DEPOSITION OF BACTERICIDAL AgO+CuO COATINGS USING HIGH-POWER PULSED MAGNETRON SPUTTERING TECHNOLOGY (HPIMS) ON POLYPROPYLENE SUBSTRATE.

[1]Joanna KACPRZYŃSKA-GOŁACKA, [1]Sylwia SOWA, [1]Monika ŁOŻYŃSKA, [1]Wioletta BARSZCZ, [2]Piotr WIECIŃSKI, [1]Jerzy SMOLIK, [3]Andrzej KRASIŃSKI

[1]Łukasiewicz Research Network – Institute for Sustainable Technologies, Radom, Poland, EU,
joanna.kacprzynska-golacka@itee.lukasiewicz.gov.pl

[2]Faculty of Chemistry, Warsaw University of Technology, Warsaw, Poland, EU,

[3]Faculty of Chemical and Process Engineering, Warsaw University of Technology, Warsaw, Poland, EU.

https://doi.org/10.37904/metal.2022.4488

Abstract

This paper present the issue of plasma treatment of the surface of polypropylene (PP) using AgO+CuO coatings in order to antimicrobial activity. The analyzed coatings were deposited using High Power Impulse Magnetron Sputtering (HPIMS). This method is characterized by high power density, high ionization and high plasma density, which enables the production of high-quality multi-component coatings. All CuO+AgO coatings, formed on the polypropylene (PP) surface by MS-PVD magnetron sputtering with various parameters, were tested in terms of morphology, chemical composition, mechanical properties and antibacterial properties. The conducted analysis showed a significant influence of the chemical composition on the structure, density and mechanical properties of the obtained coatings. The analysis of the continuity of structure different CuO+AgO coatings showed that its depending on chemical composition. Furthermore, different growth mechanism of the coatings are observed. It was also found that plasma treatment of polypropylene (PP) with CuO+AgO layers allows to provide good antimicrobial properties.

Keywords: Polypropylene, plasma treatment, silver and copper oxides, antibacterial properties

1. INTRODUCTION

Polymer materials are one of the key materials in many areas of industry, which is widely used in the production of various types of elements such as filters, construction elements or packaging [1-2]. The increasing use of polymeric materials in industry is related to their low production cost, easy of processing and good mechanical properties. At the same time, polymeric materials are non-toxic and completely chemically inactive [3-4], which makes them exposed to the growth of various types of microorganisms on their surfaces. Polymers mainly used in the medical, pharmaceutical, food or filtration industries are exposed to this unfavorable phenomenon. Therefore, in order to give polymeric materials bactericidal properties, more and more often the possibility of modifying their surface is sought, which will contribute to a significant increase in their usefulness.

The conducted analysis of the state of knowledge [5-8] showed, that the bactericidal properties of polymeric materials can be shaped either at the stage of polymer composition or by surface modification. Modification of the polymeric material at the stage of its production requires the addition of significant changes to the production process, which is usually unfavorable from an economic point of view. On the other hand, surface modification, due to the possibility of imparting functional properties to a wide range of polymer products already available on the market, seems rational and economically viable.

Magnetron surface engineering techniques can be used to modify the surface of polymers. The wide possibilities of these techniques have already been confirmed in the processes of shaping the functional properties of elements used in various industries, such as: biomedicine, electronics, textiles or optics. Due to the very large possibilities of magnetron surface engineering in terms of shaping the chemical composition of coatings, their microstructure and thickness, it is possible to produce coatings with different functional properties [9-10], also biocidal and bactericidal properties [11-12]. Such wide possibilities in shaping the functional properties of surfaces, the magnetron technologies depositon of thin coatings a promising method of shaping the properties of polymeric materials was made. This paper present the issue of plasma treatment of the surface of polypropylene using AgO+CuO coating in order to antimicrobial activity. The analyzed coatings were deposited using High Power Impulse Magnetron Sputtering (HPIMS). All CuO+AgO multi-component coatings were tested in terms of morphology, chemical composition, mechanical properties and antibacterial properties.

2. EXPERIMENT

2.1. Preparation of coatings

The High Power Impulse Magnetron Sputtering (HPIMS) method was used for the deposition of CuO + AgO coatings. For the implementation of technological processes, the Standard 3 device designed and built in the Łukasiewicz Research Network - Institute of Sustainable Technologies (Łukasiewicz – ITeE) was used. This device has been modified to create a common deposition zone from two simultaneously operating magnetrons. It was equipped with two circular flat magnetrons produced by Lesker company located on one wall of the chamber. The magnetrons used are equipped with targets with a diameter of Ø = 4.00 "(101.6 mm) on a copper backing plate. All AgO+CuO multicomponent coatings were deposited on the silicone (Si) and polypropylene (PP) surface. Process parameters of deposition the coatings are shown in **Table 1**.

Table 1 Technological parameters of deposition process of multicomponent AgO + CuO coatings on the silicon and polypropylene surface.

Target Ag	Target Cu	Pressure p [mbar]	Working atmosphere	Time t [min]
$P_{M\text{-}Ag}$ [W]	$P_{M\text{-}Cu}$ [W]			
200	200	$5x10^{-3}$	90%Ar 10%O_2	60
200	100	$5x10^{-3}$	90%Ar 10%O_2	60
200	50	$5x10^{-3}$	90%Ar 10%O_2	60
100	200	$5x10^{-3}$	90%Ar 10%O_2	60
50	200	$5x10^{-3}$	90%Ar 10%O_2	60

2.2. Coatings characterization

The microstructure and surface morphology of the coatings were characterized with the use of SU-70 Hitach electron microscope. The microstructure observations were carried out on a properly prepared sample in the form of brittle fracture. The mechanical properties of the coatings, such as hardness and Young's modulus, were investigated using the Anton Paar nanoindenter equipped with a Berkovich diamond indenter tip. The indenter was operated in the continuous stiffness mode with a maximum load of 500 mN. The applied load is 3 mN. The wettability of the samples was studied using equipment produced by Łukasiewicz - ITeE in Radom. An average value of the contact angle between the sample surfaces and a minimum of two drops was measured using the sessile drop method. The static contact angle was obtained analyzing the captured images using the Tangent Method 1 algorithm [11]. The wettability of the surface with a polar (H_2O) and non-polar (diiodomethane) solvent was analyzed. The microbiological resistance of the produced coatings was tested using the static contact method [11], and the antimicrobial effectiveness was defined as the percentage of reduction in the viability of microorganisms in relation to the control samples.

3. RESULTS

3.1. Chemical composition and microstructure studies.

Figure 1 shows the results of microstructure tests of the deposited AgO+CuO coatings. The conducted observations of brittle fractures showed differences in the microstructure between the coatings. Coatings deposited at the magnetron power of Cu target $P_{M\text{-}Cu}$=200 W and lower magnetron power values of the Ag targets, i.e. $P_{M\text{-}Ag}$=100 W and 50 W are characteristic by a nanocrystalline columnar structure with a small proportion of spherical grains (**Figures 1b,c**). On the other hand for the coating deposited at the maximum magnetron power of Ag target, i.e. $P_{M\text{-}Ag}$=200 W and lower magnetron power of Cu target, i.e. $P_{M\text{-}Cu}$=100 W and 50 W the columnar or fibrous structure with fine spherical crystallites on the entire fracture surface is visible (**Figures 1d i e**). The thickness of the columns was about 50 nm while the diameter of the spherical particles was below 10 nm. The observed differences are related to the different growth mechanism of AgO and CuO coatings, already observed in the earlier works [12,13]. The analysis of the continuity of CuO+AgO coatings on the polymer surface showed, that depending on the type of the sputtering element (Ag or Cu), there are different growth mechanisms of the coating. It depends mainly on the surface diffusion rate of atoms on the substrate. Authors have shown, that CuO monolayers are characterized by a column microstructure typical for PVD coatings, which proves the layer-by-layer growth mechanism. On the other hand, the microstructure of AgO coatings consists mainly of spherical crystallites, which indicates an island growth mechanism. Therefore, the conducted research shows that the microstructure of multicomponent AgO+CuO coatings is the result of the microstructures characteristic of one-component coatings. Depending on the percentage of AgO or CuO in the coating, a different microstructure is observed.

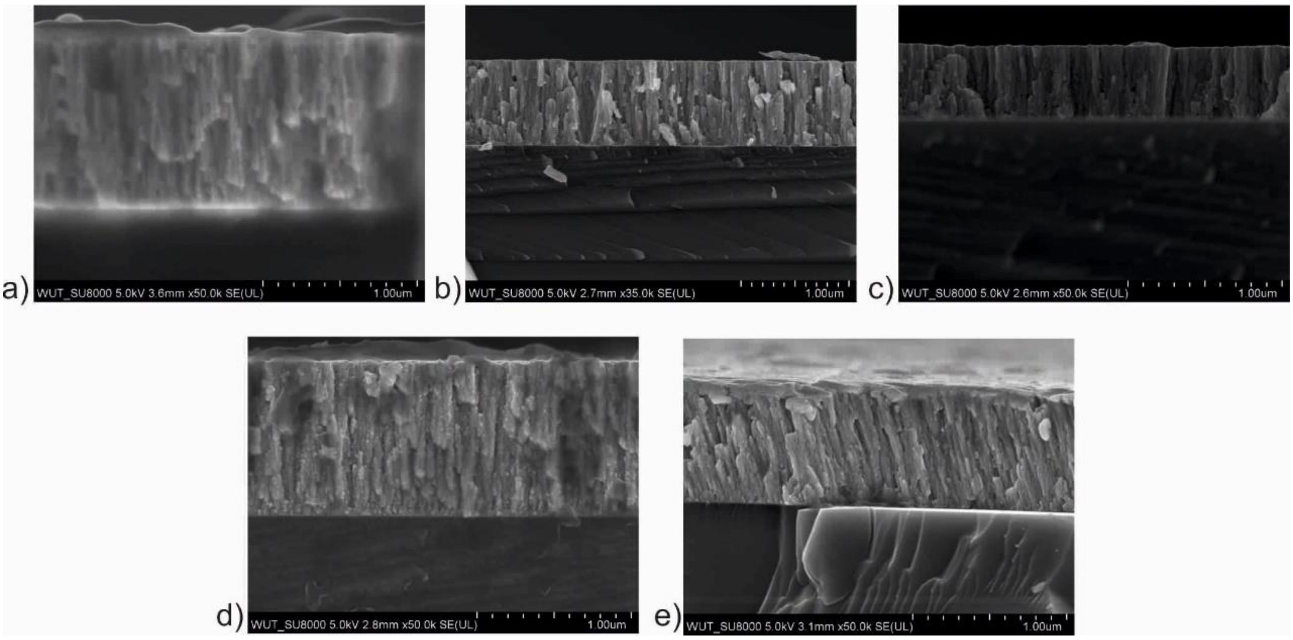

Figure 1 SEM images for CuO+AgO coatings prepared with different magnetron power $P_{M\text{-}Cu}$ and $P_{M\text{-}Ag}$:
a) $P_{M\text{-}Cu}$=200W, $P_{M\text{-}Ag}$=200W, b) $P_{M\text{-}Cu}$=200W, $P_{M\text{-}Ag}$=100W c) $P_{M\text{-}Cu}$=200W, $P_{M\text{-}Ag}$=50W,
d) $P_{M\text{-}Cu}$=100W, $P_{M\text{-}Ag}$=200W, e) $P_{M\text{-}Cu}$=50W, $P_{M\text{-}Ag}$=200W.

The chemical composition of the obtained coatings was also analyzed by means of energy-resolving EDS X-ray spectroscopy. **Figure 2** shows the chemical composition of complex coatings. Our research indicatet that the degcreasing of magnetron power can result in decrease of concentrations element in the coating. In the case of coatings produced with the same magnetron powers ($P_{M\text{-}Cu}$=200 W, $P_{M\text{-}Ag}$=200 W), the lower content of copper compared to the silver in the AgO+CuO coating indicates a lower sputtering rate of this element.

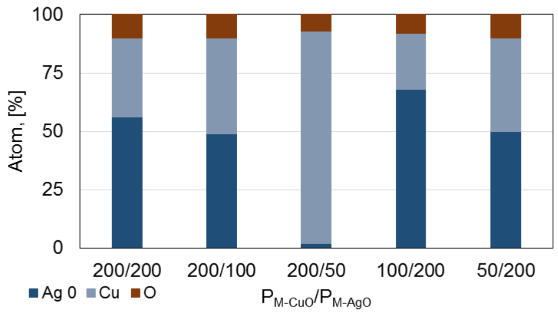

Figure 2 Chemical composition analyses of CuO+AgO coatings prepared with different magnetron power.

The analysis of the chemical composition of CuO+AgO coatings showed that the microstructure among others depends on the content of CuO and AgO oxides in structure. With the increase in the percentage of CuO in the coating, mainly a nanocrystalline columnar structure characteristic for PVD coatings was observed. On the other hand, in the case of coatings with increased AgO concentrations, a structure which mainly consists of spherical crystallites was observed

3.2. Mechanical properties studies

The results of the mechanical properties research are presented in **Figure 3**. They showed that the doping of CuO coatings with H_{CuO}=2,6 GPa with AgO silver oxide, which is characterized by a lower hardness (H_{AgO}=1,4 GPa), did not significantly reduce the hardness of the composite CuO+AgO coatings. At the same time, it was observed that multicomponent CuO + AgO coatings characterized by a higher Young's modulus compared to CuO monolayers (E_{CuO}=77 GPa). This indicates an improvement in the plastic deformation resistance of composite shells. This is an important feature in the context of using the coating to modify flexible polymeric materials.

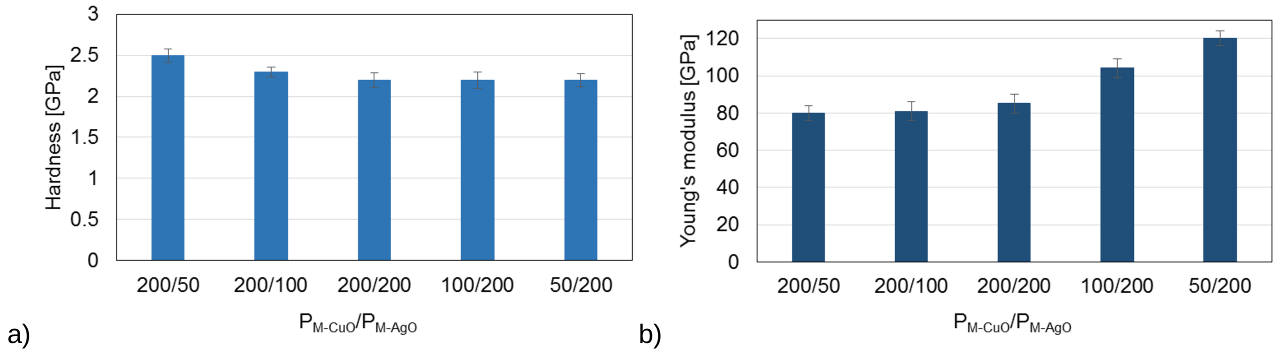

Figure 3 Results of measurements of the mechanical properties of CuO + AgO coatings: a) hardness tests, b) Young's modulus tests.

3.3. Wettability studies

The obtained results of the wettability analysys (**Figure 4**) showed that all tested coatings characterized by a wetting angle in relation to the polar liquid (H_2O) higher than pure polymer up to 105º in some cases. The non-polar liquid wettability analysis (DJM) showed a decrease in the wetting angle compared to the pure polymer.

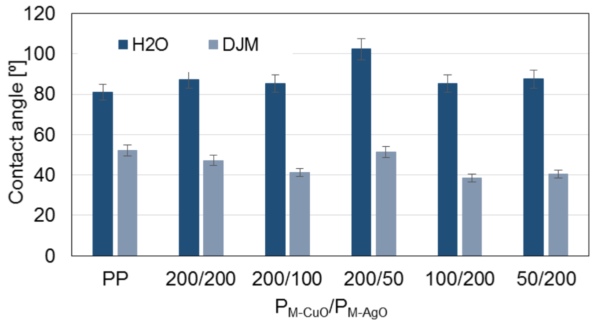

Figure 4 Results of measurements of wettability of thin CuO + AgO coatings obtained on a polymer substrate

3.4. Bactericidal properties studies

The obtained results of bactericidal properties tests (**Figure 5**) confirmed the high antibacterial effectiveness of the AgO-CuO coatings against both Gram negative (*Escherichia coli*) and Gram positive (*Staphylococcus aureus*) bacteria. Metal oxide compounds (Ag and Cu) included in the coating contributed to a complete reduction in the viability of microorganisms compared to the sample made of pure polypropylene (PP).

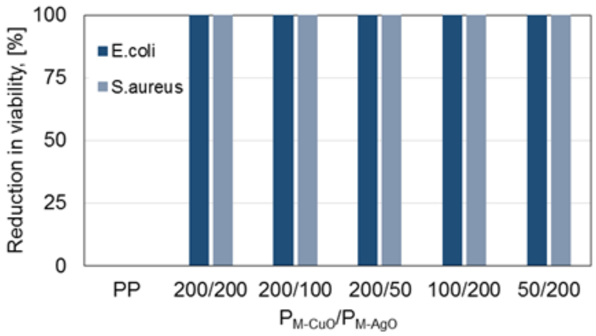

Figure 5 The degree of reduction in the viability of (*Escherichia coli*) and (*Staphylococcus aureus*) after contact with the tested samples in relation to the polypropylene sample (PP) after 24 h.

4. CONCLUSION

The high power impulse magnetron sputtering (HPIMS) process has been successfully used for the deposition of bactericidal coating on polymer substrate. The AgO+CuO coatings were deposited by magnetron sputtering method using various process parameters which resulted the differences in their chemical composition. The conducted analysis showed a significant influence of the chemical composition on the structure, density and mechanical properties of the obtained coatings. The analysis of the continuity of different CuO+AgO coatings showed that it is also depending on chemical composition. Furthermore, different growth mechanisms of the coatings are observed. The microstructure of the obtained multicomponent AgO+CuO coatings is the result of the microstructures characteristic for the monolayer AgO and CuO coatings. With the increase in the percentage of CuO in coating, a nanocrystalline columnar structure characteristic for PVD coatings was observed. Such an evident structure with the coating growth mechanism layer by layer. On the other hand, in the case of coatings with increased AgO concentrations the structure, which mainly consists of spherical crystallites were observed. It indicates an island growth mechanism. In addition, the presence of larger pores in this coating was observed. It was also found that plasma treatment of polypropylene (PP) with CuO+AgO layers allows to provide good antibacterial properties. One of the factors contributing to the formation of biofilm on the surface of polymers is the hydrophilicity of the material [14]. The use of AgO + CuO coatings made it possible to obtain hydrophobic surfaces that limit the growth of microorganisms on the surface. The conducted tests showed 100% bactericidal effectiveness of all tested coatings. Thus, it can be concluded that magnetron sputtering is a convenient technique for depositing thin bactericidal films on a polymer substrate.

ACKNOWLEDGEMENTS

This work was supported by the National Centre for Research and Development in Poland carried out within the project TECHMATSTRATEG III „Long-life composite filter media for water cleaning and high efficiency separation of gas-liquid and liquid-liquid dispersions”, no. Techmatstrateg III/005/2019-00.

REFERENCES

[1] MAITZ, M.F. Applications of synthetic polymers in clinical medicine. *Biosurface and Biotribology*. 2015, vol. 1.

[2] THADEPALLI, S. Review of multifarious applications of polymers in medical and health care textiles. *Materials Today: Proceedings*. 2022, vol. 55.

[3] SORRENTINO, A.; GORRASI, G.; VITTORIA, V. Trends in food. *Science & Technology*. 2007, vol. 18, no. 84.

[4] NORTH, E.J.; HALDEN, R.U. Plastics and environmental health: the road ahead. *Rev Environ Health*. 2013, vol. 28, no. 1.

[5] SHAHKARAMIPOUR, N.; TRAN, T.N.; RAMANAN, S.; LIN H. Membranes with Surface-Enhanced Antifouling Properties for Water Purification. *Membranes*. 2017, vol. 7.

[6] LIU, L.; DI, D.W.; PARK, H.; SON, M.; HUR, H-G.; CHOI H. Improved antifouling performance of polyethersulfone (PES) membrane via surface modification. *RSC Advances*. 2015, vol. 5.

[7] OLMOS, D.; GONZÁLEZ-BENITO, J. Polymeric Materials with Antibacterial Activity: A Review. *Polymers.* 2021, vol.13.

[8] GODDARD, J.M.; HOTCHKISS, J.H. Polymer surface modification for the attachment of bioactive compounds. *Progress in Polymer Science.* 2007, vol. 32.

[9] COTO, B.; HALLANDER, P.; MENDIZABAL, L.; PAGANO, F.; KLING, K.; ORTIZ, R.; BARRIGA, J.; SELEGÅRD, L. Particle and rain erosion mechanisms on Ti/TiN multilayer PVD coatings for carbon fibre reinforced polymer substrates protection. *Wear*. 2021, vol. 466–467.

[10] MELENTIEV, R.; YU, N.; LUBINEA, G. Polymer metallization via cold spray additive manufacturing: a review of process control, coating qualities, and prospective applications. *Additive Manufacturing*. 2021, vol. 48.

[11] TAN, G.-L.; TANG, D.; DASTAN, D.; JAFARI, A.; SHI, Z.; CHU, Q.-Q.; SILVA, J. P.B.; YIN X.-T. Structures, morphological control, and antibacterial performance of tungsten oxide thin films. *Ceramics International*. 2021, vol. 47.

[12] RASHID, S.; VITA, G.M.; PERSICHETTI, L.; IUCCI, G.; BATTOCCHIO, C.; DANIEL, R.; VISAGGIO, D.; MARSOTTO, M.; VISCA, P.; BEMPORAD, E.; ASCENZI, P.; CAPELLINI, G.; SEBASTIANI, M.; DI MASI, A. Biocompatibility and antibacterial properties of ticu(ag) thin films produced by physical vapor deposition magnetron sputtering. A*pplied Surface Science*. 2022, vol. 573.

[13] WOSKOWICZ, E.; ŁOŻYŃSKA, M.; KOWALIK-KLIMCZAK, A.; KACPRZYŃSKA-GOŁACKA, J.; OSUCH-SŁOMKA, E.; PIASEK, A.; GRADOŃ L. Plasma deposition of antimicrobial coatings based on silver and copper on polypropylene. *Polimery. 2020*, vol. 65.

[14] KACPRZYŃSKA-GOŁACKA, J.; KOWALIK-KLIMCZAK, A.; WOSKOWICZ, E.; WIECIŃSKI, P.; ŁOŻYŃSKA, M.; SOWA, S.; BARSZCZ, W.; KAŹMIERCZAK, B. Microfiltration Membranes Modified with Silver Oxide by Plasma Treatment. *Membranes.* 2020, vol. 10.

[15] KACPRZYŃSKA-GOŁACKA, J.; ŁOŻYŃSKA, M.; BARSZCZ, W.; SOWA, S.; WIECIŃSKI, P.; WOSKOWICZ, E.; ŻYCKI M. Influence of deposition parameters of TiO2+CuO coating on the membranes surface used in the filtration process of dairy wastewater on their functional properties. *Membranes.* 2021, vol. 11.

[16] KUSZELNICKA, I.; RUDAWSKA, A.; GINTER-KRAMARCZYK, D.; MICHAŁKIEWICZ, M.; ZAJCHOWSKI, S.; TOMASZEWSKA, J. Wpływ zwilżalności powierzchni kompozytów polimerowo-drzewnych na tworzenie biofilmu w procesach oczyszczania ścieków. *Polimery*. 2018, vol. 63.