

## IDENTIFYING THE OPTIMUM METHOD FOR MODIFYING THE ZINC OXIDE SURFACE IN ORDER TO OBTAIN A HIGH DEPOSIT DEGREE OF THE FUNCTIONING AGENT

MARIA SÖNMEZ<sup>1</sup>, DENISA FICAI<sup>2</sup>, ANTON FICAI<sup>2</sup>, OVIDIU OPREA<sup>2</sup>, IOANA LAVINIA ARDELEAN<sup>2</sup>, ROXANA TRUȘCĂ<sup>2</sup>, LAURENȚIA ALEXANDRESCU<sup>1</sup>, MIHAELA NIȚUICĂ<sup>1</sup>, MARIA DANIELA STELESCU<sup>1</sup>, MIHAI GEORGESCU<sup>1</sup>, DANA GURĂU<sup>1</sup>

<sup>1</sup>INCDDP–Division: Leather and Footwear Research Institute, 93 Ion Minulescu St., Bucharest, Romania, maria.sonmez@icpi.ro

<sup>2</sup>Politehnica University of Bucharest, Faculty of Applied Chemistry and Material Science, 1-7 Polizu St., Bucharest, Romania

The aim of this study is to identify the optimal method of surface modification of ZnO nanoparticles in order to obtain a high deposition rate of the polydimethylsiloxane (PDMS) functionalizing agent. Thus, in order to identify the optimal route, the surface of ZnO nanoparticles were functionalized by 3 methods, ultrasonic, magnetic stirring and vacuum adsorption, followed by advanced powder characterization, FTIR, SEM, EDS, DSC-TG. The FTIR analysis recorded on the surface modified ZnO powder highlights the functional groups in the PDMS, regardless of the synthesis method, which confirms that the functionalization took place. However, based on the intensity of PDMS functional groups, it can be concluded that the highest deposition rate is obtained in the case of ultrasonography, followed by the magnetic stirring and vacuum adsorption method. This different deposition rate can be attributed to the fact that ultrasonication leads to ZnO particles being broken down into smaller particles, resulting in a higher contact surface with PDMS. The SEM image obtained on the commercial ZnO powder and the ZnO / PDMS powder, highlights their extremely varied morphology and demonstrates that the modification does not influence either the shape or size of the ZnO. EDS analysis confirms that functionalization took place due to the presence of the Si element alongside the other Zn and O major elements. The DSC-TG analysis obtained on the ZnO / PDMS powder indicated an organic mass loss, from the organosilane structure, of 5.51% in the range of 365-530°C. The results obtained provide the premise that these functionalized ZnO nanoparticles in addition to antibacterial properties will improve compatibility / dispersibility in various polymeric matrices.

Keywords: functionalization methods, zinc oxide, polydimethylsiloxane.

## INTRODUCTION

Infectious diseases caused by a high number of bacteria pose a serious threat to human health. One of the major bacteria that causes 1.5 million deaths annually due to food and beverage contamination is *Sigella flexneri* (Kotloff *et al.*, 1999). Other bacterial strains, which frequently infest food and slop a high number of illnesses, has *Escherichia coli*, *Campylobacter jejuni*, *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Enterococcus faecalis*, *Salmonella types*, and *Clostridium perfringens*, (Sirelkhatim *et al.*, 2015; Stegarus *et al.*, 2017). To deactivate or kill these bacterium, numerous metallic salts, nanoscale metals and metallic oxides have been tested as promising inorganic antimicrobials. Metal oxides are used in many applications, Catalysis, sensors, medicine, varistors, rubber and plastics, cosmetics, personal care products, etc. (Oprea *et al.*, 2014). The most frequent metal oxides, use as anti-bacterial agents, in various products, are TiO<sub>2</sub>, CuO, ZnO, MgO, etc. (Mahmoodi *et al.*, 2018). Of these, ZnO is considered the most promising safe and anti bacterial agent (Zhao *et al.*, 2018). In addition to the bacterial properties, ZnO is frequently used as an agent of inorganic reinforcement in various polymers, with a view to improving the thermal properties, mechanical and chemical (Simões *et al.*, 2017; Cetin *et al.*, 2018). ZnO is

often used in various polymeric films, for the manufacture of the active antimicrobial packaging (Naveed ul Haq *et al.*, 2017). The most common polymers / mixtures of polymers in which ZnO is used, in order to obtain thin films are, PET- poly(ethylene terephthalate) / PBS-poly(butylene succinate), co-polymer (Threepopnatkul *et al.*, 2014), - PET/PEG - poly(ethylene glycol) (Ji *et al.*, 2015), polyurethane - PU (Chen *et al.*, 2013), cases - PP (Hadi *et al.*, 2016), etc. The main problem in obtaining homogeneous composite materials is very difficult because ZnO possesses a large surface area and a surface energy increases, leading to an agglomeration in the matrix of copolymers / polymers, altering the physico-mechanical properties. In order to reduce the agglomeration of ZnO in the polymeric matrix, it is necessary to modify its surface. The most used coupling agents are: oleic acid (Aysa *et al.*, 2017), stearic acid (Ji *et al.*, 2015), 3-aminopropyltrimethoxysilane - APTS, 3 - thiolpropyltrimethoxysilane - TPTS, (El-Nahhal *et al.*, 2016; Lu *et al.*, 2018), etc.

## MATERIALS AND METODS

### Materials

The materials used in this study were the following: zinc oxide nanopowder, <100nm particle size, molecular weight - 81.39, assay ~ 80% Zn basis, surface area - 15-25 m<sup>2</sup>/g; 2-propanol (isopropanol), grade - anhydrous, assay - 99.5%, molecular weight - 60.10, vapor density – 2.1 (vs air), vapor pressure – 33 mmHg (20°C) and 44 mmHg (25°C); poly (dimethylsiloxane) (PDMS), grade - analytical standard, vapor pressure - 153 mmHg (20°C), density - 0.82 g/mL, molecular weight - 236.53 wt.%.

### Method

Surface modification of ZnO particles with PDMS was performed by three methods:

**Method a** - consists in the modification of the ZnO surface with PDMS by ultrasonography, using 1 g of the commercial ZnO powder, over which has been added, 10 ml of isopropanol (with the role of reaction /scattering medium). Mixture containing ZnO and isopropanol has been inserted into the plastic tubes with a volume of 50 mL and immersed in the ultrasonic bath, previously heated to 40°C. After 5 minutes of mixing ZnO with isopropanol, using an automatic syringe, 1 mL of PDMS were added, and allowed to mix/react for 2h. After 2 h, the centrifuge tubes were removed from the ultrasonic bath, left at room temperature, approximately 10-15 minutes, filtered and washed with isopropanol in abundance to remove unreacted PDMS followed by drying in a hot air oven at 80°C for 4-6 hours followed by milling and morpho-structural characterization (SEM, EDAX, DSC-TG, FTIR).

**Method b** - is similar to that described above, with the mention that in this case the surface modification of ZnO with PDMS has been achieved by the magnetic stirring, with the possibility of adjusting the temperature (40°C) and the rotational speed (300 rpm).

**Method c** - in this case the nanoparticles surface modification has been achieved by the adsorption method under vacuum, using a special container glass, equipped with a special connection for the vacuum pump and a glass funnel with plastic lid, where the isopropyl alcohol and PDMS solution is injected. In this container, over 1 gram of ZnO powder, a solution consisting of 5 mL of isopropyl alcohol and 1 mL PDMS introduced under vacuum, using a syringe was added. After adsorption, container has been placed

in a thermostated bath at 40°C for 2 h. The following stages are identical to those described above.

## RESULTS AND DISCUSSION

### FTIR Spectrometry

FTIR spectrometry was used for the purpose of investigating the bonds which are formed between the molecules of PDMS and the ZnO powder surface. In the Figure 1 are shown the spectra recorded on the commercial ZnO powder and those of ZnO powder functionalized with PDMS, by the 3 methods described. The IR spectra obtained on the ZnO powder modified with PDMS, through all 3 methods, they highlight the bands characteristic to functional groups of organosilane, namely the band with from the 2904  $\text{cm}^{-1}$  is assigned to groups CH<sub>3</sub>, band from 1089-1015  $\text{cm}^{-1}$  are assigned to stretching groups of Si-O-Si and those of approx. 1259  $\text{cm}^{-1}$  are characteristic to -CH<sub>3</sub> deformation groups, from Si-CH<sub>3</sub> bond. The band at 796  $\text{cm}^{-1}$  is characteristic to stretching bond Si-C- originating from Si-CH<sub>3</sub>. The ZnO band can be observed at approx. 436  $\text{cm}^{-1}$ . As it can be seen, the method of using ultrasonic bath, seems to be optimum, because a higher deposition rate of PDMS on the surface of ZnO is obtained compared to the use of the magnetic stirring method and the one under vacuum adsorption. This can be confirmed by the much higher bandwidth intensities of the bending CH<sub>3</sub> groups originating from Si-CH<sub>3</sub> bond, Si-O-Si groups (1089-1015  $\text{cm}^{-1}$ ) and the stretch Si-C bonds from CH<sub>3</sub> (791  $\text{cm}^{-1}$ ) in the case of ZnO/PDMS powders modified by ultrasonography compared with the use of other methods. A possible explanation for depositing a more thick layer of PDMS could be attributed to the fact that ultrasonography would facilitate the breakage of ZnO particles into smaller particles, which would lead to an increase in the specific surface area, and implicitly to a higher net deposition rate PDMS.

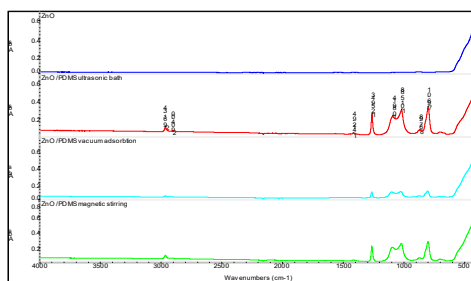


Figure 1. The FTIR spectra of ZnO powders functionalized with PDMS, by the 3 methods

### Scanning Electron Microscopy (SEM)

The Scan electronic microscopy (SEM) images have been recorded both on the simple powder of ZnO and modified with PDMS. As you can see in Figure 2 image A, recorded on the un treated powder of ZnO, to a 50000x magnification, particle size varies in the range 63.81 - 279 nm, with particles shapes extremely varied: acicular, in the form of canes, rectangular, etc, and very well defined (monodisperse without

agglomeration). In the case of ZnO / PDMS powder (image B), it is noted that the presence of organo-silane do not affect significantly, the shape and size of the particles. More than that, sharp contours between the particles of ZnO are observed.

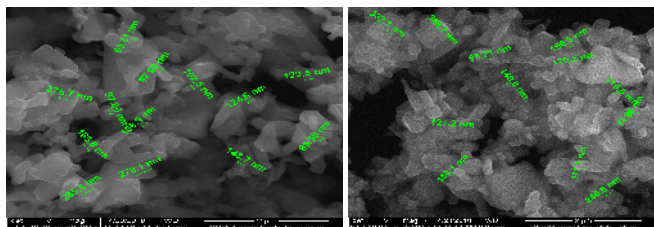


Figure 2. SEM image of commercial ZnO (left) and ZnO /PDMS powder obtained by ultrasonography (right)

### Energy Dispersive Spectroscopy (EDS) Analysis

EDS analysis is an effective method of identifying the constituent elements and their relative proportions (atomic, weight), present in a sample. As shown in Figure 3, in the case of the spectrum recorded on the pure ZnO powder, the following elements could be identified, Zn and O. Peak corresponding to the Zn, appears in the spectrum at different intensities, which shows that he represents the main component which can be found in the sample. Other items in addition to Zn and O could not have been identified, which show that the ZnO powder used, is of high purity. Quantitative analysis of ZnO powder is shown in Table 1, and shows as the percentage, the weight and nuclear content of the 2 types of components.

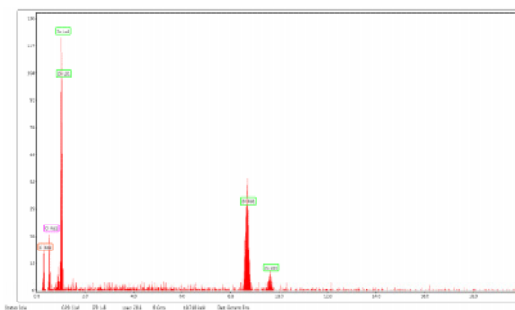


Figure 3. The EDS spectrum of the commercial ZnO powder

Table 1. Quantitative analysis of commercial ZnO powder

Element	Weight, %	Atomic, %
O K	28.23	61.65
Zn K	71.77	38.35

The spectrum shown in Figure 4, obtained on the ZnO/PDMS powder by ultrasonography, indicates the presence of the following components, Zn, Si, and O. It should be noted that the relative strength between peaks varies significantly, and is the

most intense for Zn. The presence of an extra peak namely Si, confirm once again the results obtained by FTIR, DSC-TG and demonstrates that ZnO surface functionalization was conducted successfully. The percentage and atomic weight between the three elements (O: Si: Zn) is shown in Table 2.



Figure 4. The EDS spectrum of the ZnO/PDMS powder, ultrasonic

Table 2. Quantitative analysis of ZnO/PDMS powder, ultrasonic

Element	Weight, %	Atomic, %
O K	22.82	52.64
Si K	5.04	6.62
Zn K	72.15	40.74

### Complex Thermal Analyses

Thermal analysis recorded on the ZnO/PDMS powder, Figure 5, shows a good stability up to 365°C (losing only 0.35 percent of the mass). There is a single-stage of decomposition, in accordance with the TG curve in the range 365-530°C, with the onset to 395.7°C, when there is a loss of mass of 5.51% accompanied by a slightly exothermic effect, with maximum at 411°C. The residual mass is 93.96%.

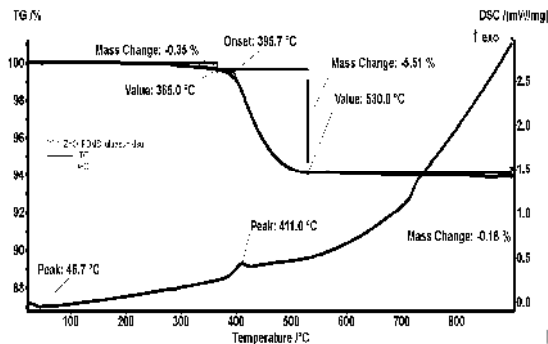


Figure 5. Thermal analysis of ZnO/PDMS powder

## CONCLUSIONS

The morpho-structural and thermal analyzes obtained on the ZnO powder modified with PDMS, demonstrates that depending on your chosen route may get different deposition degrees of organo-silane. The results obtained provide the premise that these nanoparticles of functionalized ZnO, in addition to the bacterial properties will improve the compatibility / dispersability in various polymeric matrix (PET, PVC etc.).

## Acknowledgements

This research was financed through PN 18 23 01 01/2018 project: “Antibacterial polymeric nanocomposites with thermoplastic matrix and TiO<sub>2</sub>/ZnO hybrid nanoparticles for medical and food industry applications” supported by MCI.

## REFERENCES

- Aysa, N.H. *et al.* (2017), “Preparation and surface modification of zinc oxide nanoparticles”, *Journal of Babylon University/Pure and Applied Sciences*, 25, 497-503.
- Cetin, G. *et al.* (2018), “A novel antibacterial nanofibers mat made of co-axial electrospun polycaprolactone/silver nitrate/ zinc oxide composites”, *Advanced Nano-Bio-Materials and Devices*, 2, 275-86.
- Chen, H. *et al.* (2013), “Dispersivity of modified ZnO and characterization of polyurethane/ZnO composites”, *Polymer Composites*, 35, 237-44, <https://doi.org/10.1002/pc.22655>.
- El-Nahhal, I.M. *et al.* (2016), “Synthesis & characterization of silica coated and functionalized silica coated zinc oxide nanomaterials”, *Powder Technology*, 287, 439-46, <https://doi.org/10.1016/j.powtec.2015.09.042>.
- Hadi, N.J. *et al.* (2016), “Rheological behavior of waste polypropylene reinforced with zinc oxide nanoparticles”, *WIT Transactions on Engineering Sciences*, 105, 201-11, <https://doi.org/10.2495/AFM160171>.
- Ji, P. *et al.* (2015), “Influence of surface modification of zinc oxide nanoparticles on thermal behavior and hydrophilic property of PET-PEG composites”, *Polymer Composites*, 37, 1-9.
- Kotloff, K. *et al.* (1999), “Global burden of Shigella infections: implications for vaccine development and implementation of control strategies”, *Bull World Health Organ*, 77, 651-66.
- Lu, P.J. *et al.* (2018), “Methodology for sample preparation and size measurement of commercial ZnO nanoparticles”, *Journal of Food and Drug Analysis*, 26, 1-9, <https://doi.org/10.1016/j.jfda.2017.07.004>.
- Mahmoodi, S. *et al.* (2018), “Copper nanoparticles as antibacterial agents”, *J Mol Pharm Org Process Res*, 6, 1-7.
- Naveed Ul Haq, A. *et al.* (2017), “Synthesis approaches of zinc oxide nanoparticles: the dilemma of ecotoxicity”, *Journal of Nanomaterials*, 1-14, <https://doi.org/10.1155/2017/8510342>.
- Oprea, O. *et al.* (2014), “ZnO Applications and Challenges”, *Current Organic Chemistry*, 18, 1-12, <https://doi.org/10.2174/13852728113176660143>.
- Simões, D.N. *et al.* (2017), “Thermoplastic elastomers containing zinc oxide as antimicrobial additive under thermal accelerated ageing”, *Materials Research*, 20, 325-30, <https://doi.org/10.1590/1980-5373-mr-2016-0790>.
- Sirelkhatim, A. *et al.* (2015), “Review on zinc oxide nanoparticles: Antibacterial activity and toxicity mechanism”, *Nano-Micro Lett*, 7, 219-42, <https://doi.org/10.1007/s40820-015-0040-x>.
- Stegarus, D.I. and Lengyel, E. (2017), “The antimicrobial effect of essential oil upon certain nosocomial bacteria”, *International Multidisciplinary Scientific GeoConference Surveying Geology and Mining Ecology Management, SGEM*, 17(61), 1089-1096, <https://doi.org/10.5593/sgem2017/61/S25.142>.
- Threepopnatkul, P. *et al.* (2014), “Effect of TiO<sub>2</sub> and ZnO on thin film properties of PET/PBS blend for food packaging applications”, *Energy Procedia*, 56, 102-11, <https://doi.org/10.1016/j.egypro.2014.07.137>.
- Zhao, S.W. *et al.* (2018), “The preparation and antibacterial activity of cellulose/ZnO composite: a review”, *Open Chem*, 16, 9-20, <https://doi.org/10.1515/chem-2018-0006>.