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Corrosion Behaviour of CuSn- and CuZnNi-coated Polypropylene Nonwoven

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Abstract

The intended purpose of metallised nonwovens is architectural shielding against electromagnetic fields. Therefore the aim of this work was to systematically investigate the corrosion behaviour of metallic layer/polypropylene nonwoven systems in the contact with an aggressive environment (3% NaCl solution). In the work, a thermo-bonded polypropylene nonwoven was used as a substrate for CuSn and CuZnNi thin layer deposition. Nonwoven metallisation was carried out using the magnetron sputtering process. Additionally to enhance the durability of these barrier materials, their surfaces were covered with a thin, hydrophobic coating of polydimethylsiloxane. Evaluation of the corrosion resistance was made by means of potentiodynamic polarisation tests. Furthermore the degree of loss of the metallic layers was checked using an optical metallographic microscope and quantitative microanalysis by the method of Energy Dispersive X-ray Spectroscopy. It was found that the CuZnNi metallic layer deposited onto the polypropylene nonwoven shows higher corrosion resistance as compared to CuSn. In both cases, the metallic layers are the most susceptible to degradation within the nonwoven “waves”. Regardless of the layers’ chemical composition, the polydimethylsiloxane coating increases their corrosion resistance in 3% NaCl solution.

Key words: polypropylene nonwoven, metallic thin layers, CuSn, CuZnNi, polydimethylsiloxane, magnetron deposition, corrosion resistance, potentiodynamic polarisation.

Introduction

Modern textile composites are more and more often obtained by combining different techniques, and also by the use of those which have not been applied to textiles yet. In recent years, they were joined by PVD (Physical Vapour Deposition) methods, particularly the increasingly popular magnetron sputtering technique. So far magnetron sputtering has been applied on a large scale in optoelectronics, particularly in photovoltaics, e.g. for the deposition of low-emissive coatings onto plastic films and glass, as well as in the packaging industry for deposition of aluminum onto paper and labels. The variety of technological capabilities of this technique is still very high, which in turn leads to imparting materials the exploitation characteristics desired. In this way, textile composite materials possessing many functions can be produced, which is often unattainable by other methods. Additionally the technique (being effluent-free) is in line with the trend of reducing waste water from finishing processes, according to the Best Available Technology – BAT and Best Environmental Practice for Wet Processes in the Textile Processing Industry – BEP directives.

Studies on the use of the magnetron sputtering technique to modify textiles are carried out in various research centres. The anti-fungal and anti-bacterial properties of selected groups of elements were

investigated by Scholz et al. [1]. The use of Cu and Ag sputter deposited coatings on conductive textiles was studied by Wei et al. [2], Hegeman et al. [3] and Pawlak et al. [4]. In the same papers, Wei et al. [2] reported the influence of the coating on the pore size of the textile material, and Hegeman et al. [3] also showed the anti-bacterial activity of Ag coatings. The use of the magnetron sputter deposition of Cu coating for the production of textile screens against electromagnetic fields was studied by Bula et al. [5]. For the coatings thus obtained, only selected traits, mainly adhesion, were tested.

It is generally believed that coatings deposited by PVD methods exhibit good operating properties, including very good tribological and corrosion resistance. Such studies with respect to PVD coatings applied on metal substrates are conducted and published quite often [6 - 11]. On the other hand, in the research [5, 12 - 14], where the magnetron technique was applied to deposit metals or metal alloys onto textile substrates in order to obtain conductive and/or shielding materials, attention was paid mainly to the quality and features of the resultant coatings expected. The problem of the corrosion resistance of metallised textiles – materials of spatial structure has not, to our knowledge, been undertaken so far. However, knowledge of the sustainability of this type of material in aggressive environments where they may be used is

extremely important, particularly for the development of their new applications.

Therefore the aim of this work was to systematically investigate the corrosion behaviour of CuSn and CuZnNi thin layers deposited by magnetron sputtering onto polypropylene (PP) nonwoven. The intended purpose of the resulting metallised PP nonwovens is architectural shielding against electromagnetic fields. Additionally to enhance the durability of these barrier materials, their surfaces were covered with a thin, hydrophobic coating of polydimethylsiloxane (PDMS), which is known to form effective protective layers against the contact of water based corrosive media [15, 16].

Experimental

Sample preparation

The metallisation of a substrate – PP nonwoven was carried out by magnetron sputtering of CuSn (composition by weight: 80% Cu, 20% Sn) and CuZnNi (composition by weight: 53.5 – 56.5% Cu, 25 – 30% Zn, 17 – 19% Ni) alloy targets. The thermo-bonded polypropylene nonwoven used, with a weight of 150 g/m², was manufactured under the trade name of “Termonina” by Textron, Zgierz, Poland. The deposition of metallic layers was conducted under the conditions summarised in **Table 1**. Features of the magnetron device used and the deposi-

tion process itself have been presented elsewhere [5,13].

Hydrophobic coating was deposited by plasma polymerisation (at ZEM-POLMO Ltd., Łysomice, Poland) using the liquid precursor – hexamethyldisiloxane, known under the trade name “Glipoxan”. Polymerisation was carried in a time of 300 s, according to the procedure described in [17]. The intention of the use of such a short time was to obtain a possibly thin (nano-sized) protective coating which would not affect the conductive and simultaneous shielding properties of the metallised nonwoven. Then it was possible to register potentiodynamic characteristics (polarisation curves) of the materials investigated and to determine their resistance to electrochemical corrosion.

Characterisation

Evaluation of the corrosion resistance was made by means of potentiodynamic polarisation tests using an Atlas 9833 potentiostat. The measurements were carried out in a three-electrode cell with the sample as a working electrode. A saturated standard calomel electrode (SCE) and platinum were applied as reference and counter electrodes, respectively. Sodium chloride solution ($\text{pH} = 6.5, t = 25 \pm 1 \text{ }^\circ\text{C}$) was used as the corrosive medium. It is known that solutions containing chloride ions are one of the most aggressive corrosive media, also with regard to architectural constructions. Generally the corrosion rate increases with an increase in the concentration of chloride ions. However, above a concentration of *ca.* 3%, the growth rate of the corrosion rate decreases. Therefore 3% NaCl solution was chosen for these studies. The exposed area of each sample was 0.3 cm^2 . Prior to the beginning of the polarisation tests, the samples were kept in an electrolyte for 10 min. The measurements were carried out at a scan rate of 0.001 V/s . Such conditions (stabilisation time and scan rate) were chosen to prevent electrolyte leakage through the highly porous substrate (polypropylene nonwoven). The tests were repeated at least three times for each sample until obtaining similar polarisation curves. The corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were estimated with the use of the Tafel extrapolation method [18].

The corroded areas and those not treated with the corrosive medium were ob-

Table 1. Parameters of CuSn and CuZnNi deposition processes; *Effective power – power generated directly onto the sputtered material at intervals (pulse phases). The sputtering effectiveness can be modified by changing its value. **Flying power – a value which describes “mismatching” between the output resonant circuit of the feeder and the impedance of glow discharge. The value of the flying power can be affected by the gas type and its composition, e.g. content of reactive gas, changes in the total pressure, electric properties of reaction products covering the target surface, changes in the density of the effective power resulting from changes in the target geometry due to its gradual etching. The above definitions apply only to pulse feeding due to the feeder with a resonant circuit.

Sample	Velocity of the substrate drift, mm/s	Effective power*, kW	Flying power**, kW	Number of cycles
CuSn/PP	15	3.95 – 4.05	1.72 – 1.75	15
CuZnNi/PP		2.02 – 2.07	0.58 – 0.63	

served with an optical metallographic microscope (MM), Nikon MA-200 with CF160 optics. In the description of the results obtained by MM, the following terms were introduced: “weave” as the equivalent of the crossing points of the polypropylene fibres, and “overpress” understood as the area located between the four “weaves” and corresponding to the site of the thermal joint of the unwoven fabric.

Furthermore the degree of loss of the metallic layer components was also tested using quantitative microanalysis by the method of Energy Dispersive X-ray Spectroscopy (EDX). The microanalyses were conducted in a vacuum environment at a pressure equal to $2 \times 10^{-5} \text{ Pa}$. The voltage accelerating the electron beam (probe) applied was 20 kV . Analysis of the chemical composition was performed, in every case, on equal surface areas of the samples (magnification:

$1000\times$) within both “weaves” and “overpresses” untreated and treated with 3% NaCl solution.

Results

Corrosion behaviour of CuSn based systems

Figure 1 shows the polarisation curves registered for CuSn/PP and PDMS-CuSn/PP (additionally coated with a polysiloxane protective coating) samples in 3% NaCl solution. On the graph, two potentiodynamic characteristics obtained for each sample have been set together in order to confirm the reproducibility of the results and thus the uniformity of the layers deposited on the polypropylene substrate.

Analysing the polarisation curves obtained for CuSn/PP (black lines), one can distinguish three specific anodic areas, which were also observed during elec-

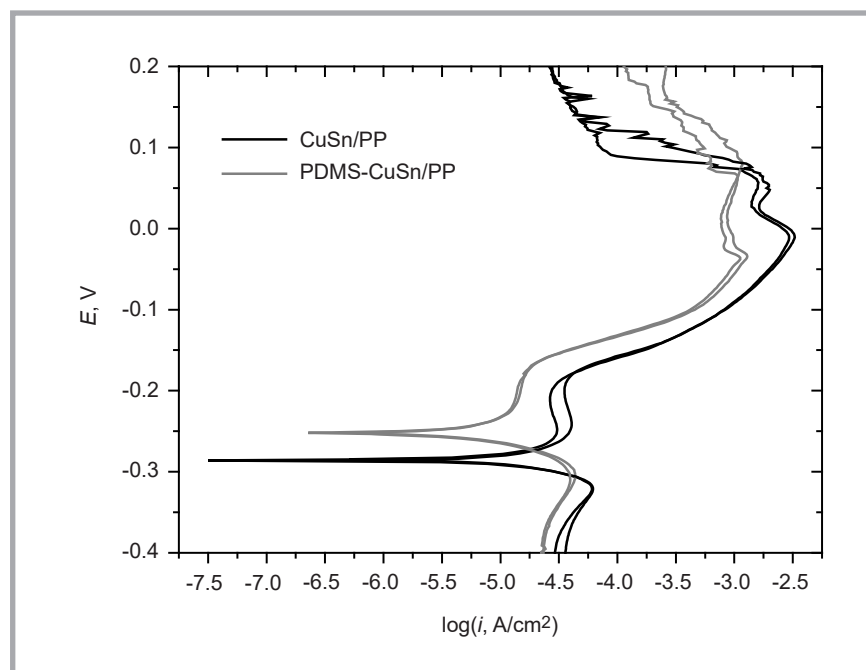


Figure 1. Polarisation curves of CuSn/PP and PDMS-CuSn/PP samples in 3% NaCl solution.

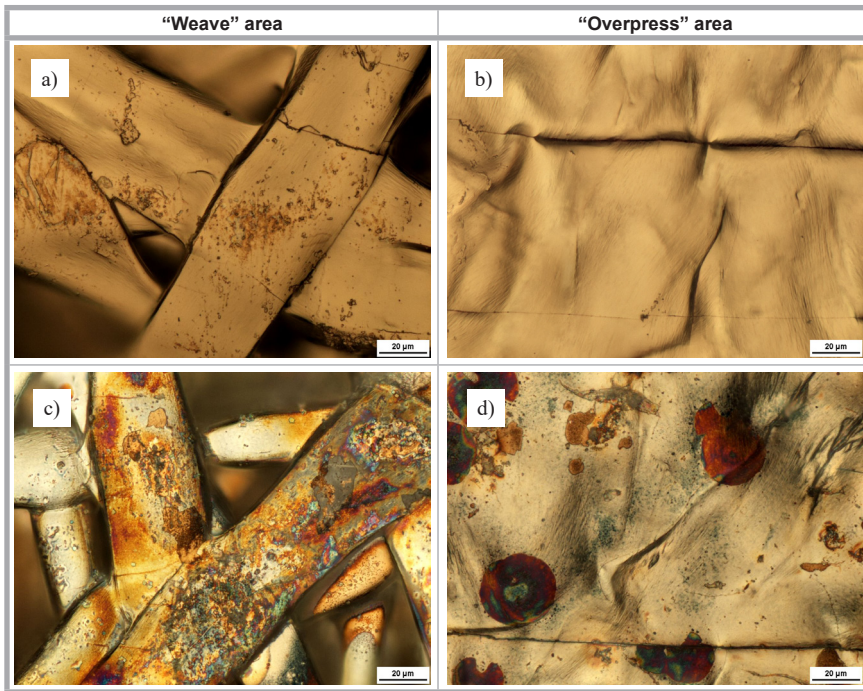


Figure 2. MM images of CuSn/PP: not treated (a, b) and treated (c, d) with 3% NaCl solution.

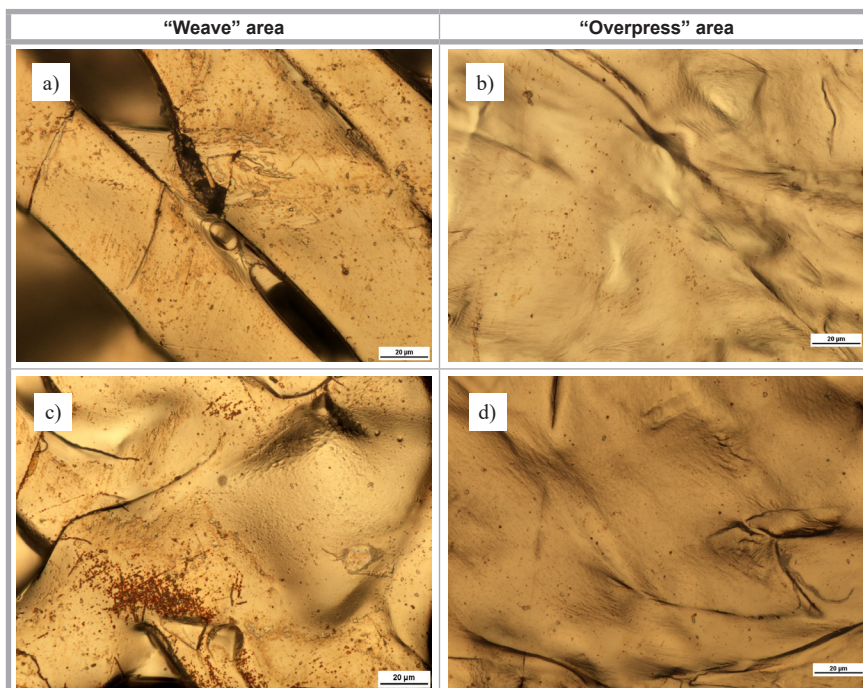


Figure 3. MM images of PDMS-CuSn/PP: not treated (a, b) and treated (c, d) with 3% NaCl solution.

trochemical studies of bronze carried out in aerated NaCl aqueous media [19, 20]. They correspond to the following: (I) dissolving the components of the CuSn metallic layer, which extends from the corrosion potential $E_{\text{corr}} = -0.281$ V up to about $E = -0.250$ V, (II) the active-passive transition, and (III) the current plateau observed up to a potential value of about -0.195 V. The occurrence of the

plateau is attributed to the formation of a blocking layer on the bronze surface, constructed with oxidation products of alloy components. After crossing $E = -0.195$ V, the current density increases sharply, which is connected with a breakdown of the blocking layer. In addition, in the final stage of the measurements, the continuity of the metallic

layer was likely disturbed, resulting in a decrease in the current density values.

Polarisation curves obtained for metalised nonwoven additionally coated with a thin coating of poly(dimethylsiloxane) (grey lines) are shifted towards higher potential values, indicating greater corrosion resistance of the sample in 3% NaCl, compared to CuSn/PP. The corrosion potential determined for PDMS-CuSn/PP equals -0.252 V. Furthermore a significant decrease in the current density after $E = -0.050$ V, suggesting a lack of continuity of the metallic layer and/or lack of electrical contact, was not observed in this case. Moreover comparison of the corrosion current densities (i_{corr} – quantity directly proportional to the speed of the corrosion process) which equal $i_{\text{corr}} = 3.9 \times 10^{-6}$ A/cm² and $i_{\text{corr}} = 3.1 \times 10^{-6}$ A/cm² for CuSn/PP and PDMS-CuSn/PP, respectively, shows that the presence of thin PDMS coating contributes to slowing down the dissolution of the CuSn layer components in the corrosive medium applied.

Figure 2 presents MM images obtained for CuSn/PP. Microscopic observations were carried out for both areas termed as “weaves” and “overpresses”. Thereafter the images captured for a corroded area of the sample were compared with those taken for an area not treated with the corrosive medium. The CuSn layer exposed to the corrosive agent - 3% NaCl solution, exhibits a significant change in surface topography compared to the initial material. Within the “weave”, except the reaction products generated during the corrosion process, mainly Cu₂O and SnO₂ [21], losses of the metallic layer located on the most exposed fibres are visible (see **Figure 2.c**). In the case of “overpress”, CuSn losses are rather small, but the localised outbreaks of corrosion can be clearly distinguished there.

In the case of the PDMS-CuSn/PP sample (**Figure 3**), pristine areas and those treated with the electrolyte demonstrate a similar surface structure. There are no serious defects observed within the metallic layer, which may indicate that the process of its delamination is significantly limited. This confirms the observations made on the basis of potentiodynamic measurements that the CuSn layer deposited on the PP nonwoven and covered with PDMS maintained continuity in the corrosion process conducted.

Table 2. EDX microanalysis of CuSn/PP.

"Weave" area		"Overpress" area	
Areas of the sample not subjected to the corrosive medium			
Element	Wt %	Element	Wt %
C	9.57	C	8.40
O	1.74	O	0.86
Cu	76.15	Cu	78.81
Sn	12.54	Sn	11.93
Total	100.00	Total	100.00
Areas of the sample subjected to the corrosive medium			
Element	Wt %	Element	Wt %
C	42.83	C	16.73
O	24.82	O	19.29
Cl	3.10	Cl	3.22
Cu	16.38	Cu	43.68
Sn	12.88	Sn	17.08
Total	100.00	Total	100.00

The results of the chemical analysis (EDX microanalysis) are shown in **Tables 2** and **3**, for CuSn/PP and PDMS-CuSn/PP samples, respectively. The values shown in the tables are expressed in % by weight and they correspond to the mutual proportions between the different elements. Carbon was identified predominantly as a component of the polypropylene substrate. The tables highlight the participation of copper as the main component of the metallic layer in the reference sample not treated with the corrosive agent as well as in all corroded specimens, pointing to the evolution of its contents.

On the surface of the pristine CuSn/PP sample, elements Cu, Sn, C and O were detected in both the "weave" and "overpress", wherein the amount of oxygen absorbed within the "weave" is slightly higher than that of the "overpress", which is associated with a greater extension of the sample surface in this area. One can also not exclude the presence of small amounts of oxide Cu (I). Our previous studies on the crystallographic structure and composition of thin CuSn layers deposited on polypropylene nonwoven showed that the formation of Cu₂O crystallites is possible under the conditions of the deposition process applied [22]. MM micrographs, included in this work (**Figure 2.a** and **Figure 3.a**), also suggest slight chemical changes in the surface of samples not exposed to the corrosive agent.

After the process of forced electrochemical corrosion, Cl was additionally detected in CuSn/PP, which may constitute a component of the reaction products of Cl⁻ ions with a metallic layer, mainly

with Cu [23]. Furthermore the following was observed: (I) both the "weave" and "overpress" areas are significantly depleted in copper; (II) the oxygen content increases, which can be attributed to the formation of Cu and Sn oxides, and (III) the tin content is not subjected to significant changes wherein the surface of the "overpress" appears to be relatively enriched in compounds containing Sn. Therefore it may be assumed that the selective dissolution of Cu occurs in the corrosion process, being more pronounced within the "weaves". A similar phenomenon of decuprification was observed for bronze treated with NaCl [20, 21]. The increase in the relative content of C is related to the partial unveiling of the polypropylene nonwoven, particularly in the "weave", which is fully consistent with the microscopic observations.

Analysis of the chemical composition performed for the PDMS-CuSn/PP sample (**Table 3**) not treated with the corrosive medium showed the presence of silicon, and an increased relative contribution of oxygen in comparison to the initial CuSn/PP sample. Both of these elements are parts of the polydimethylsiloxane chain. However, it should be noted that due to the "nanometric" thickness of the PDMS layer deposited, estimation of the Si content may be affected by a high measurement error. On the other hand, the complete absence of the signal originating from Si in the areas subjected to the corrosion process may indicate par-

Table 3. EDX microanalysis of PDMS-CuSn/PP.

"Weave" area		"Overpress" area	
Areas of the sample not subjected to the corrosive medium			
Element	Wt %	Element	Wt %
C	10.95	C	6.30
O	3.29	O	4.37
Si	0.21	Si	0.56
Cu	74.12	Cu	76.49
Sn	11.42	Sn	12.29
Total	100.00	Total	100.00
Areas of the sample subjected to the corrosive medium			
Element	Wt %	Element	Wt %
C	15.70	C	5.31
O	5.16	O	2.35
Cu	69.07	Cu	79.58
Sn	10.70	Sn	12.76
Total	100.00	Total	100.00

tial or complete damage/delamination of the protective layer. However, the metallic layer itself seems to be intact within the "overpress" area, and there is a slight copper depletion observed within the "weave". A simultaneous increase in the C signal suggests local damage to the CuSn layer and the unveiling of the substrate material.

Corrosion behaviour of CuZnNi based systems

Figure 4 shows the polarisation curves obtained for the CuZnNi/PP and PDMS-CuZnNi/PP samples. The curves show a similar shape to those registered for CuSn/PP and PDMS-CuSn/PP. How-

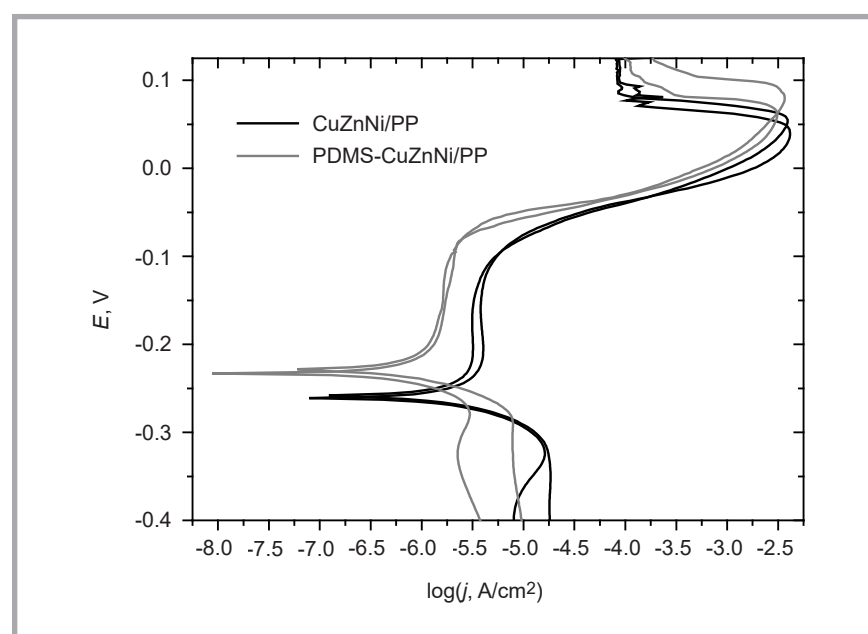


Figure 4. Polarisation curves of the CuZnNi/PP and PDMS-CuZnNi/PP samples in 3% NaCl solution.

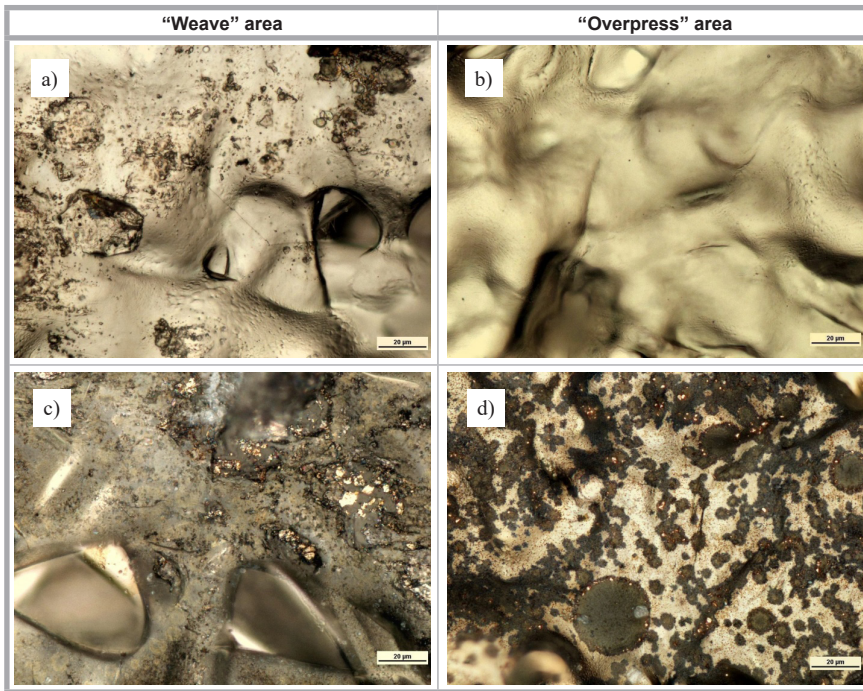


Figure 5. MM images of CuZnNi/PP: not treated (a, b) and treated (c, d) with 3% NaCl solution

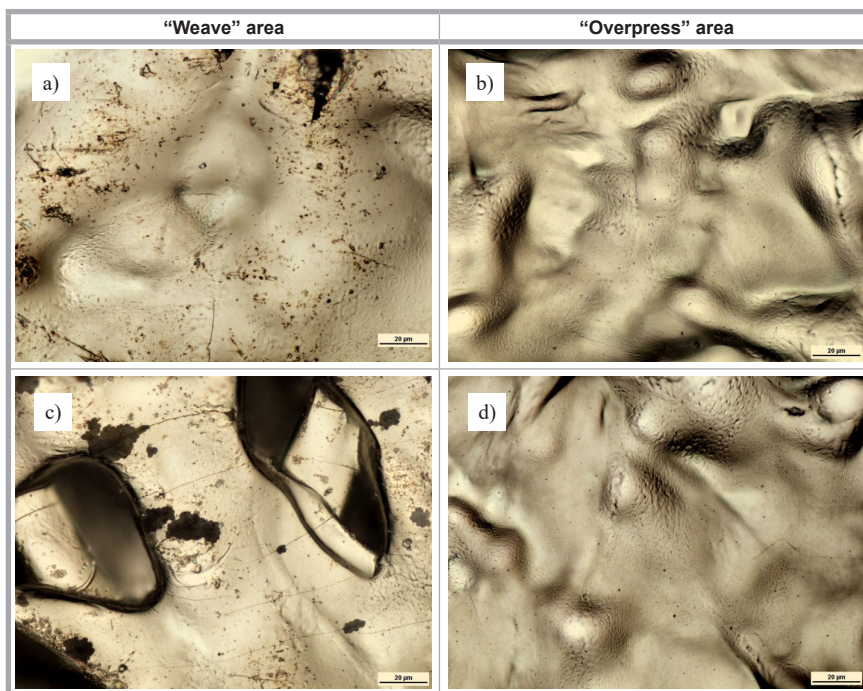


Figure 6. MM images of PDMS-CuZnNi/PP: not treated (a, b) and treated (c, d) with 3% NaCl solution.

ever, in both cases of the samples obtained from CuZnNi alloy, i.e. uncovered and covered with the PDMS protective coating, the corrosion potentials are shifted towards higher values and equal $E_{\text{corr}} = -0.256$ V for CuZnNi/PP and $E_{\text{corr}} = -0.218$ V for PDMS-CuZnNi/PP, respectively. At the same time, the higher E_{corr} obtained for the covered sample and lower, in this case, corrosion cur-

rent density ($i_{\text{corr}} = 0.84 \times 10^{-6}$ A/cm²) as compared to the CuZnNi/PP ($i_{\text{corr}} = 0.19 \times 10^{-6}$ A/cm²), are a confirmation of the protective properties of the polydimethylsiloxane coating.

Furthermore a hitherto wider current plateau was observed for both samples of this series, extending up to a potential of *ca.* $E = -0.100$ V and *ca.* $E = -0.075$ V

for the samples uncoated and coated with PDMS, respectively. Both of these features: a higher E_{corr} and wider current plateau provide better stability of the nonwovens metallised with CuZnNi alloy in the corrosive environment utilized, as compared to those based on CuSn. On the basis of research carried out on copper alloys rich in nickel, one can conclude that the presence of this particular element facilitates the formation of a stable protective passive layer in contact with various types of electrolytes [24, 25].

In the potential range above -0.050 V, a decrease in the anodic current density for both samples was observed, which might suggest a lack of continuity of the CuZnNi metallic layer. However, it should be noted that the layers were obtained using almost twice less target sputtering power than in the case of CuSn, while maintaining other process parameters the same. Therefore it is possible that the amount of material deposited onto polypropylene nonwoven was not sufficient to ensure proper electrical contact during the whole corrosion process, even in the presence of the PDMS protective layer.

Figure 5 shows MM images obtained for the CuZnNi/PP sample before and after the corrosion process, respectively. On the surface of the CuZnNi layer treated with 3% NaCl solution (**Figure 5.c** and **Figure 5.d**), highly defected areas can be observed, clearly visible also within “overpresses” that are not present in the pristine material (**Figure 5.b**). The reason for their formation may be the oxidation of metallic layer components, which leads to the creation of copper and nickel oxides. However, the dezincification process of CuZnNi also cannot be excluded. Dezincification, i.e. the preferential dissolution of zinc, is a typical course of corrosion of the CuZn alloys used e.g. for the preparation of porous copper structures [26, 27]. The slightly higher loss of Zn within the “overpress” (in comparison to other elements of the metallic layer) that occurs in the forced corrosion process of the CuZnNi/PP sample was confirmed by EDX microanalysis (see **Table 4**). Within the “weave”, considerable losses of the metallic layer take place, similar to the CuSn/PP sample, which is clearly seen in **Figure 5.c**.

Table 4. EDX microanalysis of CuZnNi/PP.

"Weave" area		"Overpress" area	
Areas of the sample not subjected to the corrosive medium			
Element	Wt %	Element	Wt %
C	26.72	C	26.33
O	7.80	O	6.01
Ni	11.06	Ni	10.01
Cu	36.44	Cu	39.30
Zn	17.98	Zn	18.26
Total	100.00	Total	100.00
Areas of the sample subjected to the corrosive medium			
Element	Wt %	Element	Wt %
C	82.07	C	68.42
O	13.79	O	11.69
Ni	0.11	Ni	3.11
Cu	3.30	Cu	11.80
Zn	0.74	Sn	4.98
Total	100.00	Total	100.00

Table 5. EDX microanalysis of PDMS-CuZnNi/PP.

"Weave" area		"Overpress" area	
Areas of the sample not subjected to the corrosive medium			
Element	Wt %	Element	Wt %
C	41.90	C	25.21
O	5.92	O	8.62
Si	0.41	Si	0.23
Ni	8.49	Ni	10.68
Cu	28.94	Cu	35.79
Zn	14.34	Zn	19.47
Total	100.00	Total	100.00
Areas of the sample subjected to the corrosive medium			
Element	Wt %	Element	Wt %
C	48.17	C	37.77
O	6.54	O	5.51
Si	0.41	Si	0.53
Ni	6.99	Ni	10.25
Cu	25.35	Cu	29.91
Zn	12.53	Sn	16.03
Total	100.00	Total	100.00

Microscopic observations carried out for the PDMS-CuZnNi/PP sample treated with 3% NaCl (**Figure 6**) revealed corrosion changes occurring in "weaves" located mainly in the vicinity of cracks in the metallic layer. In contrast, no distinct defects were found within "overpresses" with the use of this method. This applies to both samples: subjected and not subjected to the corrosive medium.

On the other hand, EDX microanalysis performed for CuZnNi/PP and PDMS-CuZnNi/PP, the results of which are given in **Tables 4** and **5**, revealed a significant content of carbon and oxygen in all cases investigated. This indicates the occurrence of stochastically distributed losses in the metallic layer, within both

"weave" (which is also clearly visible in **Figure 5.a** and **Figure 6.a**) and "overpress" areas of the pristine and corroded samples. In the case of the "weave" of the CuZnNi/PP sample treated with 3% NaCl solution, the high percentage of C and O is accompanied by a very low content of Cu, Zn and Ni, which makes it impossible to conduct a thorough analysis of the relationship between losses of individual elements of the metallic layer. Nevertheless one can assume that the CuZnNi component is destroyed as a whole, which is consistent with the microscopic observations described above and the polarisation curves (their course in the upper range of potentials) obtained for the CuZnNi/PP sample.

The protection of the CuZnNi/PP sample with the polydimethylsiloxane coating reduces losses in the metallic layer within the "weave" and "overpress" areas. However, this effect is not as clear as in the case of CuSn-based systems. Attention shall be paid to the presence of Si (as a component of PDMS) in the PDMS-CuZnNi/PP sample subjected to the corrosion process. Therefore it cannot be ruled out that in this case a local delamination of the PDMS/CuZnNi layer system occurs, which is also confirmed by the microscopic observation (see **Figure 8.c**). As a result, this phenomenon may be the cause of a decrease in the anodic current density observed during potentiodynamic tests in the range of potentials above -0.050 V (see **Figure 4**).

Conclusions

On the basis of the corrosion resistance studies performed for the metallised polypropylene nonwovens in 3% NaCl solution, it was found that:

- CuSn deposited as a thin layer on PP nonwoven corrodes in accordance with the mechanism characterising, in general, the corrosion of bronzes,
- a CuZnNi metallic layer deposited on PP nonwoven shows higher corrosion resistance in the corrosive environment utilised as compared to CuSn, which is consistent with the results obtained for copper alloys rich in nickel,
- regardless of the type of alloy used for the metallisation, the metallic layers deposited are more susceptible to corrosion (degradation) within the nonwoven "weaves" than in the "overpress" areas,

- regardless of the chemical composition of the metallic layers, a protective PDMS coating additionally deposited increases their corrosion resistance in contact with aqueous corrosive media rich in Cl⁻ ions,
- in the technological aspect, process parameters used during the CuSn deposition – with almost twice as large target sputtering power than in the case of CuZnNi – seem to be more advantageous for the stability of the PDMS/metallic layer system during the corrosion process,

Additionally knowledge of corrosion processes occurring in thin alloy coatings deposited onto textile substrates by magnetron sputtering will allow the rational use of such composites in practice.

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Programme

08. 09.2016 Thursday		09.09.2016 Friday	
8.00 – 9.00	Registration	9.00 – 10.15	Session 5. Biodeterioration of historical objects stored underwater. Chairperson: Brenda Little
9.00 – 9.30	Opening ceremony	10.15 – 11.15	Poster session and coffee break
9.30 – 10.45	Session 1. Biodeterioration of historical buildings, monuments, frescos & wall paintings. Chairperson: Christine Gaylarde	11.15 – 12.30	Session 6. Methods of investigation. Chairperson: Katja Sterflinger
10.45 – 11.45	Poster session and coffee break	12.30 – 13.45	Session 7. Protection, disinfection & conservation methods. Chairperson: Thomas Warscheid
11.45 – 13.00	Session 2. Biodeterioration of archival documents, paper & photos. Chairperson: Flavia Pinzari	13.45– 14.45	Closing ceremony
13.00 – 14.15	Session 3. Biodeterioration of historical textiles. Chairperson: Beata Gutarowska	14.45 – 15.45	Lunch
14.15 – 16.15	Lunch	16.00	Sightseeing of Łódź
16.15 – 17.30	Session 4. Biodeterioration of historical wood. Chairperson: Kale Pilt		
19.00	Conference dinner		

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