

## ANTIBACTERIAL POLYMERIC NANOCOMPOSITES WITH MATRIX OF PET AND TiO<sub>2</sub> FUNCTIONALIZED NANOPARTICLES WITH APPLICATION IN MEDICAL AND FOOD INDUSTRY

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Thermoplastic polyesters represent an important class of polymers used in a variety of products and applications, one of which is poly (ethylene terephthalate) (PET). Currently, PET is the most cost-effective polyester. PET can be processed in a variety of domestic and industrial shapes and products by melt processing techniques such as spinning, extrusion, injection, blowing, thermoforming. Polymer composite materials are systems consisting of one or more discontinuous phases dispersed in a continuous phase. In this paper, elastomeric nanocompound materials were selected, due to performance properties such as: antimicrobial, resistance to aggressive chemical agents, mechanical properties, especially hardness which, depending on the degree of plastification, can present values from very low to high 30 -100°Sh D, thermal, impermeability, resilience, low density, elasticity, thermostability, processability, impact resistance etc. The new compounds produced by a simple and efficient technology for obtaining polyethylene terephthalate (PET) composite, TiO<sub>2</sub> functionalized nanoparticles, provide flexibility in adapting superficial chemistry and molecular structure to the polymer / nanoparticle interface. These nanomorphous 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 interface compatibility and bonding.

Keywords: nanocomposites; functionalized nanoparticles; antibacterial.

### INTRODUCTION

Thermoplastic polyesters represent an important class of polymers used in a variety of products and applications, one of which is poly (ethylene terephthalate) (PET). Currently, PET is the most cost-effective polyester and used of about 95 % of the total consumption worldwide, the approximately 25 million tons per year (Fakirov, 2002; Johnson, 2005; Bartolome, 2012). PET has applications in various fields: fiber for clothing, bottles and jars for packaging, the textile component in the tires, safety belts, bags, technical, including non-woven textile, audio/video tapes, medical objects, etc. One of the main reasons for the widespread use of PET is the possibility of obtaining in a single polymerization plant several types of products with a different degree of polymerization. PET can be processed in a variety of domestic and industrial forms and products by melt processing techniques such as filler, extrusion, injection, blowing, thermoforming (Chand, 2008; Tsai, 2013). The polyethylene terephthalate (PET) was used more than 50 years in medical and food devices. Current PET applications include implanted sutures, surgical meshes, vascular grafts, sleeves for heart valves, and percutaneous components for access devices, bottles, food packaging boxes, disposable glasses, and so on. The notable characteristics of PET are bioscience, promoting tissue ingestion, a well-characterized biotic response, and a long history of human implantation (Tayel, 2011; Mekonnen, 2013).

Polymeric composite materials are systems that consist of one or several discontinued phases, dispersed in a continuous phase. Thus, at least two different materials, which are completely immiscible, are mixed to form a composite. Additionally, additives such as compatibilizers, plasticizers, pigments, temperature

stabilizers and UV radiation, nanoparticles are additionally added to improve certain properties. The type and geometry of the discontinuous phase of the composite gives enhanced properties, such as high specific strength, stiffness and hardness, antimicrobial, etc. (Deng, 2012).

There are different types of nanoparticles which may be incorporated in the polymeric matrix, selected according to their properties and their application. ZnO found various applications in everyday life, such as the rubber and plastic industry, medical packaging, cosmetics, medical devices (Saehana *et al.*, 2013), dentistry, and orthopedics, antibacterial coating (Arenas *et al.*, 2013), the textile industry (Bazant *et al.*, 2014; Alexandrescu *et al.*, 2017), etc. Antibacterial activity has been proven on various bacterial strains (*Staphylococcus aureus*, *Staphylococcus epidermidis*, *E. coli*, *Listeria monocytogenes*, *Bacillus subtilis*, *Pseudomonas fluorescens*, *Pseudomonas aeruginosa*, *Salmonella enteritidis*, *Salmonella typhimurium* etc.) (Stegarus and Lengyel, 2017). The particles normally have a higher surface / volume ratio, which ensures more efficient antibacterial activity. Its role is particularly important in terms of antimicrobial and UV protection. The properties of composite materials depend on the compatibility method. For this purpose, the external surface of the nanoparticles can be functionalized with different agents, the most common functionalizing agents being organo-functional siloxanes or sodium oleate. Functioning agents are used to improve adhesion between the polymer matrix and nanoparticles, protect surfaces against internal stresses that can cause cracks, stabilize the interface layer, improve wetting and increase hydrophobicity.

## EXPERIMENTAL

### Materials

All composites contain the same components: polyethylene terephthalate recycled Green Tech company in Buzau, with the following characteristics: Melt Flow Index (260°C/10 kg), and 44,4 g/10 min; melt temperature-Vicat, 201°C and density-1,33 g/cm<sup>3</sup> and EPDM - Ethylene-Propylene Diene-Monomer, was purchased from Du Pont - NORDEL IP-3745 P, with the following characteristics: ethylene content - 70%, polypropylene content -30% and density-0,88 g/cm<sup>3</sup>. Other components: TiO<sub>2</sub>, white powder, with particle size of 21 Nm, molecular mass - 79,87 g/mol, the specific area 23 m<sup>2</sup>/g, density - 4.26 g/ml and concentration - 99.5%, functionalized with PDMS, polydimethylsiloxane, produced by Sigma-Aldrich, plasticizer - dipropyl heptyl phthalate produced by Bayer, stabilizer - calcium stearate, antioxidant - Irganox 1010, the last two components from the company Ciba Geigy.

### Method

PET, TiO<sub>2</sub> functionalized with PDMS, plasticizer - dipropyl heptyl phthalate, calcium stearate, EPDM and antioxidant -Irganox 1010 were mechanically mixed in a Brabender Plasti-Corder PLE-360 at 30-100 rotations/min, for 3 min. at 230°C to melt the plastomer, mixed for 5 min. at 248°C and 2 min. at 210°C for homogenisation. The total processing time was 10 minutes. Table 1 shows tested formulations. Continue mixing at a speed of 100-110 revolutions per minute and 248°C for 3 minutes until the ingredients are embedded and the mixture is uniform. Remove the composition from the

mixer and press into specimen molds for physico-mechanical, chemical and microbiological characterizations.

Table 1. Polymeric composites based on PET, plasticized 10% with dipropyl heptyl phthalate and TiO<sub>2</sub> nanoparticles functionalized with PDMS

Compound	E1	E21	E22	E23
PET	285	285	285	285
TiO <sub>2</sub> /PDMS	-	3	9	21
Dipropyl heptyl phthalate	10	10	10	10
Calcium stearate	3	3	3	3
EPDM	15	15	15	15
Irganox 1010	3	3	3	3

The Brabender mixing diagrams, figures 1 and 2, show that the mixing chamber temperature increases by only 3°C from 248 to 251°C for control sample E1, with a maximum torque of 56 N / mm at 190s. When adding nanoparticles, both the mixing force increases (65 N/mm-E21, and 90N/mm-E23) and the time it takes to reach maximum change. Decreasing proportionally with the amount of TiO<sub>2</sub> added in the mixture, from 180s to 170 s (E21 and E22), higher than the control and 260s-E23.

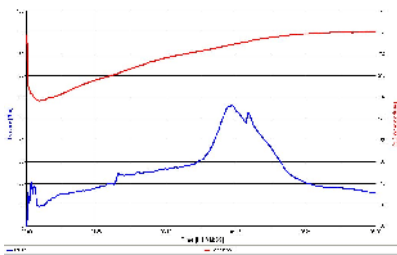


Figure 1. Brabender mixing diagram for control sample E1 polymeric composite based on PET plastified with 10% dipropyl heptyl phthalate –DPHP

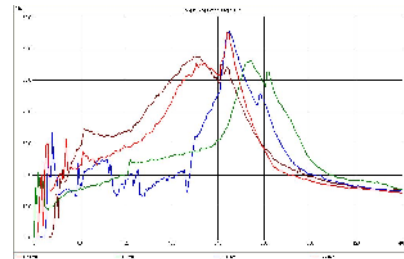


Figure 2. Brabender mixing diagram for polymeric composite based on PET plastified with 10% dipropyl heptyl phthalate –DPHP and 1, 3, and 7 % TiO<sub>2</sub> nanoparticles

### Testing Methods

Tensile strength 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 “D” Durometer according to SR ISO 7619-1:2011.

Melt flow index. Samples were tested using a Melt Flow Index device – Haake that displays values for the melt volume rate (MVR – cm<sup>3</sup>/10min) as well as melt flow rate (MFR- g/10min). Working temperature (chamber temperature up to 350°C), 2 heating areas, operating according to ISO 1133 standard.

Shock resistance tests were conducted using an INSTRON equipment with pendulum hammer, which can carry out Izod or Charpy tests with a wide range of testing capacity (0.7-27.847 J), according to STAS 7310-87.

FT-IT 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>.

## RESULTS AND DISCUSSION

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 2. Analyzing the values of physical-mechanical tests reveals the following:

Hardness of the control sample is 82°Sh D, when the nanoparticles are added, it increases by several units up to 85°Sh D. This is demonstrated by the fact that the hardness increases with the amount of filler in the mixture.

Table 2. Physico-mechanical characteristics for polymeric composites based on PET, plasticized 10% with dipropyl heptyl phthalate and TiO<sub>2</sub> nanoparticles functionalized with PDMS

Mixtures	E1	E21	E22	E23
Normal				
Hardness 0Sh D	82	83	83	85
SR ISO 7619-1:2011				
Tensile strength, N/mm <sup>2</sup>	6,6	7,4	8,7	9,0
SR ISO 37:2012				
Density, g/cm <sup>3</sup>	1,02	1,02	1,02	1,02
SR ISO 2781:2010				
Izod shock resistance, [KJ/m <sup>2</sup> ]	1,46	1,70	1,82	2,02
STAS 7310-87				
Melt flow index - 230°C, 5 Kg, g/10min	27,2	26,7	26,4	25,8
Elongation at break, %	1,47	1,60	1,69	1,78
SR ISO 37:2012				

Tensile strength ranges from 6.6 to 9.0 N/mm<sup>2</sup>, higher values show PET/TiO<sub>2</sub> composites and increase proportionally with the amount of nanoscale filler.

Elongation at break shows high values compared to rigid materials, and increases proportionally with the amount of nanoparticles introduced into the composite. Similar to tensile strength, higher values show for TiO<sub>2</sub> nanoparticle composites.

To estimate the fragility of polymeric nanocomposite, they were tested by the Izod Impact Resistance Method (SR EN 179-2: 2010). The values are small, the control is at the limit of fragility, and by the addition of functionalised nanoparticles, increases with approx. 3-5%.

In order to establish technological parameters for the processing composites in finished products, tests were carried out for melt flow index at 245°C and a force of 10 kg. The values of the flow indices are small and close to the control sample, with a decrease of approx. 3% and are in the range: 27.2-control sample and 23.7-26.7. Values decrease when adding ZnO and TiO<sub>2</sub> nanofillers into composites.

FT-IT spectroscopy. IR spectrum represents 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  $\mu\text{m}$ . IR domain for usual organic chemistry is between 2.5 and 25  $\mu\text{m}$ . The structural determinations were carried out on an IR molecular absorption spectrometer with double beam, in the range of 4000-600  $\text{cm}^{-1}$ , 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:

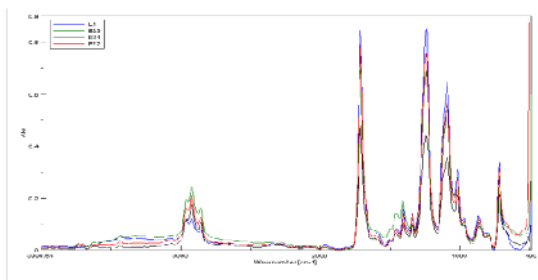


Figure 3. Composites based on PET / EPDM / DPHF and / or reinforced with 1, 3 and 7%  $\text{TiO}_2$ /PDMS nanoparticles

If analyzing blends based on polyethylene terephthalate (PET) / 5% ethylene propylene diene terpolymer (EPDM) plasticized with 10% dipropyl heptyl phthalate reinforced with 1, 3 and 7% of  $\text{TiO}_2$  nanoparticles surface functionalized with PDMS (Figure 3), can be identified, both PET functional groups and EPDMs at different wavelengths.

Thus, the main characteristic bands assigned to PET are: the carbonyl group  $\text{C} = \text{O}$  (derived from the terephthalic acid ester) at 1712  $\text{cm}^{-1}$ , the asymmetric  $\text{C}-\text{C}-\text{O}$  group at 1241  $\text{cm}^{-1}$  and the stretch at 1091  $\text{cm}^{-1}$ ,  $\text{C}-\text{H}$  vibration bond (pendulum) from the aromatic structure to 721  $\text{cm}^{-1}$ . The presence of the EPDM can be identified based on the presence of the two intense peaks occurring at approximately 2920 and 2851  $\text{cm}^{-1}$  and are assigned to the stretching vibrations of asymmetric and symmetric  $\text{CH}_3$  groups.

Numerous other peaks can be identified at 721  $\text{cm}^{-1}$ , the deformation vibration pattern of the  $\text{CH}_2$  (rotation), 1343  $\text{cm}^{-1}$  - characteristic for the deformation vibration of the  $\text{CH}_2$  bond outside the plane (pendulum) and the 1463  $\text{cm}^{-1}$  deformation vibration of the of the  $\text{CH}_3$ (shear) bond. The vinyl  $-\text{C} = \text{C}$  group derived from the EPDM structure can be observed around 988  $\text{cm}^{-1}$ , and the one assigned to the  $\text{RR}'\text{C}-\text{CH}_2$  group can be identified at about 865  $\text{cm}^{-1}$ .

As can be seen from Figure 3, if the mixture consists of PET / EPDM / plasticizer (E1) or PET / EPDM / plasticizer / 1%  $\text{TiO}_2$ -PDMS (E21) the carbonyl group-specific bands are very intense and are not affected by their presence. In contrast, when higher than 3 and 7% of  $\text{TiO}_2$  / PDMS nanoparticles are used, the intensity of the carbonyl group decreases considerably, probably due to the fact that these carbonyl groups come from the plasticizer and during the processing of the mixture under the influence of temperature and screws speed this is adsorbed into the nanoparticle structure.

Also, a decrease in the intensity of the asymmetric C-C-O group from PET at 1241 cm<sup>-1</sup> is observed, as the ZnO / PDMS nanoparticles amount increase, probably due to specific interactions that occur between the components in the mixture.

## CONCLUSION

The paper presents the study of the new nanostructured polymer composites based on chemically functionalized nanoparticles dispersed in the elastomer matrix. Hybrid TiO<sub>2</sub> nanoparticles (filler) dispersed in PET 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 subjected to physico-mechanical and spectrometric tests. Prototypes of biomedical applications will be obtain from nanocomposites, and will be microbiological tested for a further examination.

## Acknowledgements

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