THE ANTIMICROBIAL AND PHOTOCATALYTIC ACTIVITY EVALUATION OF THE POLYMER/TITANIUM(IV) OXO-COMPLEX COMPOSITES

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Introduction

Antibiotic resistance is a problem that is increasingly beginning to affect us personally. This is the result of human action, which directly contributed to a drastic increase in the problem of antibiotic resistance. Unfortunately, it is not easy to overcome it, and one of the directions of research is to search for new materials showing high antimicrobial activity. The solution we propose is to use titanium(IV) oxo-complexes (TOCs). The aim of the study was the synthesis of (TOCs) with the $\{Ti_3O\}$ and $\{Ti_4O_2\}$ core as well as the synthesis of composite materials, by introducing oxo-complexes into the polymer matrix. The most important stage was to examine the microbiological and photocatalytic activity of the obtained composites. The structures we obtained have a chance to be used in the production of antibacterial surfaces.

Materials and Methods

Titanium(IV) oxo-complexes were synthesized as a result of the 4-hydroxybenzoic acid, 4-aminobenzoic acid and 9-fluorecarboxylic acid reaction with titanium(IV) isopropoxide as well as 4-hydroxybenzoic acid with titanium(IV) isobutoxide. Composite materials were produced by the incorporation of 20 wt.% oxo-complexes into the polymer matrix. The products were subjected to thermal analysis (STA 449 FS NETZSCH), infrared spectroscopy (FT-IR Spectrometer SPECTRUM 2000, Perkin Elmer), and Raman spectroscopy analysis (RamanMicro 200, Raman Microscope, Perkin Elmer). Microbiological tests were conducted for the following bacteria: *Escherichia coli*, *Staphylococcus aureus* and yeast: *Candida albicans*. The photocatalytic activity of produced composite materials was studied on the base of the methylene blue (MB) degradation procedure, in accordance to ISO 10678; 2010.

Results and Discussion

The oxo-complexes (TOCs) were synthesized in the direct reaction of titanium(IV) alkoxides ($Ti(O^iPr)_4$ and $Ti(O^iBu)_4$) and selected organic acids in 4:1 alkoxide/acid molar ratio, using a standard Schlenk technique under an argon atmosphere and room temperature (RT). The following organic acids were used in our experiments: 9-fluorenecoarboxylic acid ($HOOCC_{13}H_9$)), 4-aminobenzoic acid ($HOOC\text{-}p\text{-}PhNH_2$), and 4-hydroxobenzoic acid (HOOC-p-PhOH)). Analysis of IR and Raman spectra of synthesized oxo-complexes confirmed that their structure consists of $\{Ti_3O\}$ and $\{Ti_4O_2\}$ cores, according to the results of our earlier structural studies [1-3]. The photocatalytic activity estimation were carried our using polymer/TOCs composite foils produced by the dispersion of TOCs in the polymer solution (poly(methyl methacrylate) (PMMA)) and slow evaporation of the solvent. Scanning electron microscopy (SEM) confirmed the presence of uniformly dispersed microcrystalline powders of studied oxo-complexes in the composite films of 25-50 μm thick. The photocatalytic activity of synthesized trinuclear Ti(IV) oxo-complexes have been estimated basing on the UV photoinduced degradation process of methylene blue (MB), in accordance to ISO 10678; 2010 standard. The results of experiments carried out confirmed that all produced materials revealed the photocatalytic activity, however the best activity was found for $PMMA/[Ti_4O_2(O^iBu)_{10}(O_2C\text{-}PhOH)_2]$ system.
Microbiological studies proved that the composites obtained have good antimicrobial properties, each of the complexes tested caused a decrease in the number of microorganisms (TABLE 1).

TABLE 1. Antibacterial and antifungal properties of the PMMA film enriched with oxo-clusters, tested using the *S. aureus*, *E. coli* strains as well *C.albicans* ATCC 10231, in accordance with the EN ISO 22196 standard. The degree of microbial reduction [%]

	PMMA	PMMA+4-amino {Ti3O}	PMMA+4-hydroxy {Ti4O2}	PMMA+9-fluoro {Ti3O}	PMMA+ TiO_2 + 4-hydroxy {Ti4O2}
E. coli ATCC 8739	28,57 %	99,71%	100,00%	83,07%	100,00%
E. coli ATCC 25922	- 10,00 %	99,95%	100,00%	96,50%	100,00%
S. aureus ATCC 6538	- 105,56%	100,00%	100,00%	99,73%	100,00%
S. aureus ATCC 25923	- 310,00%	100,00%	100,00%	96,60%	100,00%
C. albicans ATCC 10231	- 20,00 %	82,00%	100,00%	81,00%	100,00%

Conclusions

The research results showed that oxo-complex $[Ti_4O_2(O^iBu)_{10}(O_2C\text{-}PhOH)_2]$ exhibits the best photocatalytic properties (decolorization of MB solution in the presence of the $polymer/[Ti_4O_2(O^iBu)_{10}(O_2C\text{-}PhOH)_2]$ composite sample, which was irradiated by UVA light). Simultaneously, the microbiological assays revealed that this composite caused a reduction in the number of microorganisms by almost 100%, which indicate on the high antimicrobial activity of this material.

References

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