MULTINUCLEAR TITANIUM(IV)-OXO COMPLEXES AS THE NOVELTY ANTIMICROBIAL AGENTS

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Introduction

Excessive and misuse of antibiotics and antimicrobials led to a spread of microorganisms resistant to most currently used agents. The resulting global threats became an impulse in searching for new materials with optimal antimicrobial activity and their application in various areas of our lives. Our research focused on the formation of composite materials produced by the dispersion of multinuclear titanium(IV)-oxo complexes (TOCs) in polymer matrices, which exhibit optimal antimicrobial activity.

Materials and Methods

The TOCs, of the general formula $[Ti_aO_b(OR)_c(O_2CR')_{4a-2b-c}]$ (R = ^{i}Pr, ^{i}Bu; R' = $PhNH_2$, PhOH, and $C_{13}H_9$) were isolated from the mother liquors consisted of $Ti(OR)_4$ and organic acids (HO_2CR') accordingly procedure earlier described [1-3]. Analysis of X-ray diffraction data and spectra registered using diffuse reflectance infrared Fourier transformation (DRIFT) and Raman spectroscopy allowed on their structure confirmation [1-5]. The isolated TOCs microcrystalline powders were dispersed in the polymer matrices (PMMA, PCL, and epoxide resins), thus forming composites (polymer + *n*TOCs), containing *n* = 2, 5, 10, and 20wt% of the oxo-complex. The presence of TOCs in (polymer + TOCs) composites and their structural stability during the fabrication of composite samples has been confirmed by the registration of Raman microscope maps and Energy dispersive X-ray spectroscopy (SEM EDX). Moreover, the possible changes in thermal properties of studied composites, caused by the addition of TOCs, were estimated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The photocatalytic activity was estimated on the basis of methylene blue solution (MB) decolorization, during the irradiation with visible light by 30 h. EPR spectroscopy was used to detect paramagnetic species on the surface of the synthesized materials. Antibacterial and antifungal activities of composite samples was studied against Gram-positive (*Staphylococcus aureus* ATCC 6538 and *S. aureus* ATCC 25923) and Gram-negative (*Escherichia coli* ATCC 8739 and *E. coli* ATCC 25922) bacteria and yeasts of *Candida albicans* ATCC 10231.

Results and Discussion

he results of our investigations allowed us to develop methods for the synthesis of multinuclear Ti(IV)-oxo complexes (TOCs) with different $\{Ti_aO_b\}$ core architecture, as well as their structural characteristic [1-5]. Obtained results proved the hydrophobic nature of TOCs crystals and powders; additionally, they revealed a low sensitivity to hydrolysis processes. It caused that in all our photocatalytic and biological experiments, the (polymer + TOCs) composites produced by the TOCs dispersion in the polymer matrix, were used. The preliminary spectral (IR, Raman) investigations confirmed the structural stability of TOCs during the composite sample production and the photocatalytic experiments. Moreover, we have noticed a clear relationship between the $-O_2CR'$ group type, stabilizing the oxo-core, and TOCs photocatalytic activity. It should be noted that in all our experiments, the samples were illuminated with UV irradiation (UVB-UVA range). However, in some cases, e.g. TOCs stabilized by the 9-fluorenecarboxylic or benzoic carboxylic species ligands, the broad absorption band also covers the visible range. In this case, it was possible to use visible light as a factor inducing photocatalytic processes. It suggests that the TOCs micro-grain samples excited by the visible light can generate the reactive oxygen species (ROS) as the potential microbicidal factors. The results of our preliminary studies on the antimicrobial activity of the (polymer + TOCs) composites (polymer = PMMA, TOCs = complexes containing $\{Ti_3O\}$ and $\{Ti_4O_2\}$) showed promising properties of this system as a microbiocidal agent [6,7]. Moreover, it was established that the antimicrobial activity of the (polymer + TOCs) composite was the result of the oxo-complexes introduction into the polymer matrix.

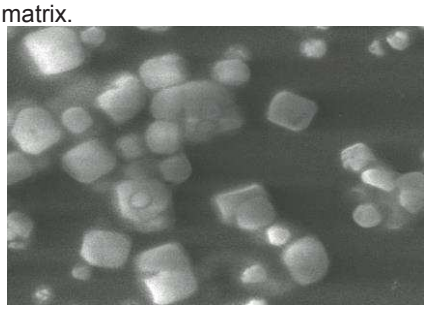

FIG. 1. The SEM image of the (PMMA + TOCs) composite sample.

Conclusions

The results of our investigations on TOCs synthesis, their physicochemical properties, and photocatalytical activity revealed that these compounds might be of vital importance for novel bioactive inorganic-organic composite materials formation. A significant was determining the dependency between the TOCs' structure, their photocatalytic activity in the visible light range, manifested by the generation of identified ROS, and their antimicrobial properties. Successful results of the future detailed microbiological tests and excluding cytotoxic properties of composites produced by dispersion of selected TOCs in polymer matrices will allow for designing new devices/coatings with the visible light-induced to solve differentiated problems related to the control of microbial pathogens.

References

[1] Janek, M.; Radtke, A.; Muzioł, T.M.; Jerzykiewicz, M.; Piszczek, P. Materials 2018, 11, 1661.
[2] Piszczek, P.; Kubiak, B.; Golińska, P.; Radtke, A. Int. J. Mol. Sci. 2020, 21, 9663.
[3] Janek, M.; Muzioł, T.M.; Piszczek, P. Materials 2019, 12, 3195.
[4] Piszczek, P.; Radtke, A.; Muzioł, T.; Richert, M.; Chojnacki, J. Dalton Trans. 2012, 41, 8261-8269.
[5] Radtke, A.; Piszczek, P.; Muzioł, T.; Wojtczak, A. Inorg. Chem. 2014, 53, 10803-10810.
[6] Piszczek, P.; Kubiak, B.; Golińska, P.; Radtke, A. Int. J. Mol. Sci. 2020, 21, 9663.
[7] Kubiak, B.; Radtke, A.; Topolski, A., Wrzeszcz, G.; Golińska, P.; Kaszkowiak, E.; Sobota, M.; Włodarczyk J.; Stojko, M.; Piszczek, P. Int. J. Mol. Sci. 2021, in press.