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ANTIMICROBIAL MODIFICATION OF POLYPROPYLENE WITH SILVER NANOPARTICLES IMMOBILIZED ON ZINC STEARATE

PROTIMIKROBNO SPREMINJANJE POLIPROPILENA Z NANODELCI SREBRA, IMOBILIZIRANIH NA CINKOVEM STEARATU

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The microwave synthesis of Ag nanoparticles on zinc stearate (ZnSt/Ag) was performed to obtain an antimicrobial additive for a polypropylene matrix. Thermoplastically prepared polymer composites contained (1, 3, 5 and 10) % of mass fractions of ZnSt/Ag. The effect of the presence of additives on the morphology and mechanical properties of composites was studied by scanning electron microscopy and stress-strain analysis. The antimicrobial activity of the composites was studied according to the ISO 22196 standard. The results showed that sufficient antimicrobial activity of the composites against both Gram-positive and Gram-negative bacterial strains was observed in the case of the composites with the highest filling studied.

Keywords: antibacterial, polypropylene composite, zinc stearate, Ag nanoparticles

Izvedena je bila sinteza nanodelcev Ag na cinkovem stearatu (ZnSt/Ag) z mikrovalovi, da bi dobili protimikrobni dodatek polipropilenski osnovi. Termoplastično pripravljeni kompozit polimera je vseboval (1, 3, 5 in 10) % masnega deleža ZnSt/Ag. Vpliv prisotnosti dodatkov na morfologijo in mehanske lastnosti kompozitov je bil proučevan z vrstično elektronsko mikroskopijo in analizo napetost-raztezek. Protimikrobna aktivnost kompozita je bila proučevana skladno s standardom ISO 22196. Rezultati so pokazali, da je primerna protimikrobna aktivnost pri sevih, gram pozitivnih in gram negativnih bakterij, dosežena v primeru kompozita z največjim proučevanim dodatkom.

Ključne besede: protibakterijsko, polipropilenski kompozit, cinkov stearat, nanodelci Ag

1 INTRODUCTION

Antimicrobial modifications of polymers are used to prevent or inhibit the growth of microorganisms on its surface. Such a modification may find utilization in food packaging, medical applications and especially in hygienic materials or textile production. Nowadays, a commonly used method for the modification of polymers is an addition of an antimicrobial agent/additive directly into the polymer matrix. Currently, silver-based (Ag) additives have received significant attention due to the low toxicity of the active Ag ion to human cells as well as for being a long-lasting biocide with high thermal stability and low volatility.[1,2] Microwave (MW) synthesis is one of the well-known effective methods for the preparation of Ag NPs.[3,4] The immobilization of Ag NPs by MW synthesis on various organic substrates has been studied by P. Bazant et al.[2] The authors successfully immobilized nano-silver, nanostructured ZnO and hybrid nanostructured Ag/ZnO on a wood flour (WF) surface by MW synthesis. Subsequently, the modified WF was compounded into a PVC matrix (5 % of mass fractions loading) and the antimicrobial activity was tested while the most efficient system was the hybrid nanostructured Ag/ZnO. N. Iqbal et al.[1] described the surface modification by the MW synthesis of Ag NPs on the surface of inorganic substances. The Ag NPs were successfully bonded on hydroxyapatite and caused antimicrobial activity of the prepared system.

The antimicrobial modification of polypropylene with Ag NPs prepared by MW synthesis and immobilized on a zinc stearate surface was studied in this work. The prepared composites were characterized by scanning electron microscopy, stress-strain analysis and antimicrobial testing according to the ISO 22196 standard.

2 EXPERIMENTAL PART

2.1 Materials

Polypropylene (PP) resin (C706-21 NA HP, density = 0.9 g.cm^{-3}, MFR = 21 g.10 min^{-1}) used in this work was a product of the Braskem company (Brazil). Zinc stearate (ZnSt) was supplied by Sigma Aldrich (USA). Silver nitrate ($AgNO_3$), Hexamethylenetetramine (HMTA) and ethanol were purchased from PENTA, Czech Republic.

2.2 Preparation of hybrid ZnSt/Ag particles and PP composites

Hybrid ZnSt/Ag particles were prepared under reflux in the MW open vessel system MWG1K-10 (RADAN,

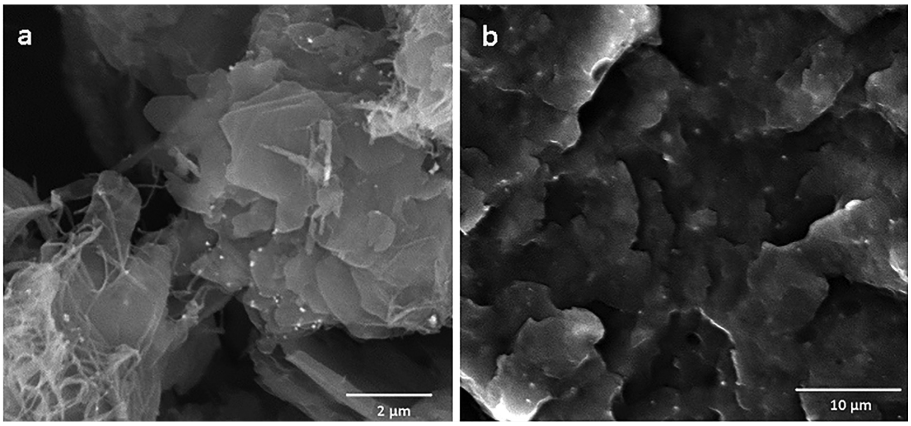

Figure 1: Scanning electron micrographs of: a) ZnSt/Ag particles and b) PP 10 % of mass fractions of ZnSt/Ag composite. The Ag nanoparticles can be recognized as white dots.
Slika 1: Posnetka z vrstičnim elektronskim mikroskopom: a) ZnSt/Ag delci in b) kompozit PP z 10 % masnega deleža ZnSt/Ag. Nanodelci Ag se kažejo kot bele točke.

Czech Republic; 1.5 kW, 2.45 GHz) operating in continuous mode (zero idle time) with an external cooler. First, 200 mL of $AgNO_3$ (0.85 g) solution in water and 450 mL of ZnSt (11.02 g) dispersion in ethanol were transferred into a 1000 mL reaction bottle. The reaction mixture was heated in a MW oven for 2 min. After that, 100 mL of HMTA (7.00 g) solution in water was added and the MW heating continued for 10 min under continuous stirring (250 min^{-1}). The reaction product was collected by suction microfiltration and left to dry in a laboratory oven (50 °C) up to the constant weight. The prepared ZnSt/Ag system contained 2.4 % of mass fractions of Ag (determined by atomic absorption spectroscopy, Agilent DUO 240FS/240Z/UltrAA). The prepared hybrid particles were incorporated into the PP matrix by twin screw micro-compounder DSM Xplore (15 mL chamber volume). The temperature of all three zones was 200 °C, speed 100 min^{-1} and time of mixing 10 min. The concentration of the filler was from 1 % to 10 % of mass fractions.

2.3 Characterization methods

The structure of the prepared samples was observed by scanning electron microscopy (VEGA IILMU, TESCAN). The specimens were coated with a thin Au/Pd layer. The microscope was operated in vacuum mode at an acceleration voltage of 10 kV.

The mechanical characterization of the samples (dog-bone shaped specimens) was performed with a M350-5 CT Materials Testing Machine. The cross-head speed was 10 mm/min. Each test consisted of seven replicate measurements. Antimicrobial testing was performed according to the ISO 22196:2007 international standard against *Escherichia coli* and *Staphylococcus aureus*.

3 RESULTS AND DISCUSSION

SEM micrographs of the ZnSt/Ag additive and PP 10 % ZnSt/Ag composite are shown in **Figure 1**. Immobilized Ag particles with a size below 100 nm are visible in the case of the pure additive (**Figure 1a**) as well in the composite (**Figure 1b**). The size and shape of the MW prepared Ag NPs correspond to the results published by Bazant et al.[2] where Ag NPs were immobilized on a wood flour. Furthermore, the SEM analysis reveals that immobilized Ag NPs have good cohesion to the ZnSt substrate, even after thermoplastic processing.

The mechanical properties of the composites were noticeably influenced when the loading of the filler was above 5 % of mass fractions. However, the addition of 1 % of mass fractions of ZnSt/Ag improved the tensile strain by approximately 16 % in comparison with neat PP, while the tensile strength remained unchanged. In the case of the composites containing 10 % of mass fractions of ZnSt/Ag the Young's modulus, tensile strength and tensile strain were reduced by approximately 35 %, 20 %, and 81 %, respectively (**Table 1**). The mechanical properties of the composites are most dependent on the

Table 1: Summary of stress-strain analysis results of prepared PP/ZnSt/Ag composites
Tabela 1: Zbir rezultatov analiz napetost-raztezek pripravljenih kompozitov PP/ZnSt/Ag

	Young's modulus (MPa)	Tensile strength (MPa)	Strain at break (%)
PP	217 (± 27)	22 (± 1.7)	187 (± 47)
PP 1 % ZnSt/Ag	179 (± 25)	22 (± 0.5)	217 (± 23)
PP 3 % ZnSt/Ag	172 (± 12)	22 (± 1.1)	68 (± 12)
PP 5 % ZnSt/Ag	155 (± 29)	21 (± 1.2)	54 (± 17)
PP 10 % ZnSt/Ag	143 (± 10)	18 (± 0.8)	35 (± 3)

Table 2: Antimicrobial activity of prepared composites determined according to ISO 22196
Tabela 2: Protimikrobna aktivnost pripravljenih kompozitov, določena po ISO 22196

Sample	*S. aureus*		*E. coli*	
	CFU/cm^2	*R*	CFU/cm^2	*R*
PP	2,4E+05	–	7,2E+05	–
PP + 5 % ZnSt	1,1E+05	0.4	1,9E+05	0.6
PP + 10 % ZnSt	9,6E+04	0.4	5,0E+04	1.2
PP + 5 % ZnSt/Ag	1,6E+05	0.2	5,5E+04	1.1
PP + 10 % ZnSt/Ag	9,5E+02	2.4	0,0E+00	7.0

ZnSt content without the effect of the Ag NPs presence on it. Changes of the mechanical properties correspond to the results observed in the case of the composites based on PP and unmodified ZnSt.[5]

The antimicrobial activity of the composites is summarized in **Table 2**. There is a slight inhibition of growth of both bacterial strains when the concentration is 5 % of mass fractions of ZnSt (corresponding to 0.08 % of mass fractions of Ag). The samples with the highest filling studied (0.16 % of mass fractions of Ag) exhibit a noteworthy activity against *Escherichia coli* and *Staphylococcus aureus*. Antimicrobial activity is in agreement with studies describing incorporation of Ag NPs into hydrophobic polymer matrices.[2]

4 CONCLUSIONS

The hybrid systems of ZnSt and Ag nanoparticles were prepared by MW synthesis and incorporated into a PP matrix. The prepared composites showed a promising antimicrobial activity at concentration above 5 % of mass fractions. The mechanical properties were noticeably influenced at 10 % of mass fractions of the ZnSt/Ag loading into the PP matrix. However, a noticeable improvement of tensile strength of the composites was observed already at 1 % of mass fractions of ZnSt/Ag, while the tensile strain remained unchanged in comparison with the unmodified PP.

The proposed antimicrobial modification of commonly used additives, such as zinc stearate, represents a promising way of nanoparticle handling and applications.

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