness was obtained. Further crust leather was finished using the coating processes described in [9]. Leather with acrylic coating of various thicknesses from 22 up to 122 μm was produced by spraying opaque pigmented acrylic emulsion (Durlin, Austria) with compressed air (50 g/m^2) at 100 °C temperature and 75 bar pressure. Leather for footwear lining was produced by the same tanning, retanning, and fatliquoring technologies as upper leather, after which it was shaved and grounded. The structures of both leathers used are presented in ***Table 1***.

Textile laminates for footwear lining of different composition, thickness and comfort-related parameters were selected for investigations, most of which (DL, LL, TL and CL) were used as purchased. These laminates differ in the chemical composition of fibres (polyester, polyamide or cotton) as well as in the layer structure and thickness (***Table 1***), which were combined by thermal or chemical means. Most of the textile laminates chosen comprise liner fabric, which comes in contact with the foot, bottom fabric from knitted or nonwoven textile, and an insulating middle layer – polyurethane foam or nonwoven fibre with countless microscopic open pores allowing air to circulate, to render a cushioning effect, and to create a comfortable micro-climate around the foot. Additionally some textile laminates comprise water vapour permeable microporous or hydrophilic membranes, such as Tepor, from Tepor s.p.s., Italy, (TL), Puratex, from Freudenberg, Germany, (PL), and LTI, from FTMC Textile institute, Lithuania, (LL), allowing perspiration to move away from the foot. In order to determine the influence of breathable membrane on the properties of textile laminates, Puratex microporous polyurethane membrane was hot laminated in a laboratory to a Dryliner laminate (DL) at a temperature of (90 ± 5) °C and pressure of (35 ± 2) kPa for (20 ± 2) s, and Puratex laminate or PL was obtained. Additionally a two-layer lining laminate (Cambrelle laminate or CL) with abrasion resistant fabric (available commercially as Cambrelle®, from DuPont de Nemours, USA) that exhibits high moisture transport properties was used. This fabric is formed from staple, bicomponent polyamide fibres (nylon 6 & nylon 6,6 and their sheath/core fibres) that are composed into a nonwoven web and thermally point bonded. Further Cambrelle® fabric was laminated to flexible high density polyurethane foam. LTI laminate (LL), instead of polyurethane foam, has a nonwoven polyester layer attached by a polyamide adhesive mesh using rollers heated at (130 ± 5) °C.

Evaluation of breathability

Before testing, all samples of leather and textile laminates were conditioned in a standard atmosphere at a temperature of T = 23 °C ± 2 °C and relative humidity RH = 50% ± 5% in accordance with the requirements of the EN 12222 standard. The water vapour permeability (WVP) and water vapour absorption (WVA) was measured according to the requirements

Table 1. *Structure and characteristics of footwear upper and lining materials investigated.* ***Note:*** ** WVP – water vapour permeability; WVA – water vapour absorption.*

Material cross-section and thickness	Material layers	Samples	Density, kg/m³	WVP*, mg/cm²·h	WVA, mg/cm²
LEATHER					
	1 – grounded leather (h ≈ 1.15 mm) 2 – acrylic coating (h_c ≈ 0-122 μm)	Upper leather	crust leather		
			450	4.3	3.3
			coated leather (coating thickness of 22-122 μm)		
			590-650	4.0-2.5	3.4-7.9
	1 – grounded leather, uncoloured, uncoated	Lining leather	490	4.3	8.5
TEXTILE LAMINATES					
	1 – cotton nonwoven (h ≈ 1.30 mm) 2 – polyurethane foam (h ≈ 1.00 mm) 3 – polyester and polyurethane blend knit DryLiner® (h ≈ 0.50 mm)	Dryliner laminate (DL)	110	133.0	2.3
	1 – cotton nonwoven fabric (h ≈ 1.30 mm) 2 – polyurethane foam (h ≈ 1.00 mm) 3 – polyester and polyurethane blend knit DryLiner® (h ≈ 0.50 mm) 4 – hydrophilic polyurethane membrane Puratex® laminated to textile (h ≈ 0.20 mm)	Puratex laminate (PL)	140	15.1	2.2
	1 – polyamide knit (h ≈ 1.10 mm) 2 – polyester nonwoven (h ≈ 1.30 mm) 3 – microporous polyurethane membrane, (h ≈ 0.03 mm) 4 – polyester knit (h ≈ 0.60 mm)	LTI laminate (LL)	220	3.2	5.7
	1 – polyamide knit (h ≈ 0.75 mm) 2 – polyurethane foam (h ≈ 2.90 mm) 3 – nonporous hydrophilic polyester membrane Tepor® (h ≈ 0.015 mm) 4 – polyester knit (h ≈ 0.35 mm)	Tepor laminate (TL)	160	4.3	5.8
	1 – nonwoven bicomponent polyamide fibres fabric Cambrelle® (h ≈ 0.75 mm) 2 – polyurethane foam (h ≈ 5.00 mm)	Cambrelle laminate (CL)	50	13.1	7.6

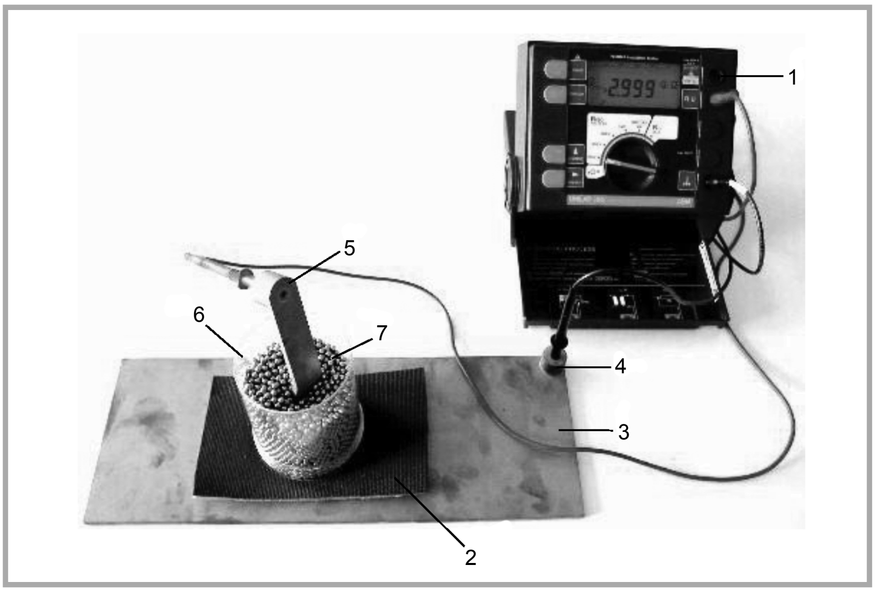


Figure 2. *Electrical resistance testing set: 1 – tester, 2 – test specimen, 3 – copper contact plate, 4 – external electrode, 5 – internal electrode, 6 – nonconductive plastic cylinder, 7 – stainless steel balls.*

Table 2. *Dependence of footwear material's electrical resistivity at different relative humidity.*

Material	Resistivity (Ω) at 100 V and different relative humidity		Resistivity (Ω) at 500 V and different relative humidity	
	50%	95%	50%	95%
Upper leather (crust, uncoated)	$4.3\ 10^{8}$	$6.7\ 10^{6}$	$4.0\ 10^{8}$	$5.3\ 10^{6}$
Lining leather (uncoated)	$2.0\cdot10^{8}$	$8.1\ 10^{4}$	$1.8\ 10^{8}$	$7.6\ 10^{4}$
DL	$>3.0\cdot10^{10}$	$7.1\cdot10^{6}$	$>3.0\cdot10^{10}$	$6.9\cdot10^{6}$
PL	$>3.0\cdot10^{10}$	$1.1\cdot10^{7}$	$>3.0\cdot10^{10}$	$1.0\cdot10^{7}$
TL	$>3.0\cdot10^{10}$	$>3.0\cdot10^{10}$	$>3.0\cdot10^{10}$	$3.1\cdot10^{9}$
LL	$>3.0\cdot10^{10}$	$3.4\cdot10^{8}$	$>3.0\cdot10^{10}$	$1.8\cdot10^{8}$
CL	$>3.0\cdot10^{10}$	$>3.0\cdot10^{10}$	$>3.0\cdot10^{10}$	$2.3\cdot10^{9}$

of EN ISO 20344 at the same atmospheric conditions. A detailed description of the leather samples and textile laminates' test procedures are presented in [5, 9, 21].

Evaluation of electrical resistivity

In order to check the influence of ambient humidity on the electrical properties, the test pieces were placed in airtight containers and kept for 7 days at ae temperature of (20 ± 2) °C and relative humidity RH = (50 ± 5)% and RH = (95 ±5)%. The dimension of the test pieces was 100 mm × 100 mm.

The measurement set used for whole shoe resistance determination according to the requirements of Standard EN ISO 20344 was adjusted for resistance *R* measurements of flat test samples. The measurements were carried out using a multifunctional insulation tester – Unilap ISO (LEM Norma GmbH, Austria) with electrical resistivity from 10 Ω up to 30 GΩ and the measuring voltage in the range of 50-1000 V DC at a 1 mA measuring current and temperature of (23 ± 2) °C and relative humidity RH = (50 ± 5)%. Test piece *2* was placed on the copper contact plate *3*, which was connected to the external electrode *4* and internal electrode *5*. This electrode was inserted into the isolating plastic cylinder *5* filled with conductive stainless steel balls *6* with a diameter of 5 mm (***Figure 2***). The insulation resistance values were measured applying a test voltage of (100 ± 2)V DC and (500 ± 2)V DC between the copper plate and steel balls for about 1 min. Insulation resistance measurements of footwear are usually performed at 100 V voltage, but in order to detect subtle weaknesses in the insulation, measurements above normal working voltages – at 500 V were performed as well.

Results and discussion

The footwear materials chosen for investigation vary in physical, mechanical and electrical properties. It is evident that their electrical properties depend not only on the nature and structure but also on the ability to accumulate moisture. The water uptake of the leather mainly depends on the packing density of the fibrils bundles, influenced by the leather quality and its manufacturing procedures [5, 9]. A polymer top coating from impermeable polymeric materials increases leather resistance to water penetration and lowers moisture transport properties. It was determined that the upper leather's water vapour permeability (WVP) decreases about 1.7 times (from 4.3 mg/cm$^2\cdot$h to 2.5 mg/cm$^2\cdot$h) and water vapour absorption (WVA) about 2.4 times (from 3.3 mg/cm^2 to 7.9 mg/cm^2) when a coating thickness of 122 µm is formed on an uncoated crust leather surface (***Table 1***). The increase in water vapour absorption can be attributed to the decrease in the porosity degree of coated leather, the interaction of water molecules with the leather collagen, and to the coating of acrylic polymer [5, 9].

WVP depends on the structure and type of textile laminate [21, 22]. As can be seen from ***Table 1***, for textile laminates TL and LL, WVP values are close to leather permeability values. Significantly higher values of permeability are characteristic for CL and PL laminates (13-15 mg/cm$^2\cdot$h), while DL shows about 10 times higher permeability compared to that of previously-mentioned laminates, and consequently DL has lower water vapour absorption ability than PL, CL and TL laminates, i.e. *ca.* 2 mg/cm^2 compare to that of 6-8 mg/cm^2.

The electrical resistivity of the footwear materials investigated at different measuring voltages is shown in ***Table 2***. It can be seen that upper and lining leathers possess antistatic properties at 50 % humidity. However, an increase in relative humidity by 45% (from 50% up to 95%) causes a decrease in leather resistivity by two and four orders of magnitude for upper and lining leather, respectively. At this level of humidity lining leather became conductive. With an increase in moisture content, the leather ionization degree increases, due to polar group interaction with water molecules. It may be supposed that the difference between upper and lining leather resistances at high relative humidity can be explained by the tighter packaging of lining leather fibrils and the higher polar group amount per unit volume. On the other hand, the measuring voltage change from 100 V

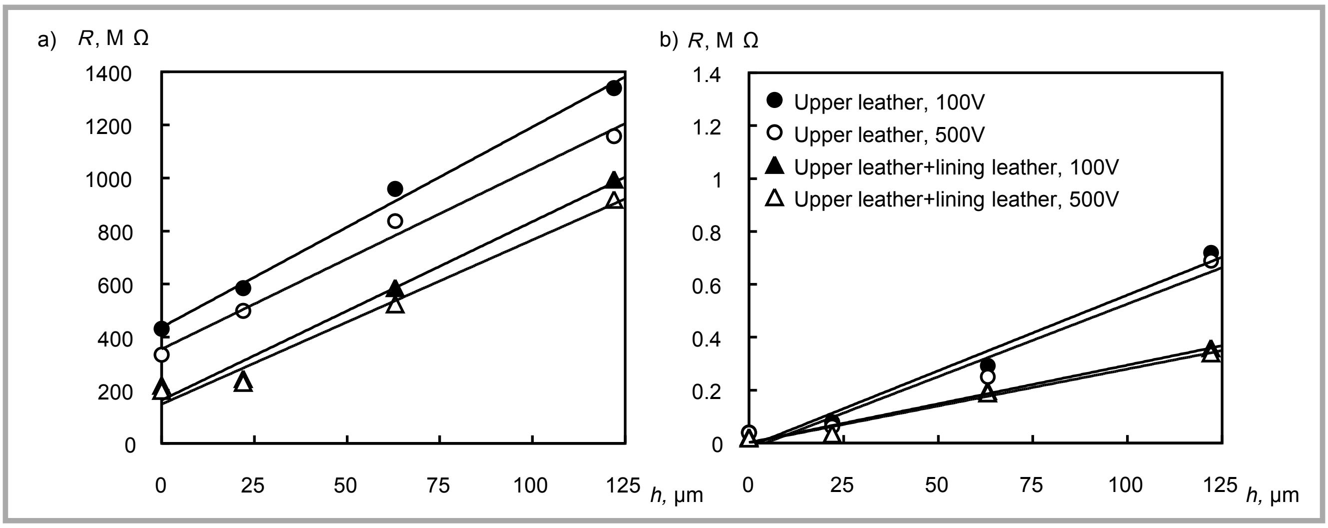


Figure 3. *Influence of coating thickness on the electrical resistivity of upper leather and its composition with lining leather at different relative humidity: a) 50%, b) 95%.*

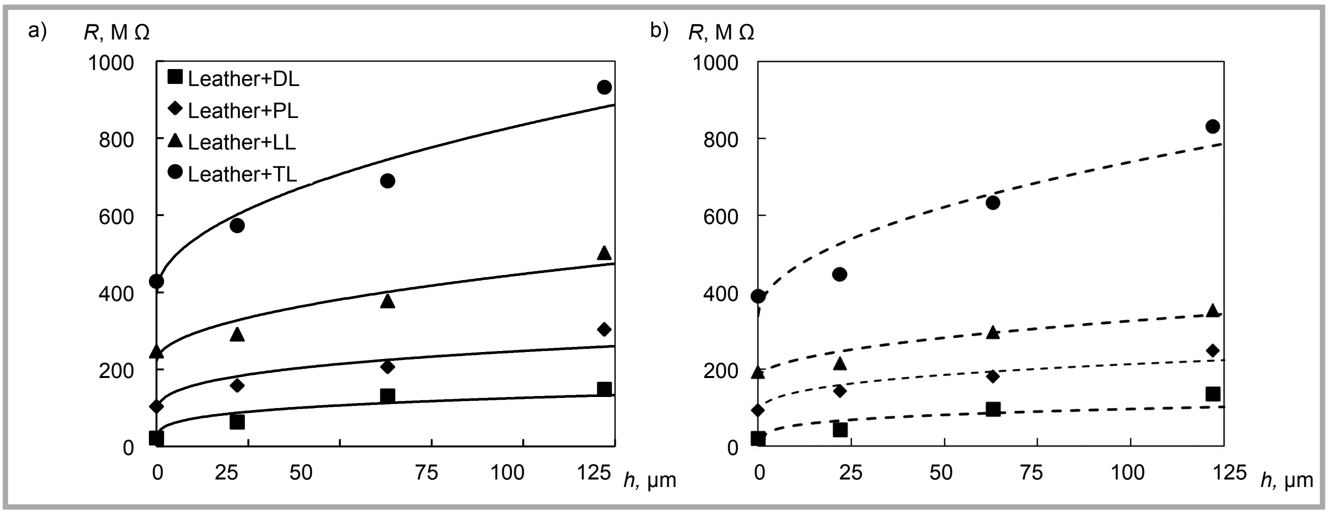


Figure 4. *Dependence of electrical resistivity of the upper leather and textile laminate composition upon leather coating thickness at a relative humidity of 95% and different measuring voltages: a) 100 V, b) 500 V.*

up to 500 V only slightly affects the electrical resistivity of leather, i.e. resistivity decreases by 10-20%.

The electrical resistivity of insulating textile laminates is extremely high (in the order of 10^{15} Ω [18]) and cannot be measured with the testing set used. However, an increase in relative humidity from 50% to 95% considerable decreases textile laminate resistance, while the change intensity depends on the laminate's construction, layer thickness and chemical composition of fibres. A lowest resistivity was obtained in the case of DL laminate, which is composed of natural (cotton) and synthetic (polyester and polyurethane) materials. Meanwhile the PL and LL laminates of closed thickness show higher resistance by one and two orders of magnitude, respectively. It can be supposed that such a difference to be caused by a higher content of synthetic materials in the laminate's structure [18]. The data indicate that the difference in the laminate's resistivity is caused not only by the fibre's chemical composition and humidity but also by the laminate thickness. The highest insulation ability is shown by the CL laminate, whose thickness is 1.5-2 times higher than the other laminates. Moreover the voltage only negligibly influences the electrical resistivity of laminates DL, PL and LL, which are of a similar chemical nature, but in the case of laminates TL and CL, the voltage influences the resistivity change by one or more orders of magnitude, which can be related to the influence of the high thickness of the polyurethane foam layer. However, no direct influence of the laminate's ability to accumulate moisture on the electrical properties was observed.

The dependence of the electrical resistivity of the upper leather as well as its system with lining leather at different relative humidity is presented in ***Figure 3***. It can be seen that the formation of acrylic coating of 122 μm thickness on a crust leather surface increases its resistivity by more than 3-times in both cases of measuring voltage. The resistivity of the system of upper leather – lining leather is lower compared to that of single upper leather, showing the same tendency of changes in coating thickness. In this case, the composition's resistivity increases by approx. 5 times, i.e. from 199 MΩ up to 995 MΩ at 100 V. Electrical resistivity values are lower by approx. 10-15% at a measuring voltage of 500 V.

Humidity drastically, by three orders of magnitude, decreases coated leather resistivity. As can be seen from ***Figure 3.a***, a higher decrease intensity is possessed by the system of upper leather-lining leather. The higher the leather thickness, the higher the amount of polar groups in collagen fibres; therefore a lower value of electrical resistivity is obtained. At a humidity of 95% the measuring voltage only slightly influences leather resistivity (***Figure 3.b***).

Upper leather-lining textile laminate systems for footwear show insulating behaviour at 50% humidity. Therefore in this case the influence of the coating thickness of the leather surface on the electrical resistance was measured only at 95%. From ***Figure 4*** it is clear that the laminate structure's influences the footwear upper-lining system's electrical resistivity; however, as can be expected, the intensity of change in the leather coating thickness is lower compared to that of the system with lining leather (1.5-2 times compared to 5 times). The system's resistivity increases with an increase in the laminate thickness applied. As can be supposed, the leather system with the laminate of the lowest thickness DL shows the lowest resistivity, and at 100 V voltage it changes from 63 MΩ up to 148 MΩ as the coating thickness increases from 22 μm to 122 μm (***Figure 4.a***).

Meanwhile, using a similar structure PL, resistivity values are two times higher due to the influence of the hydrophilic polyurethane membrane. The upper leather system with the higher thickness laminate TL possesses several times higher resistivity – 573 MΩ and 933 MΩ at a thickness of 22 μm and 122 μm, respectively. In the case of the CL laminate, the system showed insulating behaviour even at high humidity when measurement was performed at 100 V voltage. ***Figure 4.b*** demonstrates that, as in the case of leather, the measuring voltage influence on resistivity is only negligible – at 500 V measuring voltage the resistivity of the upper leather-textile lining laminate systems possess approx. 10% lower values.

Conslusions

- The electrical properties of protective footwear can be influenced by the upper and lining materials' structure, thickness, relative humidity, and voltage.
- The electrical resistivity of leather drastically decreases in a high humidity environment due to the free ion generation under the interaction of water molecules with polar groups of leather. The antistatic behaviuor of leather changes to conductive, or close to that, at 95% relative humidity.
- The electrical resistivity of the upper leather-lining leather system is about 3 times lower compared to that of separate leather layers and strongly depends on the relative humidity.
- The electrical resistivity of leather is lower by more than two orders of magnitude than that of textile lining laminates.
- For footwear lining laminates composed of natural and synthetic fibres and polymer foam as insulators, the resistivity increases with an increase in synthetic fibre and/or polymer layer thickness.
- The electrical resistivity of footwear upper-lining systems only slightly depends on the working voltage.

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