Textile Composite Materials with Bioactive Melt-Blown Nonwovens for Protective Footwear

Abstract

This paper presents the results of a study into textile composite materials designed to be used for the manufacture of insoles for penetration-resistant protective footwear (all-rubber). Due to the special conditions in which the insoles are to be used, it was assumed that they should have heightened hygienic and bioactive properties with respect to bacteria and fungi, and they should also be resistant to mechanical stress. Several variants of melt-blown nonwovens were engineered on the basis of polypropylene (PP), polycarbonate (PC), and polyamide (PA) to be used in composite materials. Also a method was developed for ultrasound bonding of composite layers. A series of laboratory experiments showed bioactive composite materials based on PC melt-blown nonwovens to have optimum properties from the point of view of the application of insoles in rubber footwear. The composites are characterised by very good mechanical properties (resistance to abrasion, tearing and bond strength), hygienic properties (pH of aqueous extracts, water vapour permeability, water vapour coefficient, water absorption and desorption, thermal resistance), and microbiological properties (tests for the following bacteria: Escherichia coli and Streptococcus aureus and fungi: Candida albicans, Aspergillus fumigatus, and Trichophyton mentagrophytes).

Key words: textile composites, bioactive insoles, melt-blown nonwovens, polycarbonate.

Introduction

In order to ensure comfort to the users of footwear worn in a work environment and in everyday settings, designers and manufacturers offer specially shaped insoles made of various textile composites. Their crucial functional features include appropriate mechanical and hygienic properties. At the same time, large-scale epidemiological studies conducted in the European Union [1, 2] have shown that it is also necessary to impart good bioactive properties to insoles to prevent the development of microorganisms that grow inside footwear. A study carried out under the project Achilles [1] has revealed that tinea pedis is the most widespread condition affecting the Polish population. In certain occupations (firefighters, miners, steelworkers, sportsmen, soldiers) the incidence may be as high as 70% of the persons examined. The study has continued for different occupational populations within the project Hermes [1]. So far 2,000 persons have been examined in Poland, out of whom over 50% have been affected by some pathological changes to the skin of their feet. People over 40 wearing protective footwear at work have symptoms of advanced mycosis. The conclusions of the study point to the need for the prevention of fungal diseases, with a particular focus on research aimed at the development and manufacture of new composite materials for bioactive insoles to be used in penetration-resistant protective footwear.

Protective footwear is intended to protect workers against hazards occurring at the workplace, such as mechanical injuries to the feet, burns, or the absorption of chemicals through the skin [3, 4]. Furthermore protective footwear should not affect foot physiology, but actively participate in processes related to the thermoregulation of the body, that is, facilitate heat and moisture transport to the environment [5]. The footwear microclimate is characterised by properties of the air surrounding the foot in the footwear, that is, its temperature and relative humidity. Optimum conditions for the foot are a temperature not higher than 28 – 34 °C and a relative humidity within the range of 60 – 65% [6]. The amount of sweat perspired in the footwear changes depending on the temperature of the environment, the intensity of the work performed, the individual characteristics of the person, as well as on the type of materials used in the footwear and design thereof. According to literature data, the average human foot produces 2.5 – 3.0 g of sweat per hour [7, 8]. The greatest problems are encountered with rubber footwear. Insoles currently used are hygroscopic and retain large amounts of moisture, which diminishes their hygienic properties [9]. After an 8 h work shift, moist insoles constitute perfect conditions for the growth of microorganisms. This fact compromises the thermal insulating and hygienic properties, which is confirmed by the subjective impressions of the users, as shown in a study carried out at the CIOP-PIB [10]. On the other hand, it should be stressed that this material has good thermal insulating properties when dry, which is important from the point of view of protection against sources of heat. High temperatures and excessive humidity in rubber footwear lead to the decomposition of organic substances contained in sweat, which in turn enhances the growth of pathological bacteria and fungi. The hygienic properties of materials used inside footwear may be modelled by using products characterised by high permeability and absorption of water vapour while also having heightened microbiological resistance. The development of microorganisms is directly influenced by the microclimate of the space enclosed inside the footwear, that is, by the humidity and temperature. The relative humidity inside footwear, reaching levels of 96 – 100%, is the basic factor enhancing the growth of bacteria decomposing sweat [11]. Analysing the microbiological contamination of footwear, one should always take note of the presence of pathological bacteria and fungi. Colonisation of the interior of footwear by yeast-like fungi and dermatophytes is a separate microbiological problem related to fungal infections of the feet [12 – 18]. From the point of view of footwear hygiene, of substantial importance are also parasitic mould fungi, which usually grow in moist interdigital spaces. The development of these fungi is similar to that of bacteria – it is stimu-
lated by increased perspiration, primarily due to wearing unhygienic footwear that is impermeable to air and water vapour.

Right parameters of the microclimate inside footwear may be achieved by modelling the design of composites for insoles. Research and design work conducted to date mostly concerns the modelling of composites for everyday footwear. Falkiewicz-Dulik and Przyjemskas designed two-layer composite insoles based on softened PVC adhesively bonded to other materials, especially those based on natural components [19]. In every case, the lining material was perforated PVC foam adhesively bonded to pig leather liner, PA spun bonded nonwoven (CAMBRELLE), cotton woven fabric, and velour knitted fabric or non-perforated PVC foam adhesively bonded to the Cambrelle nonwoven or velour knitted fabric. These materials ensured unfavorable conditions for the growth of bacteria and fungi. A comparative study was conducted involving other materials used in the manufacture of insoles. However, these materials did not reveal good hygienic properties, even in spite of their natural components, which was due to the chemical structure of PVC foam and the adhesive bonding. Another study by Falkiewicz-Dulik [20] shows the influence of the adhesive applied in insoles on the two-layer systems examined. The following systems were examined: an external cotton layer and a polypropylene woven liner bonded with the following adhesives: perforated adhesive film, solvent-based PU adhesive, or PU dispersion adhesive. While the woven fabrics tested in the study cited showed unsatisfactory antimicrobial effects, the composites had the right mechanical and hygienic parameters. A paper by Gulbiniene [21] presents the results of a study on the water vapour transfer properties of footwear liners incorporating a membrane. The material studied was a multilayer insole consisting of two textile layers (a polyester knitted fabric and a cotton nonwoven) and a polyurethane layer, whose presence reduced the rate of water vapour desorption and delayed the time of footwear drying. In his patented insoles, Connor [22] used natural materials derived from *Luffa cylindrica*, a plant with sponge-like fruits, positioned in such a way as to ensure direct contact with the user’s feet in order to provide massage as well as enhance natural exfoliation, blood flow and ventilation. Few publications have been devoted to specialised

The objective of the study presented was to design new bioactive composites with heightened mechanical resistance, allowing for moisture transport and inhibiting the growth of microorganisms in chemically-resistant protective footwear.

### Experimental

#### Structure and characterisation of materials

The study concerned the modelling of three-layer composites with a view to meeting the following criteria:
- Top layer – conductive-diffusive, remaining in contact with the user’s foot;
- Middle layer – biocidal, consisting of fibres containing a bioactive component, ensuring protection against bacteria and fungi and improving the hygienic properties;
- Bottom layer – external, stiffening.

A schematic of the layers of the composite designed for protective footwear insoles is shown in Figure 1.

The system designed is a spatial structure with layers of the following characteristics:
- Top layer: two variants of two-layer woven fabric – polyester/lyocell and polypropylene/lyocell woven with an elementary warp satin weave 4/1(3). In the fabric designed, one side is dominated by warp overlap consisting of hydrophobic (polypropylene or polyester) fibres, while the other by weft overlap consisting of hydrophilic fibres (lyocell cellulose fibres) [26, 27];
- Middle layer: bioactive nonwoven produced using melt-blown technology from three kinds of commercially available polymers – MOPLEN HP 456 J polypropylene (manufactured by LyondellBasell, Germany); LEXAN Resin polycarbonate (manufactured by General Electric Plastics, USA), and AQUAMID 6 polyamide (manufactured by Aquafil Engineering Plastics, Italy), containing a biocidal substance in the form of commercially available magnesium monophosphalate (manufactured by IMPULS, Poland). A biocidal substance was added at the stage of fibre formation in a quantity of 20% per nonwoven mass, as described in previous works [28 – 30]. The bioactive agent applied was certified by the Ministry of Health for commercial

![Figure 1. Schematic of the layers of the composite for protective footwear insoles; A - hydrophobic layer of two-layer woven fabric, B - hydrophilic layer of two-layer woven fabric, C - two-layer woven fabric, D - biocidal nonwoven, E - stiffening nonwoven.](image)

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use as a biocidal product (certificate No. 2623/05).

- Bottom layer: a nonwoven consisting of polypropylene fibres of an area weight of 500 g/m² (manufactured by Filtex S.A., Poland) – a nonwoven used as a substitute for gasket felt, characterised by ease of forming into concave-convex shapes.

For the purposes of the study, technological conditions were developed for the production of melt-blown fibres using three thermoplastic polymers: PP, PC, and PA. The polymers are characterised in Table 1.

Processing procedure

The technological work was done at the CIOP-PIB Poland experimental unit. The production of melt-blown nonwovens consisted of blowing the polymer melt into elementary fibres of different fineness and length. Polymer in the form of granules was transferred from the loading hopper to the heated cylinder of the extruder. The polymer was brought to appropriate viscosity prior to extrusion from the die assembly. Compressed air was transferred from the regulator to the heat exchanger, in which it was dried and heated to the appropriate temperature. Subsequently air was directed to the nozzle assembly, and as the air exited the nozzle assembly, it blew the polymer streams to form elementary fibres. The fibres were then deposited on the collector, forming a compact, porous nonwoven web. The nonwoven production unit has a number of control points for adjusting technological parameters, which enable the modelling of the structure of nonwovens, and in particular the production of fibres of various finenesses. Depending on the nozzle temperature (T_d) and temperatures of the 1st and 2nd zones of the extruder (T_1, T_2), the viscosity of the polymer melt may be altered, which is critical for its fibre-forming properties. This can be adjusted by the air temperature (T_a) and right proportions between the polymer flow (F_p) and air flow (F_a) [28 - 30]. In adjusting the process of forming nonwovens for composite insoles, all the technological parameters given in Table 2.

In order to impart bioactive properties to the nonwovens used in the composites, it was necessary to introduce a biocidal agent at the stage of forming fibres from the polymers characterised in Table 1. A bioactive agent in the form of commercially available magnesium monopersphthalate was added at the stage of polymer fibre formation. The bioactive nonwoven variants produced are presented in Table 3.

The next stage in the formation of composites for use in protective footwear was the development of a technology for joining the layers. The ultrasonic bonding method was applied – electrical energy supplied to the generator was converted into high frequency impulses supplied to the transducer, which converted them to ultrasounds. The welding was made with a universal vertical welder with the working motion as in a pneumatic press. This kind of welder makes it possible to use simple accessories, such as welding sonotrodes, which were modified to obtain the optimum process parameters. It was possible to adjust the parameters of the welding process, including the frequency, welding time, and pressure after each welding cycle, which enabled the experimenters to arrive at the optimum settings during the welding of one sample. This was particularly important in welding composites consisting of layers of nonwovens and fabrics made from different materials. During the welding process, the constant parameters were the pressure (controlled by the air pressure in the actuator) and vibration frequency of the sonotrode (adjustable by setting the vibration generator). The variable parameter, dependent on the type of materials welded, was the time of welding. The composites were welded using the following, optimised parameters: frequency – 45 MHz, pressing force – 0.5 MPa, welding time – 7 s for polypropylene fibres, 10 s for polyamide fibres, and 12 s for polycarbonate fibres. The bond-

### Table 1. Characteristic of polymers used in the melt-blown process.

<table>
<thead>
<tr>
<th>Type of polymer</th>
<th>Symbol</th>
<th>Trade name, supplier</th>
<th>Density g/cm³</th>
<th>Melt index MLL g/10 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polypropylene MOPLEN HP 456 J</td>
<td>PP</td>
<td>Lyondell Basell</td>
<td>-</td>
<td>3.4 g/10 min</td>
</tr>
<tr>
<td>Polyamide AQUAMID 6</td>
<td>PA</td>
<td>Aquafil Engineering Plastics S.P.A.</td>
<td>1.13 - 1.14</td>
<td>-</td>
</tr>
<tr>
<td>Polycarbonate LEXAN Resins</td>
<td>PC</td>
<td>General Electric Company</td>
<td>1.2</td>
<td>-</td>
</tr>
</tbody>
</table>

### Table 2. Technological parameters of melt-blown production.

<table>
<thead>
<tr>
<th>Temperature of the 1st extruder zone T_1, °C</th>
<th>Temperature of the 2nd extruder zone T_2, °C</th>
<th>Nozzles die assembly temperature T_d, °C</th>
<th>Air temperature T_a, ºC</th>
<th>Air flow, m³/h</th>
<th>Polymer flow, g/min</th>
<th>Reception length, mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>280</td>
<td>270</td>
<td>250</td>
<td>280</td>
<td>10</td>
<td>55</td>
<td>300</td>
</tr>
<tr>
<td>290</td>
<td>295</td>
<td>290</td>
<td>300</td>
<td>10</td>
<td>70</td>
<td>300</td>
</tr>
<tr>
<td>300</td>
<td>300</td>
<td>290</td>
<td>290</td>
<td>10</td>
<td>70</td>
<td>300</td>
</tr>
</tbody>
</table>

### Table 3. Characteristics of melt-blown nonwovens used in the composites.

<table>
<thead>
<tr>
<th>Type of biocidal nonwoven</th>
<th>Average area weight, g/m²</th>
<th>Average fiber fineness, µm</th>
<th>Average nonwoven fineness, mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymide nonwoven</td>
<td>430</td>
<td>3.2</td>
<td>3.9</td>
</tr>
<tr>
<td>Polymide nonwoven</td>
<td>371</td>
<td>8.4</td>
<td>3.5</td>
</tr>
<tr>
<td>Polycarbonate nonwoven</td>
<td>314</td>
<td>3.0</td>
<td>3.7</td>
</tr>
</tbody>
</table>

### Table 4. Variants of bioactive composites produced for protective footwear insoles

<table>
<thead>
<tr>
<th>Variant</th>
<th>Structure of bioactive composites for protective footwear insoles</th>
<th>Bottom layer</th>
<th>Middle layer</th>
<th>Top layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Stiffening polypropylene nonwoven</td>
<td>Polypropylene nonwoven with a biocidal agent</td>
<td>lyocell fabric/polyester</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td></td>
<td>Polypropylene nonwoven with a biocidal agent</td>
<td>lyocell fabric/polypropylene</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td></td>
<td>Polycarbonate nonwoven with a biocidal agent</td>
<td>lyocell fabric/polyester</td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td></td>
<td>Polyamide nonwoven with a biocidal agent</td>
<td>lyocell fabric/polypropylene</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td></td>
<td>Polyamide nonwoven with a biocidal agent</td>
<td>lyocell fabric/polyester</td>
<td></td>
</tr>
<tr>
<td>VI</td>
<td></td>
<td>Polyamide nonwoven with a biocidal agent</td>
<td>lyocell fabric/polypropylene</td>
<td></td>
</tr>
</tbody>
</table>
The composites designed are characterised by good mechanical and hygienic parameters within the standard tests’ range and exhibit protective effects against selected bacteria and fungi colonising footwear.

Taking into consideration the results of standard tests, it should be stressed that all of the composites are characterized by favorable mechanical parameters important from the point of view of using the and Candida albicans according to Standards PN-EN ISO 20645:2006 and PN-EN 14119:2005 as well as for Aspergillus fumigatus and Trichophyton mentagrophytes according to Standard PN-EN 14119:2005.

Results and discussion

Average values of laboratory parameters typically determined for protective footwear in the process of type assessment for CE marking, as determined for the designed variants of bioactive composites used in protective footwear insoles, are presented in Table 5.

All variants of bioactive composites were tested for the resistance of insole layers to bond strength, heat resistance, and microbiological properties. The results are presented in Figures 2 - 5.
insoles in footwear. They are of similar thickness to commercially available composite insoles, and thus can be easily manufactured as marketable products. They are highly resistant to abrasion, meeting the requirements of Standard ISO 20345:2007 both for dry and wet rubbing. The composites also reveal substantial resistance to tearing, which confirms that they provide good material for protective footwear intended for intensive use. All the composites meet the requirements stipulated in Standard PN-EN ISO 20345:2007, concerning the levels of substances hazardous to health, with the pH of aqueous extracts at 4.2 to 4.5. The composites exhibit high water vapour permeability, which is favorable from the point of view of using the insoles in footwear (effective transport of perspiration in the form of water vapor). Furthermore very good results were obtained in respect of the water vapor coefficient – the values were several times higher than the requirements of Standard PN-EN ISO 20345:2007. In terms of water absorption – from the perspective of using the insoles in footwear – it is preferable for this parameter to be as high as possible as a function of storing humidity, and the composites studied exhibit values higher than those defined in PN-EN ISO 20345:2007. In terms of water desorption, it is important for the composite not to retain water in its structure (perspiration in liquid form) and to dry quickly by effective water transport towards the footwear. It is comparable for all the variations tested and is higher than the one required in the standard.

As can be seen from the results of the standard tests, the composite with the best properties is that containing a PC nonwoven with a bioactive agent with a layer of LY/PET fabric. This system has the best mechanical and hygienic properties out of those tested in this study, which is due to the fact that PC fibres have better sorptive and mechanical properties than PP or PA fibres [31]. The composites containing PA and PP nonwovens with a bioactive agent were shown to exhibit substantially inferior levels in these respects.

Additional tests (apart from those based on the standards) were aimed at the assessment of the insulation properties of the composites, their resistance to the delamination of the layers joined by ultrasound, and the influence of the presence of a nonwoven with a bioactive agent on the inhibition of the growth of microorganisms developing inside footwear.

Resistance to the bond strength of layers

The composites studied exhibited high resistance to bond strength. This confirms the effectiveness of ultrasound bonding of the layers and suggests that the layers of composite material will not delaminate, which enhances the comfort of usage of insoles in footwear and their durability. The highest values – important from the point of view of lasting use of insoles in footwear – were obtained for the variant containing a stiffening PP
nonwoven, a PC nonwoven with a bioactive agent and a LY/PET fabric (variant III), and the lowest values were shown by that containing a stiffening PP nonwoven, a PA nonwoven with a bioactive agent, and a LY/PP fabric (variant VI).

Heat resistance
The composites designed have good isolation properties, classifying them as heat protection products, which is important for the protection of the lower limbs of fire fighters exposed to heat. Higher levels of heat resistance are revealed by variants made of stiffening PP nonwoven, PC nonwoven with a bioactive agent, and containing LY/PP fabric (variant IV) or LY/PET fabric (variant III), PA nonwoven with a bioactive agent, and LY/PE fabric (variant V). The lowest values were obtained for the composite consisting of stiffening PP nonwoven, PP nonwoven with a bioactive agent, and LY/PET fabric (variant I). It should be stressed that PC nonwovens have very good insulation properties, which translates into higher levels of heat resistance of the whole composite. PA and PP nonwovens have lower thermal insulation properties, which leads to lower values of the property studied.

Bioactive properties
All of the composite systems exhibited a high level of biological activity according to Standards PN-EN ISO 20645:2006 and PN-EN 14119:2005, the only difference being the size of inhibition zones for particular microorganisms. The best results in terms of antibacterial effects against Staphylococcus aureus were obtained for the system composed of stiffening PP nonwoven, PC nonwoven with a bioactive agent, and LY/PP fabric (variant IV). The greatest inhibition zone for Escherichia coli was observed for the system containing stiffening PP nonwoven, PA nonwoven with a bioactive agent, and LY/PET fabric (variant V). In the case of Candida albicans, the largest inhibition zone was found for systems composed of stiffening PP nonwoven, PP nonwoven with a bioactive agent, and LY/PET (variant I); stiffening PP nonwoven, PP nonwoven with a bioactive agent and LY/PP fabric (variant II); and stiffening PP nonwoven, PA nonwoven with a bioactive agent and LY/PET fabric (variant V).

For the assessment of antifungal properties of the composite systems designed, tests were conducted for Aspergillus fumigatus and Trichophyton mentagrophytes. It was found that all of the systems designed exhibited very good antifungal effects against Trichophyton mentagrophytes – they were graded level 0, which means that fungus was not detected by microscopic examination under a 50× magnification.

No growth inhibition zone was found on samples of systems consisting of stiffening PP nonwoven, PC nonwoven with a bioactive agent and LY/PET fabric (variant III), and stiffening PP nonwoven, PA nonwoven with a bioactive agent and LY/PP fabric (variant VI) – the fungus continued to grow starting from the colonies developed at the edges of the plate. The best effects against Aspergillus fumigatus were identified for the system containing stiffening PP nonwoven, PC nonwoven with a bioactive agent and LY/ PP fabric (variant IV). Better antifungal activity was found against Trichophyton mentagrophytes – the growth inhibition zone around the samples covered the entire plate, while for Candida albicans the inhibition zones around the samples were smaller than those for Trichophyton mentagrophytes. The designed bioactive systems consisting of stiffening PP nonwoven, PC nonwoven with a bioactive agent and LY/PET fabric (variant III), and those containing stiffening PP nonwoven, PA nonwoven with a bioactive agent and LY/PP fabric (variant VI) exhibit a weaker effect against Aspergillus fumigatus, but it is still defined by the relevant standard as the absence of visible growth under microscopic examination.

Conclusions
The experiments conducted tested the possibility of using bioactive melt-blown nonwovens (made of fibre-forming polymers having various mechanical properties and different liquid sorption levels) in designing composite insoles intended for protective footwear. A biocidal agent in the form of commercially available magnesium monopropylphthalate was introduced at the stage of melt-blown fibre formation in order to impart bioactive properties to the insoles. The use of the nonwovens produced in the design of composites made it possible to obtain insoles that effectively inhibit the growth of microorganisms such as Escherichia coli, Staphylococcus aureus, Candida albicans, Aspergillus fumigatus and Trichophyton mentagrophytes inside footwear, in contrast to the wool felt insoles currently used with protective footwear. To ensure good mechanical properties, directly enhancing the durability of the insoles, a method of ultrasonic bonding of composite layers was developed. The method also makes it possible to preserve the separation distance between the structural layers of the composite, thus improving the hygienic properties while keeping the optimum mechanical parameters. This method may be used as an alternative for adhesive bonding or to joining the layers of insoles by means of continuous adhesive films impermeable to water vapour or air.

Among the variants of bioactive composite insoles designed and tested, the best properties (especially in terms of good sorptive and resistance characteristics) were exhibited by composites containing a bioactive melt-blown PC nonwoven.

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