

# RIGID ANTIMICROBIAL POLIMERIC COMPOSITE WITH PVC MATRIX AND ZnO AND TiO<sub>2</sub> FUNCTIONALIZED NANOPARTICLES

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## RIGID ANTIMICROBIAL POLYMERIC COMPOSITE WITH PVC MATRIX AND ZnO AND TiO<sub>2</sub> FUNCTIONALIZED NANOPARTICLES

**ABSTRACT.** In this paper, rigid antimicrobial polymeric nanocomposites were developed - polymeric material based on chemically functionalized nanoparticles with polydimethylsiloxane (PDMS) – dispersed in a elastomer matrix. By dispersing them in elastomer matrix (polyvinyl chloride - PVC), hybrid TiO<sub>2</sub>/ZnO nanoparticles (50:50) (fillers) functionalized for good compatibility have led to the development of an advanced polymeric material with antibacterial, multifunctional and processing properties specific to plastics. Experimental polymeric materials are adapted to biomedical and food applications, therefore, they were tested for stability and long-term antimicrobial activity. The combined effects of functionalised nanoparticles and polymer on the structure and properties of new experimental materials were studied. Experimental nanocomposites were morpho-structurally, microbiologically and physico-mechanically characterized.

**KEY WORDS:** nanocomposite, antibacterial, functionalized, rigid

## COMPOZIT POLIMERIC RIGID ANTIMICROBIAN ÎN MATRICE DE PVC ȘI NANOPARTICULE DE ZnO ȘI TiO<sub>2</sub> FUNCȚIONALIZATE

**REZUMAT.** În această lucrare s-au realizat nanocompozite polimerice antimicrobiene rigide – material polimeric bazat pe nanoparticule funcționalizate chimic cu polidimetil siloxan (PDMS) – dispersate într-o matrice de elastomer. Prin dispersarea lor în matrice de elastomer (clorură de polivinil - PVC), nanoparticulele hibride TiO<sub>2</sub>/ZnO (50:50) (materiale de umplere) funcționalizate pentru o bună compatibilizare au condus la obținerea unui material polimeric avansat cu caracteristici antibacteriene, multifuncționale și proprietăți de prelucrare specifice materialelor plastice. Materialele polimerice experimentate sunt adaptate aplicațiilor biomedicale și alimentare, prin urmare, au fost testate din punct de vedere al stabilității și activității antimicrobiene pe termen lung. Au fost studiate efectele combinate ale nanoparticulelor funcționalizate și ale polimerului asupra structurii și proprietăților materialelor noi experimentate. Nanocompozitele experimentate au fost caracterizate morfo-structural, microbiologic și fizico-mecanic.

**CUVINTE CHEIE:** nanocompozite, antibacterian, funcționalizat, rigid

## COMPOSITE POLYMÉRIQUE ANTIMICROBIEN RIGIDE EN PVC ET NANOPARTICULES DE ZnO ET TiO<sub>2</sub> FONCTIONNALISÉES

**RÉSUMÉ.** Dans cet article, on a développé des nanocomposites polymères antimicrobiennes rigides – matériau polymérique à base de nanoparticules chimiquement fonctionnalisées avec du polydiméthylsiloxane (PDMS) – dispersés dans une matrice de plastomère. En les dispersant dans une matrice de plastomère (polychlorure de vinyle - PVC), les nanoparticules hybrides de TiO<sub>2</sub>/ZnO (50:50) fonctionnalisées pour une bonne compatibilité ont conduit au développement d'un matériau polymère avancé doté de propriétés antibactériennes, multifonctionnelles et propriétés de traitement spécifiques aux plastiques. Les matériaux polymères expérimentaux sont adaptés aux applications biomédicales et alimentaires. Ils ont donc été testés pour déterminer leur stabilité et leur activité antimicrobienne à long terme. On a étudié les effets combinés de nanoparticules fonctionnalisées et de polymères sur la structure et les propriétés de nouveaux matériaux expérimentaux. Les nanocomposites expérimentaux ont été caractérisés du point de vue morfo-structurel, microbiologique et physico-mécanique.

**MOTS CLÉS:** nanocomposite, antibactérien, fonctionnalisé, rigide

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## INTRODUCTION

At the global level, the trend of obtaining new advanced polymeric structures based on nanopowder reinforced elastomers offers possibilities for obtaining new materials and expanding their range of applications. In the past 5-7 years, fillers with a particle size of 1 to 10 nanometers, referred to as nanostructures, [1] are of particular interest. Nanoparticles have a high specific surface, and their antimicrobial, physical, mechanical, thermal, optical and other properties are superior compared to similar material obtained from structural elements with micron and submicron dimensions. Among the nanoscale filling materials, the most popular are the modified organic clays [2, 3], carbon nanofibres and nanotubes, nano silicon oxide, calcium, and magnesium carbonate, aluminum and titanium nanoparticles, zinc and titanium oxides, graphite, silver, etc. Therefore, new materials can be found in a wide variety of different applications, such as biomedical applications, consumer goods, health, medical or food technology, automotive and transport [4, 5]. Antibiotic resistance of bacteria increased rapidly in recent decades, especially in the hospital setting. Among hospital-acquired infections, medical device-related infections (MDIs) have been recognized as one of the rapidly growing and significant issues, especially for some permanent devices that come in intimate contact with the human body. The bacterial colonization of the medical device not only precedes the infection but can also negatively affect the function of a device [6, 7]. Polymeric materials for medical applications have a long history, leading to the fact that currently more than 50% of all medical devices are made of polymers. The polymers used are mainly polyethylene, polypropylene, polyvinyl chloride, polyester or polycarbonate, which share the fact that most surface and/or volume modifications are necessary to achieve outstanding properties [8-10]. Being one of the largest polymers, polyvinyl chloride (PVC) is widely used and essential in almost all fields. The optimal ratio of properties and costs makes PVC a material capable of competing with both natural materials and other polymers in many

areas of science and engineering. Polyvinyl chloride (PVC) is one of the most used types of polymers (40% of dedicated polymeric materials) for biomedical and food applications. Although much has been done to replace PVC in medical applications, it remains the most used polymer in medical device manufacturing. PVC applications include blood bags and tubes, intravenous containers and components, dialysis equipment, inhalation masks, examination gloves, etc. [11]. PVC-based polymeric materials are subject to continuous research for new modifications and improvements [12, 13].

Polymer composite materials are systems consisting of one or more discontinuous phases dispersed in a continuous phase. Thus, at least two different materials, which are completely immiscible, are mixed to form a composite. Additives such as compatibilizers, plasticizers, pigments, temperature and UV stabilizers, nanoparticles are frequently added to improve certain properties. The type and geometry of the dispersed phase gives the composite optimized properties such as high specific strength, stiffness and hardness, antimicrobial, etc. [14].

There are different types of nanoparticles that can be incorporated into the polymer matrix, depending on their properties and their application. ZnO has found various applications in everyday life such as the rubber and plastics industry, packaging of medicines, cosmetics, medical devices, dentistry and orthopedics, antibacterial coatings, textile industry [15, 16], etc. It is an antibacterial and antifungal agent and is one of 5 zinc compounds currently accepted by the US Food and Drug Administration (21CFR182.8991). Antibacterial activity has been demonstrated on various bacterial strains (*Staphylococcus aureus*, *Staphylococcus epidermidis*, *E. coli*, *Listeria monocytogenes*, *Bacillus subtilis*, *Pseudomonas fluorescens*, *Pseudomonas aeruginosa*, *Salmonella enteritidis*, *Salmonella typhimurium* etc). Particles normally have a higher surface/volume ratio, which provides more efficient antibacterial activity. ZnO nanoparticles even have antibacterial activity against spores resistant to high temperatures and high pressure. The rubber industry is the area where ZnO is used extensively due to its

antibacterial and antifungal activity. TiO<sub>2</sub> is used for countless applications in everyday life, such as building materials, medical devices, dental implants, textile industry, plastics, antibacterial coatings [17, 18]. Having antibacterial, antifungal and antiviral properties similar to ZnO, the medical industry is a field where TiO<sub>2</sub> is used intensively. The use of TiO<sub>2</sub> offers several advantages due to its antibacterial and UV protection. PVC is not compatible with ZnO/TiO<sub>2</sub>. The properties of composite materials depend on the compatibility method. For this purpose, the external surface of the nanoparticles can be modified with different agents, the most common functionalizing agents being organo-functional siloxanes or sodium oleate. Functionalizing agents are used to improve adhesion between the polymer matrix and nanoparticles, protect surfaces from internal stresses that can cause cracks, stabilize the interface layer, improve humidity and increase hydrophobicity. The silanolic groups present on the surface of the nanoparticle will interact with polar groups on the surface of the polymer substrate to form primary bonds. In this way, such a molecule is bifunctional, it contains polar silanolic groups capable of adhering to the surface of the nanoparticles and an R-group designed to interact with the polymeric matrix. Functional ZnO and TiO<sub>2</sub> nanoparticles offer flexibility in adapting superficial chemistry and molecular structure to the polymer/nanoparticle interface [19, 20]. These nanosize molecules form the “molecular bridges” between individually dispersed compounding agents and the continuous phase polymer matrix resulting in a maximized performance of the composite material by optimized interfacial compatibility and bonding.

## EXPERIMENTAL

### Materials and Methods

#### Materials

Materials used to obtain the polymer composites based on plasticized polyvinyl chloride and ZnO/TiO<sub>2</sub> (50:50) nanoparticles are as follows: PC with a 70K-wert value, Diisononyl

phthalate (DINOF) (density 0.984 g/cm<sup>3</sup>, pH 7, 99.5% purity), non-toxic plasticizer, mainly used by the pharmaceutical, food and cosmetics industries, PVC stabilizer - Calcium stearate (Ca content 11%, melting point 127°C), Antioxidant Irganox 1010 (pentaerythritol tetrakis (3-(3,5 di-tert-butyl-4-hydroxy-phenyl)propionate) was produced by BASF Schweiz AG (active ingredient 98%, melting point of 40°C). Functionalizing agent – polydimethylsiloxane-PDMS. ZnO, white powder, with particle size 20 nm, molecular mass – 98,87 g/mol, specific surface area – 23 m<sup>2</sup>/g, density – 4,26 g/ml, and concentration – 99,5% and TiO<sub>2</sub> white powder, with particle size 21 nm, molecular mass – 79,87 g/mol, specific surface area – 23 m<sub>2</sub>/g, density – 4,26 g/ml, and concentration – 99,5%, by Sigma Aldrich.

#### *ZnO and TiO<sub>2</sub> Nanoparticle Surface Modification by Ultrasonication*

The ZnO and TiO<sub>2</sub> (50:50) nanoparticles were functionalized in the laboratory with PDMS using an ultrasonic bath, as follows: 1 g of ZnO and TiO<sub>2</sub> (50:50) powder was introduced into 50 mL centrifuge plastic tubes, 10 mL of isopropanol (role of reaction/dispersion medium) was added. The tubes were placed in a plastic holder and immersed in the ultrasonic bath, thermostated in advance at 40°C. After a period of contact/mixing of the nanoparticles with isopropanol for about 5 minutes, 1 mL of PDMS is introduced into each tube, and allowed to react for 2h. The tubes were covered with caps to avoid alcohol evaporation during the reaction, and to maintain an equal amount of solvent for all powders. After 2 h, the centrifuge tubes were removed from the ultrasonic bath, left to rest at room temperature for about 10-15 min, filtered and washed 3 times with alcohol in abundance to remove the unreacted functionalizing agent. Afterwards it was dried in an oven with warm air at 80°C for about 4-6 hours, followed by grinding. In order to confirm the functionalization, morphological and structural characterization (SEM, EDAX, DSC-TG) was performed.

### Morpho-structural Characterization of ZnO and TiO<sub>2</sub> Nanoparticles with Modified Surface

TG/DSC – To highlight the thermal changes of the ZMO nanoparticles functionalized with PDMS, the new material, was analyzed with Pyris Diamond DSC equipment – Perkin Elmer, calibrated with Indium (99% purity), both

temperature and energy. Figure 1 shows that the sample is stable up to 365°C (losing only 0.35% of the mass). There is only one decomposition stage, between 365-530°C, with an onset at 395.7°C, when a mass loss of 5.51% occurs, accompanied by a slight exothermic effect, with a maximum of 411°C. The residual mass is 93.96%.

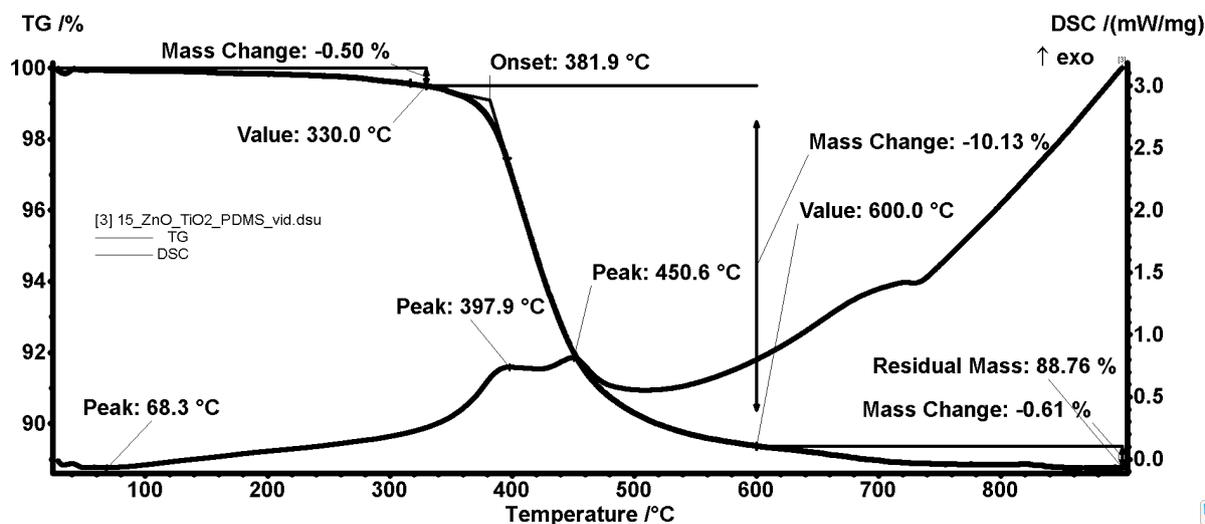


Figure 1. Thermal DSC-TG analysis for ZnO and TiO<sub>2</sub>/PDMS powder obtained by ultrasonication SEM. Simple and functionalized nanoparticles were analyzed by SEM using an ESEM QUANTA 200 instrument operating in a low vacuum equipped with an LFD detector.

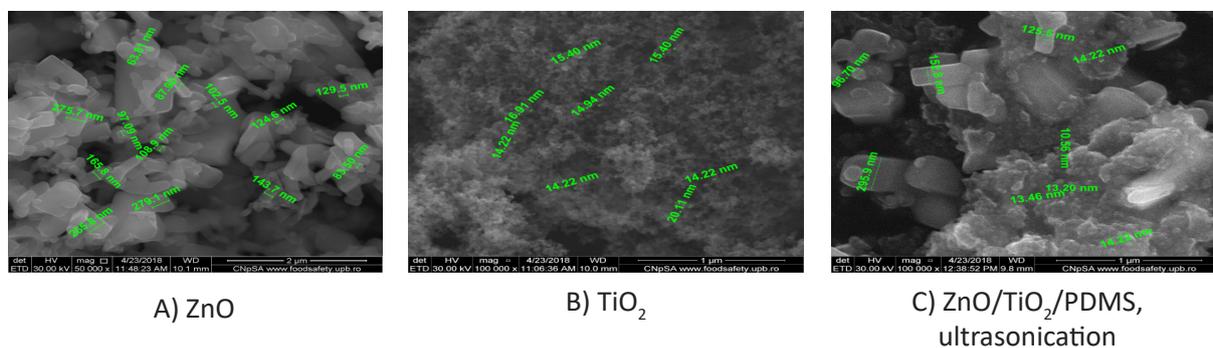


Figure 2. SEM images of simple and functional ZnO and TiO<sub>2</sub> powders

Scanning electron microscopy (SEM) images were recorded on ZnO and TiO<sub>2</sub> particles both simple and modified with PDMS. As it can be seen from Figure A and B, recorded on unmodified ZnO and TiO<sub>2</sub> particles at 50000x magnification, the particle size varies between 63.81 and 279 nm, with an extremely varied shape: acicular, canes, rectangular, etc., and very

well separated between them (monodisperse without agglomeration). In the case of ZnO and TiO<sub>2</sub> particles functionalized with PDMS (Figure C), it is observed that the presence of organosilane does not significantly affect the shape and size of the particles. Moreover, there are clear contours between ZnO and TiO<sub>2</sub> particles. In Figures 3, 4 and 5 are presented EDAX

spectra, recorded on simple ZnO, TiO<sub>2</sub> and ZnO/TiO<sub>2</sub> (50:50) nanoparticles and functionalized with PDMS. For the ZnO and TiO<sub>2</sub> functionalized

with PDMS spectrum the presence of silicon beside Zn, Ti and O is observed. This indicates that the functionalization occurred.

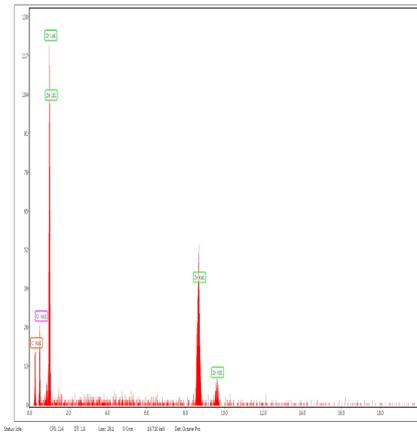


Figure 3. The EDAX spectrum recorded on the ZnO powder

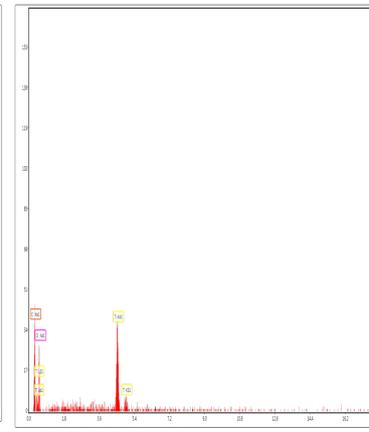


Figure 4. The EDAX spectrum recorded on the TiO<sub>2</sub> powder

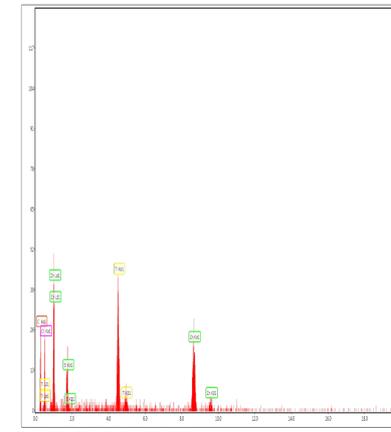


Figure 5. The EDAX spectrum recorded on the ZnO/TiO<sub>2</sub>/PDMS, ultrasonication

The EDAX spectrum in Figure 5 shows the following elements: Zn, Si, TiO<sub>2</sub> and O. It is noted that the relative intensity between the peaks varies significantly, and is the most intense in Zn and Ti. The appearance of an extra peak of Si, compared with Figures 3 and 4, confirms once again the results obtained by SEM and DSC-TG,

namely, demonstrates that the functionalization of the surface of ZnO and TiO<sub>2</sub> nanoparticles was successfully achieved by ultrasonication. The percentage of atomic, and weight content between the three elements (O: Si: Zn) is shown in Table 1.

Table 1: Quantitative analysis of ZnO/TiO<sub>2</sub>/PDMS powder, ultrasonication

Element	Weight content, %	Atomic content, %	Error, %
O K	27.97	56.87	19.49
Zn K	51.47	25.61	14.93
SiK	7.42	8.59	23.59
TiK	13.14	8.93	8.79

*Preparation of Polymer Nanocomposites based on Plasticized Polyvinyl Chloride and ZnO/TiO<sub>2</sub> (50:50)*

PVC, ZnO and TiO<sub>2</sub> functionalized with PDMS, plasticizer – Diisononyl phthalate, calcium stearate, and antioxidant – Irganox 1010 were mechanically mixed in a Brabender

Plasti-Corder PLE-360 at 30-100 rotations/min, for 5 min. at 178°C to melt the plastomer and 2 min. at 170°C for homogenisation. The total processing time was 7 minutes. Table 2 shows tested formulations. Remove the composition from the mixer and press into specimen molds for physico-mechanical characterizations.

Table 2: Polymeric composites based on PVC plasticized with 25% diisononyl phthalate, and 50:50 ZnO and TiO<sub>2</sub> nanoparticles, PDMS functionalized

Compound	B1	B31	B32	B33
PVC	240	240	240	240
ZnO/TiO <sub>2</sub> /PDMS (50:50)	-	2.4	7.2	12
Diisononyl phthalate	60	60	60	60
Calcium stearate	3	3	3	3
Irganox 1010	3	3	3	3
Total	306	308.4	313.2	318

The Brabender mixing diagrams, Figure 6, show the following: chamber temperature increases from 178 to 205°C for the control sample – B1, with a maximum mixing force of 182 N/mm in 48s. When adding nanoparticles, the mixing force decreases (158 N/mm for 1-3% mixture of ZnO and TiO<sub>2</sub> (samples B31 and B32) and 145 N/mm for 7% ZnO and TiO<sub>2</sub> – B33 mixture). The time need to reach maximum

force, increases proportionally to the amount of ZnO and TiO<sub>2</sub> mixture, from 48s –control sample to 52s – B31, 58s – B32, and 63s – B33. The temperature in the chamber decreases, at the maximum force, from 190°C – B1 control sample to 205°C – B31, 210°C – B32 and 221°C – B33. The chamber temperature increases, at the maximum force from 190°C – B1 control sample to 205°C – B31, 210°C – B32 and 221°C – B33.

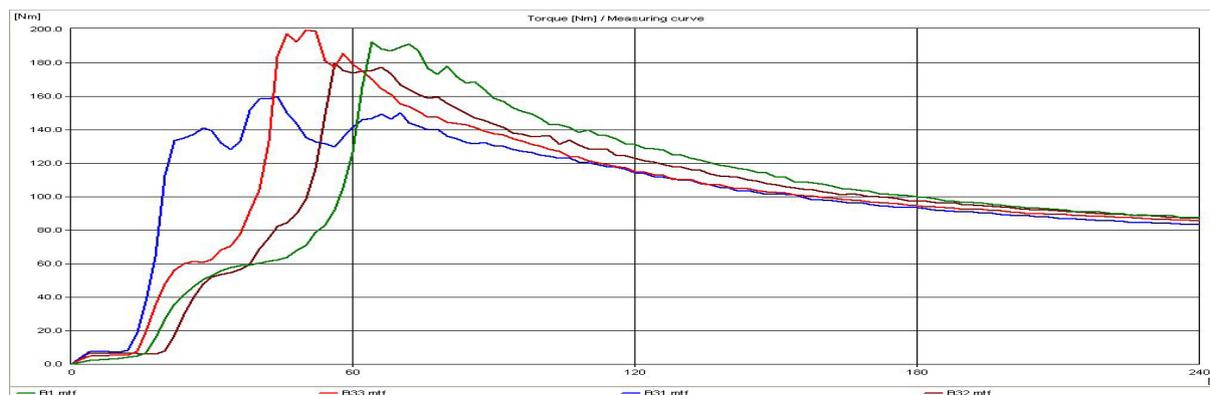


Figure 6. The overlapping Brabender mixing diagrams of control sample and PVC-based polymeric composites plasticized with 25% diisononyl phthalate – DINOF, and 1, 3, 7% ZnO and TiO<sub>2</sub> nanoparticles (50:50)

The compounds were then compression-molded (using an electrically heated laboratory press) to obtain a sheet of about 2 mm thick. Press parameters: preheating 3 min.; pressing 4 min.; cooling 13 min.; pressure 300 kN; temperature 170°C. The sheet was then cooled down to room temperature under the same pressure. The specimens were die-cut from the compression molded sheet and used for testing after 24 hours of storage at room temperature.

#### Testing Methods

Tensile tests of the samples were carried out according to SR ISO 37:2012 using a Schopper Tensile Testing machine 1445, at a constant crosshead speed of 500 ± 5 mm/min.

Hardness of the samples was measured by Shore “A” Durometer according to SR ISO 7619-1:2011.

Abrasion resistance was carried out according to ISO 4649/2010, the cylinder method,

using a pressure of 10 N. Abrasion resistance was expressed by relative volume loss in relation to calibrated abrasive paper. A wearing tester with abrasive cloth having granulation of 212–80 mm (PE 80). The samples used were obtained from rolled blends and pressed into sheets, then cutting with a rotating die and have cylindrical shape, with a diameter of 16 mm and height of min. 6 mm.

Melt flow index was determined at 180°C and a pressure force of 5 kg, with Melt Flow Index – Haake equipment.

FT-IR spectroscopy was done using the FT-IR 4200 JASCO, Herschel series instrument, equipped with ATR having diamond crystal and sapphire head within the spectrometric range 2000-530 cm<sup>-1</sup>.

The method for control of antibacterial activity is in accordance with SR EN ISO 20645/2005-Textiles materials.

## RESULTS AND DISCUSSIONS

The polymer structures obtained, in initial state and after accelerated ageing were characterized in terms of their physical-mechanical properties, and results are presented in Table 3. Analyzing the values of physical-mechanical tests reveals the following:

### Hardness

In the initial state of the control sample, B1, is 61°Sh D, when adding nanoparticles, it grows with a unit, up to 62°Sh D. This is demonstrated by the fact that the hardness increases with the amount of filler. The amount used in the mixture, being very small (max. 7%) the increase is small. At the same time, the degree of plasticization being small, the samples show a high degree of stiffness. The type of plasticizer influences very little the degree of hardness.

Table 3: Normal physico-mechanical characterization for PVC-based polymeric composites plasticized with 25% diisononyl phthalate – DINO, and 50:50 nano ZnO and TiO<sub>2</sub> mixture functionalized with PDMS

Samples	B1	B31	B32	B33
Initial State				
Hardness °Sh D, SR ISO 7619-1:2011	61	62	62	62
Elasticity %, ISO 4662:2009	16	16	16	16
Tensile strength, N/mm <sup>2</sup> , SR ISO 37:2012	23.0	24.1	24.8	25.2
Elongation at break, %, SR ISO 37:2012	260	260	300	340
Residual elongation, %, SR ISO 37:2012	84	110	116	110
Tear strength, N/mm, SR EN 12771:2003	160	142	147	149
Density, g/cm <sup>3</sup> , SR ISO 2781:2010	1.3	1.3	1.3	1.3
Abrasion resistance, mm <sup>3</sup> , SR ISO 4649/2010	97	96	99	100

### Tensile Strength

The tensile strength is in the 23-25.2 N/mm<sup>2</sup> range, in the initial state. It is worth noting the high values of this parameter, which are not found in plastics mixtures with hardness values of 60-70°Sh D.

### Elasticity

High elasticity values (16%) are observed for high values of hardness, a characteristic feature of these materials not influenced by the addition of mixed nanoparticles.

### Tear Strength

The tear strength decreases by several units proportional to the amount of nanoparticles introduced in the composite from 160 N/mm to 142 N/mm for the composite with 7% ZnO/TiO<sub>2</sub> nanoparticle.

### Abrasion Resistance

The values of abrasion resistance increase slightly from 97 mm<sup>3</sup> for the control sample up to 100 mm<sup>3</sup> for the sample with the largest quantity of nanoparticles, respectively 7%. The

values fall within the requirements imposed by the standards.

### Density

Density values do not change when the nanoparticles are added to the mixture.

### FT-IT Spectroscopy

IR spectrum represent the radiant energy absorption curve in the IR domain by the sample molecule, depending on the wave length or radiation frequency. The infrared domain of the electromagnetic radiation is between 0.8 and 200 μm. IR domain for usual organic chemistry is between 2.5 and 25 μm. The structural determinations were carried out on an IR molecular absorption spectrometer with double beam, in the range of 4000-600 cm<sup>-1</sup>, using 4200 FT-IR equipped with ATR diamond crystal and sapphire head. The solid state samples were set in the ATR and the equipment recorded the transmittance spectra of the sample and then compared it with the background spectra previously recorded. The recorded spectra of the samples were compared with the pure elastomer spectrum.

After the tests were carried out, the following were found:

Figure 7 shows the FTIR spectra recorded on the single PVC powder and shows numerous characteristic bands associated with this type of polymer. The bands of 2962, 2912, 2846  $\text{cm}^{-1}$  can be attributed to the elongation vibration of asymmetric  $\text{CH}_3$  groups, asymmetric  $\text{CH}_2$  and respectively symmetric  $\text{CH}_3$  groups of PVC. The band at 1427  $\text{cm}^{-1}$  is attributed to the planar deformation vibration of the  $\text{CH}_2\text{-Cl}$  bond, the

band at 1326  $\text{cm}^{-1}$  is attributed to outside the plane (balance) deformation bonds of the  $\text{-CH}_2$  groups. The band at 1245  $\text{cm}^{-1}$  is attributed to deformations outside the plan (balance) of  $\text{Cl-CH}$  bonds, the 960  $\text{cm}^{-1}$  band is attributed to outside the plane deformation of  $\text{C-Cl}$  bonds, and those of  $\sim 844$ , 678, and 613  $\text{cm}^{-1}$  can be attributed to  $\text{C-Cl}$  stretch groups. The band at 1091  $\text{cm}^{-1}$  is attributed to stretching bond of the  $\text{C-C}$  group of PVC.

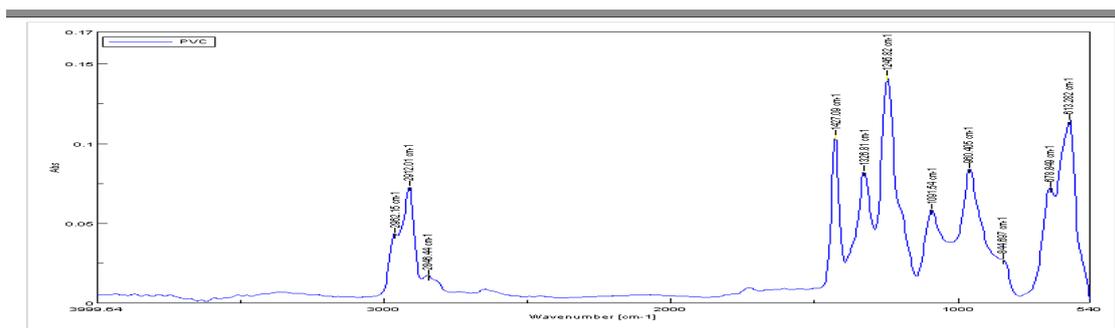


Figure 7. FTIR spectrum of pure PVC powder

The spectra obtained on the plasticized PVC mixture with 25% diisononyl phthalate (B1), composites based on DINF plasticized PVC reinforced with varying amounts (1, 3, and 7%) of nanoparticles mix ( $\text{ZnO/TiO}_2$  50:50) functionalized with PDMS (Figure 8), it can be observed that the type of nanoparticle used does not induce significant change in the structure of the spectra, probably because they are deeply embedded in the polymer matrix – PVC, and therefore cannot be identified neither on the basis of the characteristic bands derived from the nanoparticle structure nor on the basis of the functional bonds existing in the organosilane

structure. Compared to the spectrum recorded on the PVC powder, we can observe the presence of functional groups derived from the plasticizer structure, namely the carbonyl group (from about 1720 to 1121  $\text{cm}^{-1}$  for the mixture B1), and those from 1724 and 1126  $\text{cm}^{-1}$  for blends containing  $\text{ZnO/TiO}_2$  nanoparticle mixture. The presence of carbonyl functional groups shows that plasticization of PVC has been optimally achieved. Also, the bandwidth characteristic of methylene groups increases as the percentage of PDMS functionalised nanoparticles increases.

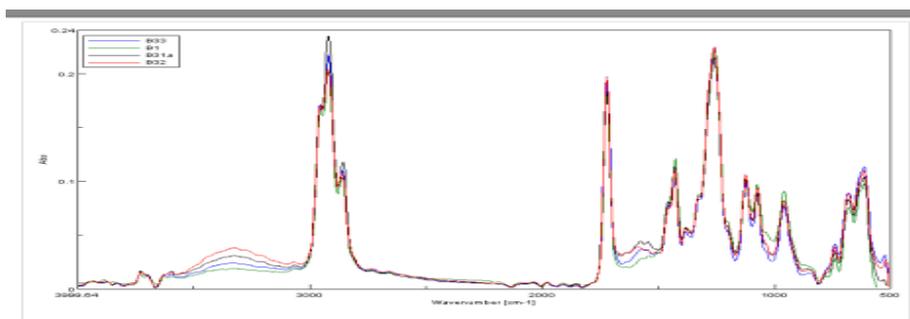


Figure 8. The FTIR spectra of composites B1 (PVC + plasticizer DINF), B31 (PVC + DINF + 1%  $\text{ZnO/TiO}_2$ /PDMS), B32 (PVC and DINF + 3%  $\text{ZnO/TiO}_2$ /PDMS), B33 (PVC and DINF + 7%  $\text{ZnO/TiO}_2$ /PDMS)

### Control of Antibacterial Activity

Test of diffusion on the gelose plate. The result is considered to have a “satisfactory effect” unless bacterial propagation is observed. The analyzed samples do not allow the development of aerobic germs for the tested bacteria (*Staphylococcus aureus*), the major inhibitory effect being presented by the samples with ZnO:TiO<sub>2</sub> – 50:50 nanoparticle mixture.

### Method

- subculturing of the bacteria used in the test: *Staphylococcus aureus*. The culture used was pure, freshly subcultured;
- dry sterilization of the laboratory glassware in the oven at 180°C;
- preparation of the culture medium, characteristic of the test bacteria used, namely: Mannitol Salt Agar for the genus *Staphylococcus aureus*; wet sterilization, autoclave and Erlenmayer glass with culture media;

- the test specimens were collected from the 2 mm thick elastomer plates and 2 cm squares, were cut into squares.

### The Test

The amount of gelose for the lower layer without bacteria is prepared. An amount of (10 ± 0,1) ml is added to each sterilized Petri dish and the gelose is allowed to solidify. The amount of gel is prepared for the upper layer and cooled to 45°C in a water bath. 150 ml of gelose is inoculated with 1 ml of bacterial working solution (1-5 × 10<sup>8</sup> ufc/ml). The container is vigorously stirred for the uniform distribution of bacteria. An amount of (5 ± 0,1) ml is introduced into each Petri dish and the gelose is allowed to solidify. The specimens are placed on the surface of the nutrient medium and then incubated at 37°C between 24h and 48h.

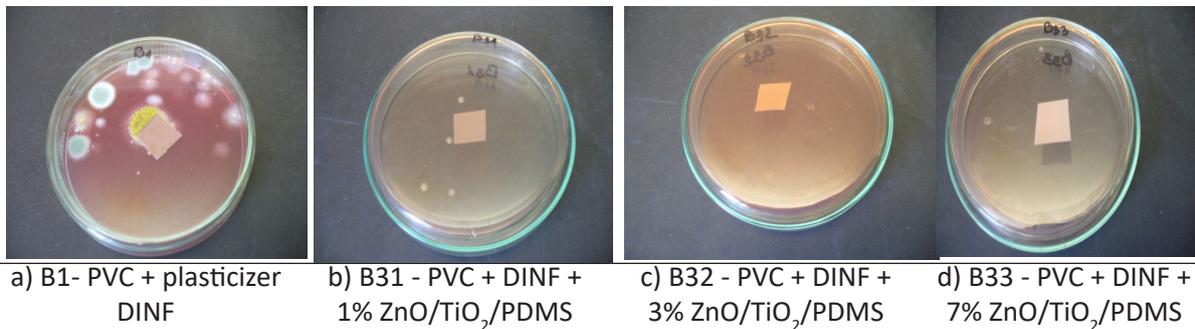


Figure 9. Effect of antibacterial treatment

The result is considered to have a “satisfactory effect” if no bacterial proliferation is noticed. Nanocomposite samples based on PVC did not allow development of aerobic germs for the tested bacterium (*Staphylococcus aureus*), exhibiting a major inhibition effect visible in samples with 50:50 ZnO:TiO<sub>2</sub> nanoparticle mixture, both around the sample and in its vicinity; the most intense effect was found in the sample with 7% ZnO/TiO<sub>2</sub> mixture – B33 (Figure 9, d), while no effect was found in the control sample – B1 (Figure 9, a).

### CONCLUSIONS

The paper presents the study of the new nanostructured polymer composites based on chemically functionalized nanoparticles

dispersed in the elastomer matrix. Hybrid ZnO/TiO<sub>2</sub> (50:50) nanoparticles (filler) dispersed in PVC matrix resulted lead to a high performance polymeric material with multi-functional antibacterial, and polymorphic processing properties. The materials are adapted for biomedical and food applications and have been tested in terms of physico-mechanical properties, spectrometry and antibacterial activity. Prototypes of biomedical applications will be obtained from nanocomposites, and will be microbiologically tested for a further examination.

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1 – Development of the national RD system, Subprogram 1.2 - Institutional Performance - RDI excellence funding projects, Contract no. 6PFE/2018, Acronym: PERFORM-TEX-PEL, and PN 18 23 01 01 project: “Antibacterial polymeric nanoparticles with thermoplastic matrix and TiO<sub>2</sub>/ZnO hybrid nanoparticles for medical and food use”.

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