Plasma deposition of antimicrobial coatings based on silver and copper on polypropylene

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Abstract: This paper addresses the issue of plasma treatment of the surface of polypropylene (PP) using sputtering of silver (Ag) and copper (Cu) and their oxides with MS-PVD in order to impart antimicrobial activity. It was found that plasma treatment of PP with Cu and Ag based layers allows to provide excellent antimicrobial properties due to a constant release of metal ions. The samples of PP treated with Cu and CuO were characterized by highest antimicrobial properties and stability of the coatings. The most stable and least effective coating against bacteria was Ag-PP sample. In turn, AgO-PP was characterized by the lowest stability in aqueous conditions and strong antimicrobial activity. It was found that leaching of metal ions from the surface of treated PP even in exceptional levels plays a crucial role in bactericidal activity.

Keywords: polypropylene, plasma treatment, silver, copper, antibacterial properties.

In the industry synthetic polymers pose the crucial production components of many materials, which are versatile in the manufacturing of all kinds of goods in packaging, medicine, filtration materials, construction elements, piping systems, etc. [1–3]. Although, the detrimental impact of polymers on environment is well-known and confirmed, they have been found to expand the area of application for almost all fields of human activity due to the low cost, ease of processing and good mechanical properties [3]. Since materials made of polymers are generally non-toxic and chemically passive, in many cases they can be easily exposed to biofouling resulting in biofilm formation on their surfaces. Some polymer materials used for the manufacturing of a wide range of products available in the industry, e.g. textiles, food packaging, biomedical devices or piping systems, can be particularly susceptible for microbial growth on their surfaces. To survive in fluctuating conditions, microbes have evolved the mechanisms of the surface attachment and living in a community. Microbial biofilms are dense, structured aggregates, where microbes are strongly bound to the colonized surface and other microbial cells in surrounding environment [4, 5]. They may form on both living or non-living surfaces and are prevalent in natural, industrial and hospital settings [6]. Biofilm appearance greatly affects industrial processes, deteriorates materials quality, limits the hygiene maintenance, causes malfunctions of devices or the increase in material and energy consumption. These lead to the reduction in the efficiency of the technology, causes the need to clean the installation com-

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ponents with strong chemical biocides [7]. Due to the high intensity of microbial pollutants on surfaces of elements during operation, the lifetime of material is significantly shortened and impaired. Therefore, the ability to resist biofouling and contributing factors are of a great significance. The common application of polymers involves manufacturing of fibrous filtration materials and membranes as well as filtration plant construction elements. The phenomenon of biofouling formation is particularly unnecessary during filtration processes as it decreases filtration and separation performance and greatly increases operating costs [8–10]. Thus, there is an increasing need to search for an appropriate method of reducing biofouling by modifications of materials coming into contact with pathogens. Recently, various methods of modification of applied materials have been extensively studied to overcome the problem of microbes forming biofilms on the surfaces of polymer materials [10, 11]. This was especially examined for materials made of polymers such as wound dressings, cotton fibres, artificial anti-inflammatory blood vessels, and many others [12–14]. Strategies used to functionalize polymer materials involve either embedding antimicrobial agents in the form of metals or their oxides into the polymer matrix or incorporation on polymer surfaces [11–16]. The functionalization of the surface is more accessible and likely to improve surface properties of final completed products made of polymers. The main aims of surface modifications are to alter several properties such as wettability, chemical inertness, cross-linking of the surface, boundary layers and impurities, surface morphology, electrical conductivity [17]. The modifications routes for imparting antimicrobial properties mainly involve incorporation of metals or their oxides especially in the form of nanoparticles. Antibacterial agents widely described in the literature are compounds containing silver and copper [15, 18]. They have already found numerous applications in water treatment, healthcare, and the industry in general since they can be toxic to wide range of microorganisms such as bacteria, algae or fungi at very exceptional levels. Compounds of copper belong to the relatively small groups of biocides that are safe to human health [19]. By testing a set of metal surfaces, it was shown that those containing copper and silver are the most effective in reducing bacterial viability [20, 21]. Today these metal based additives are found in the form of particles, ions absorbed/exchanged in different carriers, polymer matrix, etc. One recent and novel direction to further extend antimicrobial applications of these compounds and create new functional properties to materials is plasma deposition of thin layers of metals or their oxides on the surface of polymers [11, 22, 23]. Especially, the use of low temperature plasma seems the most universal method of surface modification of polymers, and its rapid development has been observed in the last years. This is particularly because plasma techniques are fast, clean and ecological [24–27]. Plasma is partially ionized gas (or a mixture of gases) consisting of equal number of electrons, ions and atoms, and electromagnetic radiation resulted from a discharges occurred in vacuum chamber. Materials subjected to plasma treatment show changes in the properties of the surface and in the chemical structure of the surface layer resulting in higher durability of an adhesive metallic coating due to its strong anchoring on the surface [17]. From a practical point of view, the stability of the functional metallic coatings deposited on the surface of polymers is an important aspect, particularly when the materials come into contact with liquids, as high levels of metal ions leached from the surface can be undesirable effect in some cases leading to serious consequences which are manifested by the pigmentation of the skin, breathing problems, allergic reactions in human body when exposed to excessive absorption of silver compounds (most commonly in the form of silver or colloidal dust) [28]. The aim of the work was to deposit thin layers of coatings based on silver (Ag, AgO) and copper (Cu, CuO) onto the surface of polypropylene using magnetron sputtering-physical vapour deposition method (MS-PVD) and examining their stability in aqueous solution and antibacterial efficiency against both Gram-positive (Staphylococcus aureus) and Gram-negative bacteria (Escherichia coli) in static and dynamic contact conditions. Furthermore, the other properties were investigated such as wettability, morphology and chemical composition of plasma treated polypropylene materials.

EXPERIMENTAL PART

Materials

Polymer materials selected to plasma treatment with MS-PVD method were raw polypropylene (PP) samples outsourced and prepared as a discs of a diameter of 2.54 cm cut with a plotter from the 5 mm thick panel. The geometry of the samples were dictated by the holders in a plasma vacuum reactor built by the ŁUKASIEWICZ Research Network-Institute for Sustainable Technologies (ŁUKASIEWICZ-ITEE). All reagents were analytical grade. Millipore-quality water was used for all solution preparations. Microbiological reagents such as Luria-Bertani broth (LB), Luria-Bertani Miller Agar (LBA) were supplied by VWR Chemicals. Chemical reagents to prepare saline buffers were purchased from Chempur.

Plasma coating deposition

Prior to plasma treatment, the polypropylene discs were washed with 96% ethanol in an ultrasonic bath for 10 min and dried. The surface of prepared PP samples were coated with metallic (Ag, Cu) layers with MS-PVD. The coatings consisting of AgO and CuO were obtained with both metallic and gaseous low temperature plasma in vaccum chamber constructed by ŁUKASIEWICZ-ITEE. This device is equipped with three circular magnetrons
The PP samples were transferred to new tubes containing dH₂O and agitated again for 1 h. The process was conducted for 18 h. The culture collections were identified with EDS microanalysis. The concentration of elements occurred within deposited layers was 30.4°, using the secondary electron detector (SE). The stability of PVD-coatings

The stability of coatings deposited on the polypropylene surface with MS-PVD was examined through the changes of the contact angle for demineralized water (dH₂O) using the static sessile drop method. The static contact angle values were automatically measured by goniometer constructed by ŁUKASIEWICZ-ITEE. For each polymer sample, 10 measurements of contact angles were taken. For each series of measurements, a Dixon’s Q test was performed to reject outliers. The mean value was calculated from 8 measurements and variability of the results characterized by the standard deviation.

Methods of testing

Contact angle

Wettability of plasma treated surface of solid PP (before and after treatment) was examined through the changes of the contact angle for demineralized water (dH₂O) using the static sessile drop method. The contact angle values were automatically measured by goniometer constructed by ŁUKASIEWICZ-ITEE. For each polymer sample, 10 measurements of contact angles were taken. For each series of measurements, a Dixon’s Q test was performed to reject outliers. The mean value was calculated from 8 measurements and variability of the results characterized by the standard deviation.

Stability of PVD-coatings

The stability of coatings deposited on the polypropylene surface with MS-PVD was examined through the measurements of leached metals (ions) into dH₂O from the treated PP samples. For this purpose each plasma treated PP solid sample (PP-Cu, PP-CuO, PP-Ag, PP-AgO) was shaken in dH₂O. The samples of solid PP were put into tubes with 45 cm³ dH₂O and agitated on the laboratory orbital shaker at 3.33 Hz for 1 h. After this time, the PP samples were transferred to new tubes containing 45 cm³ dH₂O and agitated again for 1 h. The process was conducted for 18 h. Three subsamples were tested simultaneously for each type of PP. The concentrations of Cu and CuO targets were presented in Table 1. The thickness of obtained coatings were measured with scanning electron microscope (SEM) Hitachi TM 3000.

Table 1. Parameters of MS-PVD process used to treat polypropylene

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Coating</th>
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<tbody>
<tr>
<td>Target</td>
<td>Cu</td>
</tr>
<tr>
<td>Sputtering gas</td>
<td>100%Ar</td>
</tr>
<tr>
<td>Time, min</td>
<td>30</td>
</tr>
</tbody>
</table>

located on three opposite sides of the chamber. The magnetrons were equipped with disc targets with a diameter of Ø = 140 mm and a thickness of g = 7 mm. The intensity of magnetron and the pressure in the vacuum chamber were constant and equal to 0.8 A and 0.5 Pa, respectively. An appropriate time was selected to obtain thickness of layers equal to 650 nm. The parameters of MS-PVD process used to treat PP samples were presented in Table 1. The thickness of obtained coatings were measured with scanning electron microscope (SEM) Hitachi TM 3000.

Table 2. Operating parameters of ICP-MS

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
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</thead>
<tbody>
<tr>
<td>Forward power, W</td>
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</tr>
<tr>
<td>Cool gas flow, dm³/min</td>
<td>13.956</td>
</tr>
<tr>
<td>Auxiliary gas flow, dm³/min</td>
<td>0.8021</td>
</tr>
<tr>
<td>Nebulizer gas flow, dm³/min</td>
<td>1.02464</td>
</tr>
<tr>
<td>Dwell time, s</td>
<td>0.005</td>
</tr>
<tr>
<td>Number of replicates</td>
<td>3</td>
</tr>
</tbody>
</table>

The microstructure of the plasma treated polypropylene surface was characterized via images recorded with scanning electron microscope (SEM) Hitachi electron back-scatter detector with field emission and thermal emmitter SU-70 Schottky. The analyses were carried out in vacuum conditions (1 · 10⁻⁸ Pa) at an accelerating voltage of 15 kV and a secondary electron reception angle of 30.4°, using the secondary electron detector (SE). The composition of elements occurred within deposited layers on solid PP were identified with EDS microanalysis. The tests were carried out in three sites of each polymer.

Tests of antibacterial properties

Culture and growth conditions

The antimicrobial properties of the plasma-coated PP samples were examined against two model bacterial species from the groups of Gram-negative (G⁻) – Escherichia coli (ATCC 25922) and derived from American Type Culture Collection. Prior to microbiological tests, the samples of solid polymers were disinfected with 96% ethanol and additionally sterilized under UV-C light for 30 min. Cultures of bacteria were prepared by inoculating 20 cm³ of LB containing flasks with 0.01 cm³ of a liquid culture at stationary phase of growth. The cultures were agitated at 37 °C in the incubator overnight.

Static contact

Overnight cultures of E.coli and S. aureus in the volume of 0.1 cm³ were transferred with a pipette and loop-spread onto the surfaces of the plasma treated polypropylene. As
a reference sample the untreated PP was used. All samples were placed on sterile Petri dishes in a wet chamber containing 5 cm³ of phosphate buffered saline (PBS) to maintain appropriate humidity. The samples of PP were cultured overnight without agitation and then transferred to the separate sterile flasks containing 9.9 cm³ of PBS (pH 7.0). In such conditions they were agitated in the orbital shaker for 5 min to remove attached bacteria. The serial dilutions from the agitated buffer solutions were plated on LB Miller agar. After 18 h of incubation at 37 °C the number of viable bacteria (colonies) was counted and the results were expressed as reduction in cell viability (%). Each test was performed three times (n = 3).

**Dynamic contact**

The antibacterial tests under dynamic conditions were conducted according to the procedure of ASTM E2149 (Standard Test Method for Determining the Antimicrobial Agents Under Dynamic Contact Conditions) involving slight changes of the method [29]. For the tests the potassium diphosphate (KH₂PO₄) buffer was prepared in the ratio 1 : 800 (v) from 0.25 M KH₂PO₄ stock solution (pH 7.0) and sterilized. In order to establish the concentration (1.5–3.0) · 10⁸ CFU/cm³ (CFU – colony forming unit) of bacterial working solutions in KH₂PO₄, the overnight cultures of E.coli and S.aureus were suspended in the separate buffer containing tube and the absorbance was measured

![Contact angle, °](image)

Fig. 1. Contact angle values of the solid PP samples (n = 8): untreated (PP) and plasma-treated with Cu, CuO, Ag and AgO

of the surface of AgO-coated PP significantly decreased, which was not visible for metallic Ag coating. Plasma deposition of Cu and CuO also resulted in slight and similar increase of contact angle values for dH₂O. The obtained results suggest that PP materials coated with AgO, Cu as well as CuO may reveal self-cleaning properties, which can be particularly important for the polypropylene elements exposed to pollutions including biological ones [31]. Depending on the specific final application, this change may be either positive or negative. It was found that hydrophobic character of the coating may affect biofilm formation. According to Faille et al. [32] there is a direct link between hydrophobicity and adherence of E. coli to a range of different substrates. Although this was a promising result, it was not in agreement with the study that has shown that hydrophilicity may have little effect on biofilm formation [33]. Antifouling coatings do not kill the microbes directly but instead prevent the attachment of bacteria on the surfaces that allow the formation of biofilms. Newly emerged trend to design antibacterial strategy involve creating superhydrophobic surfaces that give promising capability of reducing bacterial adhesion together with an easy removal of bacteria cells. Therefore, the selection of appropriate bactericidal compounds to be deposited via PVD techniques on the surface of polymer material may greatly contribute to both reduction of microbial attachment and release of biocides.

**RESULTS AND DISCUSSION**

**The influence of plasma treatment on contact angle changes**

Plasma treatment of PP samples with Cu, CuO, Ag and AgO enables smooth and uniform covering of their surface. The measurements of contact angle were taken from 8 points of the untreated and treated PP samples and the standard deviation was calculated. The contact angle determined the level of wettability of a solid by a liquid [30]. All of the tested coatings increased the contact angle values for dH₂O compared to the native PP (Fig. 1).

The highest contact angle values were observed for AgO-coated PP sample which was over 20° higher than untreated PP samples. This indicates that the wettability
of Cu leached from both Cu and CuO coatings was similar after each hour of the contact of PP with dH₂O. The total concentration of Cu after 18 h of agitation was similar 3.61 mg/dm³ ± 0.25 mg/dm³ and 3.43 mg/dm³ ± 0.15 mg/dm³ for both Cu and CuO coatings, respectively. Also the average increase in Cu amount for both coatings after subsequent hours of leaching was similar and equal to 0.20 mg/dm³ and 0.19 mg/dm³, respectively.

In Fig. 3 the change in the concentration of Ag leached out from PP samples treated with Ag and AgO in dH₂O was represented. Large differences in the leaching of Ag from both coatings were observed. The total concentration of Ag after 18 h of agitation was 0.365 mg/dm³ ± 0.042 mg/dm³ and 30.93 mg/dm³ ± 0.63 mg/dm³ for Ag and AgO coating, respectively. The obtained results showed that the Ag concentration was increasing over time in both cases, yet the initial concentration in dH₂O after 1 h contact with PP treated with Ag was about 85 times lower than the sample of PP treated with AgO. It was observed that the coating based on AgO showed low stability particularly in the first hours of the process, while the concentration of Ag in solutions after leaching was...
high – 29.2 mg/dm$^3$ ± 3.6 mg/dm$^3$ for 5 h, which constitutes 94% of the total concentration of Ag leached out after 18 h of the process. In the last 6 h of the leaching process, increase in Ag level was smaller and stabilized at 50 µg/(dm$^3$·h). However, for the coating based on Ag, it was observed that the increase in concentration of Ag is linear, on average about 20 µg/dm$^3$ for each hour of the leaching process.

High leaching of Ag from AgO-treated PP and its low stability in water likely relates to the state of stresses occurring in the coating [34]. The level of stresses and thus stability in the coatings is influenced by the rate of coating deposition and kinetic energy of ions in the chamber, which are dependent on the chosen method and the parameters of the deposition process [35]. Research groups so far have only been studying mechanical properties of the deposited coatings on various materials including polymers [36–39]. There is a lack of literature data on the stability and durability of plasma coatings on polymers in terms of using with aqueous conditions as well as both their antibacterial properties in conditions simulating surface attachment and biofilm formation (static contact) and flow of biologically contaminated waters (dynamic contact). Presented results are novel approach to examine stability of metallic-based coatings on polypropylene materials.

The influence of leaching on the morphology and microstructure of the PP-coating

Analyses with SEM allowed to image the morphology of polypropylene after plasma deposited coatings containing Cu, CuO, Ag and AgO (Fig. 4).

The obtained results showed that deposited layers are smooth and only several cracks were observed. After leaching process the morphology of treated PP was slightly changed. For all of the samples more discontinuities in the deposited layers were observed. Particularly, the polymer treated with Cu and CuO revealed abruptions which may be associated with the observed constant release of the metal ions from the coating.

EDS analysis showed the alterations in the composition of elements on particular PP samples expressed as atomic concentration before leaching process and after contact with dH$_2$O (Fig. 5). The presented results are average values obtained from three sites of each polymer.

The composition of samples coated with Cu were practically unchanged after contact with dH$_2$O, as the atomic concentrations of Cu were similar and equal to 98.1% Cu before and 97.4% Cu after leaching. In the case of coating based on CuO, no significant changes were observed in the atomic concentration before and after leaching process, which was 92.5% and 91.2% Cu, respectively. Ag-coated PP results showed that atomic concentration of Ag on the surface of polymer was the same for both samples before and after leaching process (98.6%). The interesting results were obtained for AgO treated polymer. The atomic concentration of particular elements

![Fig. 4. SEM images of plasma coated polypropylene samples: a–d) before leaching process: Cu, CuO, Ag, AgO, respectively; e–h) after leaching process: Cu, CuO, Ag, AgO, respectively](image)

![Fig. 5. Elements composition (at. %) of plasma treated PP samples before and after leaching process](image)
in this coating before the leaching process was different compared to the atomic composition after the leaching process. It was observed that after leaching process, the oxygen was completely removed from the coating, while the atomic percentage of silver increased (from 94.4% Ag before to 98.5% after the leaching process). This may indicate that the parameters of the AgO plasma deposition process resulted in a non-uniform structure of the coating and thus a varying degree of leached ions over time. This finding was confirmed by the results obtained for AgO treated sample during the analysis of Ag concentration in the solutions after the process of leaching (Fig. 3), while the concentration of Ag in the first hours of the process was very high. The stabilization of silver from the AgO coating during the final hours of the process may indicate that the obtained coating was loosely attached within the surface layer, yet its cohesion increased with the depth of the coating. Similar results of atomic concentrations of elements obtained for Ag and AgO coatings after the leaching process (98.6% and 98.5%, respectively) may indicate that the produced AgO coating might have a “layered” structure – the internal layer of the coating deposited on the PP polymer was a solid layer of Ag, and the external layer was composed of AgO characterized by loose bindings leading to higher leaching effect.

Antibacterial properties of PVD-coated samples

The antimicrobial performance of plasma treated polypropylene samples was assessed against two representative bacteria *E. coli* and *S. aureus* in static (non-stirred) conditions simulating biofouling formation on the surface of the samples and to avoid potentially forced release of metal ions. A dynamic test was performed for the same microbial species to assess the bactericidal effectiveness of treated PP samples imitating their application in aqueous conditions. Both tests were performed for the originally plasma treated samples (before leaching process) and for the samples after 18 h contact (agitation) with dH2O.

Figure 6 represents the percentage reduction in cell viability of *E. coli* in static conditions before and after leaching process. It was found that Cu and CuO as well as Ag and AgO treated PP samples tested before leaching process completely eliminated *E. coli*. However, after leaching process only Ag-treated PP was significantly less effective, as it only resulted in 6% reduction of cell viability, which was probably associated with the releasing of less amount of Ag ions to the surrounding environment due to non-stirred conditions.

Figure 7 shows the performance of plasma treated samples against *E. coli* under dynamic conditions revealing that all of the samples are as same highly efficient in kil-
ling all of the bacteria regardless the samples were before or after leaching process (after contact with dH₂O).

Similar results were obtained for *S. aureus* (Fig. 8 and Fig. 9). It was noted that in static conditions all of the plasma treated samples before leaching process resulted in almost total reduction of *S. aureus* cell viability. Copper and copper oxide coated PP-samples after 18 h leaching process (agitation in dH₂O) were as same efficient against *S. aureus* as before. However, Ag and AgO coated PP samples after prior contact with dH₂O resulted in less visible bactericidal effect.

Under dynamic conditions conducted for 3 h, only Ag-treated sample did not result in strong bactericidal activity in 1 h of dynamic contact, which was similar for both types of samples: before and after leaching process (Fig. 9). It was also found that antibacterial effect of Ag-PP was increasing over time which was associated with the increasing concentration of Ag ions in the solution. This phenomena can be explained by results obtained for leaching test of Ag-PP samples, while it was confirmed that the Ag-coating is undoubtedly the most stable one, as the metal ions release in small amounts and slowest from the polypropylene surface.

These results suggest that antibacterial properties of treated samples are strongly related to the release of ions from the coatings in bacterial environment and it was more visible when the samples were agitated under dynamic conditions forcing leaching of the ions. Despite the fact that the Ag-treated PP was the most stable one, the levels of ions leaching out from the polymer samples was sufficient to kill bacteria. There are various theories on the action of silver on microbes to cause the microbicidal effect. One of them is that ions can interact with the thiol groups of many vital enzymes of bacteria and inactivate them. The bacterial cells in contact with silver take in silver ions, which inhibit several functions in the cells. It was also proposed that generation of reactive oxygen species, which are produced possibly through the inhibition of a respiratory enzyme by silver ions may attack the cell themselves [40]. This clearly confirms that releasing of ions and their concentration plays a major role in eliciting bactericidal properties of surface-modified materials. However, *S. aureus* (G+) was less prone to the Ag ions compared to *E. coli* (G-) as it was reported that it created a defense system against the inhibitory effects of Ag ions [41, 42]. Antibacterial assay conducted in the study revealed that copper ions released from Cu and CuO coatings turned out to be highly efficient against both G+ and G- bacteria independently the tested samples were before or after leaching process. This might be associated with the constant release of the same bactericidal concentration of ions in time as it was shown in previous section. In the

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![Fig. 8. Reduction in *S. aureus* viability after 18 h static contact with the plasma treated PP samples before and after leaching (*n* = 3)](image)

![Fig. 9. Reduction in *S. aureus* cell viability after 1, 2 and 3 h of dynamic contact with plasma treated PP samples: a) before, b) after leaching (*n* = 3)](image)
case of copper-based surfaces it was found that particularly Cu⁺ play a key role in creating defects in microbial cells by changing conformational structure of nucleic acids and proteins, besides reactive oxidative stress generation [43]. Various laboratory and clinical studies have confirmed that solid copper surfaces promote rapid killing of both G- and G+ bacteria. In antibacterial activity performance of antibacterial compounds the crucial issue involves the differences in the thickness of bacterial cell wall between species. It has been already concluded that biofilms of G- species with a thinner cell wall are inactivated more rapidly with several microbicidal agents than biofilms of G+ bacteria with a thicker cell wall [42, 44]. Generally, the mechanism underlying antibacterial behavior of metals includes the attachment of metal particles to the surface of cell membrane, catalyzed radical formation and release of metal ions [15]. Metal-based coatings deposited on the surface of polymers provide a versatile path to take advantages of their antibacterial properties manufacturing new generation biocide materials and allowing the extension of potential applications. Surface treatment of polymer involving slow and constant release of metal ions greatly contributes to antimicrobial behavior.

CONCLUSIONS

In the study a novel approach combining interdisciplinary science such as materials, physics, chemistry and biotechnology was presented to give an insight into new trends toward development of polymer-based materials. Surface engineering technologies including MS-PVD technique enables imparting novel functional properties to a range of polymeric materials. In the present work, polypropylene samples were coated using MS-PVD with silver- and copper-based layers so as to provide antimicrobial properties to the polymeric material. The samples of polypropylene functionalized with plasma deposited silver and copper compounds were examined in terms of wettability, morphology, composition and stability of the coatings in aqueous solution. It was found that the hydrophobicity for all of the samples treated with metals and their oxides increased as compared to unmodified PP sample, except Ag-PP which resulted in contact angle similar to that of original PP. The obtained Cu-PP and CuO-PP coatings did not vary to each other significantly in terms of wettability, morphology, composition and stability. The exposure of Cu and CuO plasma treated samples to dH₂O showed that ions of metals were linearly released in time, and their concentrations in aqueous solution were sufficient to completely eliminate both G+ and G- bacteria using static and dynamic contact method. However, the properties of Ag-PP and AgO-PP were significantly different. The leaching of silver ions from Ag-PP during contact with dH₂O was relatively low and was about 20 µg/(dm²-h). Nevertheless, the dynamic contact of inoculum with Ag-treated PP showed that the concentration of leached ions was sufficient to completely remove E. coli before contact of Ag-PP with dH₂O, but insufficient to kill S. aureus for both before and after contact of Ag-PP sample with dH₂O (leaching). It was demonstrated that antimicrobial activity of the material was maintained at similar level after the leaching process. Antibacterial activity against S. aureus was higher as the contact time of the Ag-PP sample with bacterial inoculum was longer, which was due to the linear dependence of silver ions release (constant increase in ions concentration over time). Although the Ag-PP samples were characterized by high antibacterial performance against two bacterial strains before leaching, this activity significantly decreased after leaching process in static contact. It resulted from avoiding mechanically forced leaching of ions (static contact method) from the polymer surface. The sample of AgO-PP due to its low stability under water conditions resulted in complete removal of both E. coli and S. aureus bacterial cells in static and dynamic conditions. The ion leaching in dH₂O over time was changing and in the final hours of the leaching process reaching about 50 µg/(dm²-h) and it was sufficient to completely remove E. coli in both static and dynamic contact, but too low to remove S. aureus in static conditions. The morphology and composition of AgO-PP sample after the leaching process and the study on its bactericidal properties revealed that selected parameters of MS-PVD treatment were not appropriate to obtain AgO over the entire depth of the coating. It is likely due to the mixture of Ag and AgO occurring within the coating, which was confirmed by the similar atomic concentrations of the elements on the surface of PP obtained for both Ag (before and after the leaching process) and AgO coating (after the leaching process). This was also confirmed by bactericidal tests using static contact method resulting in lower concentration of silver ions available for bacteria to elicit appropriate toxicity compared to dynamic contact method.

The reason of the differences in the results on antimicrobial activity between the same samples are due to the methodological variations within static and dynamic conditions, which used together complement understanding the mechanism underlying antimicrobial activity of material produced via surface treatment with plasma. It was found that the key aspects of bactericidal properties of plasma treated polypropylene are the leaching of metal ions from the surface of the material, their amount released into the environment of bacterial cells, operating conditions of plasma deposition as well as the type of bacterial strain. Due to some differences in their cell structures and developed defense mechanisms, they may have different sensitivity to certain metal ions.

To sum up, plasma treatment of polymers showed bactericidal properties and may be potentially used in many sectors. Further research is necessary to support the development of innovative biocide-based materials to be used in medicine, pharmacy and food industry, preventing attachment of variety of microorganisms, biofilm formation and potentially associated diseases. Future area of inves-
tigations should include scaling up the process for a particular application, optimization, control of ion leaching along with safety and potential toxicity to human health.

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