POLYMER NANOCOMPOSITE BASED ON SILICONE RUBBER REINFORCED WITH NANOPARTICLES PROCESSED BY VULCANIZATION

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The aim of this work was to obtain polymer nanocomposites based on silicone rubber reinforced with ZnO and TiO₂ nanoparticles. The technology of making polymer nanocomposites reinforced with nanoparticles is vulcanization (in strict compliance with the order of introduction of ingredients). Embedding the ZnO and TiO₂ nanoparticles in the polymer composite mixture helps to increase the physical-mechanical and chemical properties of the nanocomposite. The obtained polymer nanocomposites were tested in terms of physical-mechanical properties (normal state and accelerated aging), chemically by immersion in environments such as ethyl alcohol (70%), distilled water and cooking oil, and biologically, according to standards in force.

Keywords: polymer nanocomposite, silicone rubber, ZnO and TiO$_2$, nanoparticles

1. Introduction

There is an emerging trend to develop new composites reinforced with nanoparticles, based on silicone elastomer (silicone rubber), with antimicrobial properties determined by the chemical nature and structure of the matrix and disperse phase, by the processing and vulcanization conditions, using highly innovative technologies and resulting in competitive products, leading to the

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development of new products for the food, pharmaceutical and medical industries [1].

Silicone elastomer is preponderantly used in the development of products for the food, medical and pharmaceutical industries due to its resistance to high temperatures (from -100°C to +315°C), specific to the sterilization operation [2-4]. Vulcanization of elastomers is a main operation stage with a major impact on the final properties of the products [5]. The amount and type of vulcanization agent, time, temperature and vulcanization pressure are important factors controlling the crosslinking degree and the properties of the final product. The vulcanization system and the amounts of vulcanization agents required are selected depending on the elastomer used and the envisaged characteristics [6,7]. The applications of vulcanized silicone rubber are vast, but the preferred areas are the medical, food and pharmaceutical industries, because, compared to rubber blends based on other elastomers, the former are free of restricted toxic substances [8- 13].

Qualitative performance and superior physical-mechanical properties, required by standards in force, particularly in terms of elasticity, resistance to aggressive chemicals, thermal stability and antimicrobial, antibacterial and antifungal protection, can be achieved by determining the optimal amount of nanometric reinforcing agent (for antimicrobial, antibacterial and antifungal protection purposes), of filler and ingredients in the structure of silicone rubber-based compounds used in the food, medical and pharmaceutical industries and by establishing optimal processing conditions [15-17]. This paper, therefore, deals with the development of a new elastomeric nanocomposite processed by vulcanization based on silicone rubber, plasticizer (stearin), nanometric reinforcing agents (ZnO and TiO_2 – for antimicrobial, antifungal, antibacterial protection purposes), filler (chalk) and crosslinking agent (dicumyl peroxide) [18, 19].

The resulting polymer nanocomposites were physico-mechanically and chemically tested by immersion in specific working environments and also biologically characterized.

2. Materials properties and Methods

The following materials were used:

(1) silicon rubber, Elastosil R701/70-OH: polydimethylsiloxane with vinyl groups, dynamic viscosity over 9.000.000 mPa*s, in the form of paste, density – 1.32 g/cm^2, colour – opaque;

(2) stearin, (white flakes, moisture - 0.5% max, ash – 0.025 % max);

(3) zinc oxide microparticles (ZnO – precipitate 93-95%, in the form of white powder, density – 5.5 g/cm, specific surface – 45-55 m^2/g);

(4) zinc oxide nanoparticles (ZnO – in the form of white powder, 99.99 % trace metals basis);

(5) titanium dioxide nanoparticles (TiO_2 – white nanopowder, assay $\geq$ 99.5 % trace metals basis);

(6) chalk ($CaCO_3$ precipitate – white powder, molecular weight 100.09);

(7) di(tert-butylperoxyisopropyl) benzene, powder 40% with calcium carbonate and silica (PD) - Perkadox 14-40B (1.65 g/cm^3 density, 3.8% active oxygen content, pH 7, assay: 39.0-41.0%).

Polymeric nanocomposites based on silicone rubber reinforced and crosslinked with PD were made by mixing on a laboratory-scale electric roll mill with temperature adjustment, mixing capacity of about 1 kg, strictly following the order of introduction of ingredients (Table 1). The resulting formulations were then rheologically tested using the Monsanto rheometer and finally processed into plates by moulding using the electrical press, according to the optimal technological processing parameters determined upon rheological testing. Pressing parameters are as follows: pressing temperature 170°C, for 2 minutes at 300 kN pressure and cooling for 2 minutes. After conditioning for 24 hours at room temperature, specimens were cut out from the plates and tested physico-mechanically: normal state (at room temperature) and accelerated ageing at 70°C for 168 hours) – Fig. 1.

Table 1

Polymer nanocomposite compositions based on silicone rubber

Sample code							
Material	UM	CS_1	CS_2	CSZ_1	CSZ_2	CSZ_3	CSZT
Silicone rubber: Elastosil R701/70-OH	g	100	100	100	100	100	100
Stearin – flakes	g	5	5	5	5	5	5
ZnO – active (powder)	g	4	4	3	2	1	1
ZnO – nanoparticles (powder)	g	-	-	1	2	3	3
TiO_2 – nanoparticles (powder)	g	-	-	-	-	-	1
Chalk – $CaCO_3$ (powder)	g	10	10	10	10	10	10
PD(dicumyl peroxide – 40% - on silica and Ca CO_3 - powder substrate)	g	7.5	15	7.5	7.5	7.5	7.5

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┌─────────────────────────┐
│ Analysis and reception  │
│ of raw materials        │
└─────────────────────────┘
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│ Dosing raw materials    │
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│ Execution of            │
│ nanocomposite on        │
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      │ Rheological testing of  │
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                  │ nanocomposite               │
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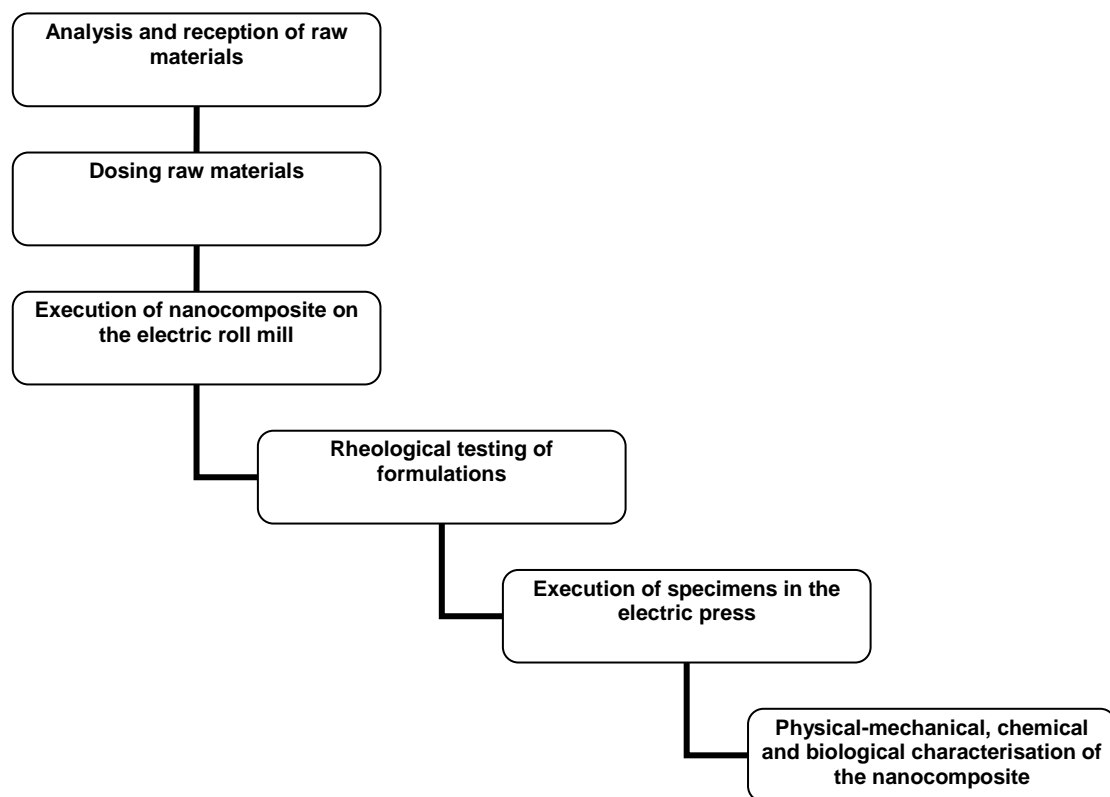
Fig. 1. Technological process for obtaining polymeric nanocomposites based on silicone rubber

Rheological analysis shows that the variation of the dicumyl peroxide concentration does not influence the vulcanization degree, as the samples are almost identical (Fig. 2).
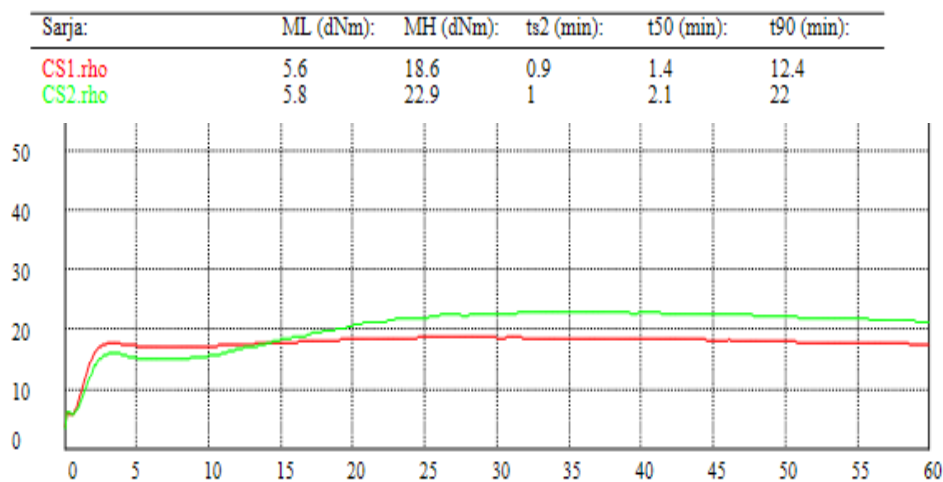
Sarja:	ML (dNm):	MH (dNm):	ts2 (min):	t50 (min):	t90 (min):
CS1.rho	5.6	18.6	0.9	1.4	12.4
CS2.rho	5.8	22.9	1	2.1	22

Fig. 2. Rheological analysis of control samples – CS_1 and CS_2

Rheological analysis of nanocomposites shows that the addition of ZnO and TiO$_2$ nanoparticles does not influence the vulcanization degree, as the samples are almost identical among themselves, compared to the control sample (Figs. 2 and 3).
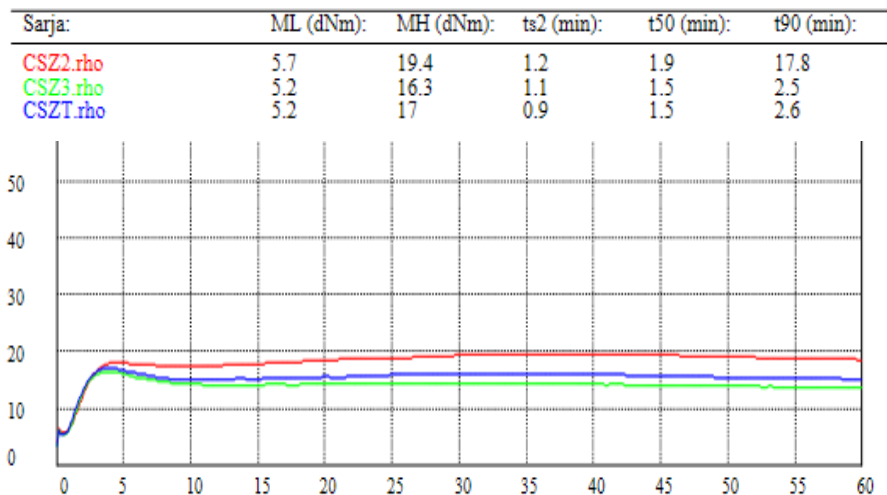

Sarja:	ML (dNm):	MH (dNm):	ts2 (min):	t50 (min):	t90 (min):
CSZ2.rho	5.7	19.4	1.2	1.9	17.8
CSZ3.rho	5.2	16.3	1.1	1.5	2.5
CSZT.rho	5.2	17	0.9	1.5	2.6

Fig. 3. Rheological analysis of samples – CSZ$_2$, CSZ$_3$ and CSZT

Polymer nanocomposites based on silicone with the composition presented in Table 1 were physico-mechanically tested (after stabilization for 24 hours at room temperature) according to standards in force (normal state and accelerated ageing at 70°C and 168 hours): hardness ^{0}ShA- SR ISO 7619:2011; elasticity - ISO 4662:2009; elongation at break -100%, residual elongation - 100%, tear strength - N/mm -SR ISO 37-2012; tensile strength, N/mm^2 - SR ISO 37-1997.

3. Results and Discussion

3.1. Physical-Mechanical Tests

Table 2 presents results of physical-mechanical tests in natural state and after thermal processing - accelerated ageing at 70^{0}C for 168 h of polymeric nanocomposites based on silicone rubber, plasticizer – stearin, reinforced with nanoparticles - ZnO and TiO$_2$, filler – chalk and crosslinked with PD – 40% - on silica and CaCO$_3$ substrate.

Table 2

Physical-mechanical characterization of nanocomposites based on silicone rubber reinforced with ZnO and TiO$_2$ nanoparticles

Material	CS$_1$	CS$_2$	CSZ$_1$	CSZ$_2$	CSZ$_3$	CSZT
Physical-mechanical characterization: normal state						
Hardness, ^{0}Sh A	65	64	63	65	65	66
Elasticity, %	12	14	12	12	12	12

Tensile strength, N /mm^2	3.4	3.8	3.4	3.8	3.8	3.8
Elongation at break, %	467	533	467	573	580	560
Residual elongation, %	36	36	37	39	42	43
Tear strength, N /mm	19.5	24.6	18.3	23	26.4	28
Physical-mechanical characterization: accelerated ageing at 70°C and 168 h						
Hardness, °Sh A	71	73	72	70	70	71
Elasticity, %	12	12	12	12	12	12
Tensile strength, N /mm^2	3.4	3.4	3.3	3.6	3.6	3.7
Elongation at break, %	427	380	420	420	460	460
Residual elongation, %	35	30	32	35	37	41
Tear strength, N /mm	17	19.5	18	18	18.5	18

For the samples based on silicone rubber filled with CaCO$_3$, crosslinked with dicumyl peroxide-PD (Perkadox - 40% - on silica and CaCO$_3$ substrate) and reinforced with ZnO and TiO$_2$ nanoparticles (CS$_1$ – control, CS$_2$ – control, CSZ$_1$, CSZ$_2$, CSZ$_3$ and CSZT):

- **Hardness** of polymer nanocomposites based on silicone rubber, reinforced and crosslinked with PD, with the addition of ZnO and TiO$_2$ nanoparticles, does not show significant changes compared to control samples CS$_1$ and CS$_2$. In the case of samples with a higher percentage of crosslinking agent due to vulcanization of silicone rubber, elasticity increases – control sample CS$_2$. After accelerated ageing hardness increases compared to hardness in normal state for all samples due to plasticizer loss,

- **Elasticity**. Similarly to hardness, with the addition of nanoparticles and crosslinking agent in various proportions, it can be seen that elasticity is constant. After accelerated ageing, elasticity remains constant in all formulations of polymer nanocomposites based on silicone rubber,

- **Tensile strength**. As a result of adding the reinforcing agent (ZnO and TiO$_2$ nanoparticles) and the crosslinking agent (dicumyl peroxide) to the formulations, tensile strength values range from 3.4 N/mm^2 to 3.8 N/mm^2. Tensile strength therefore increases compared to control sample CS$_1$ depending on the percentage of reinforcing agent added to the mixtures, and after accelerated ageing at 70°C for 168 h, tensile strength values are found between 3.4 N/mm^2 and 3.6 N/mm^2,

- **Elongation** at break in normal state increases significantly from 467% (control sample) to 560% (sample containing ZnO and TiO$_2$ nanoparticles), values proving that filler dispersion is improved in the case of using nanometric zinc oxide and titanium dioxide. After accelerated ageing, elongation at break decreases for both control sample and for samples reinforced with nanoparticles, due to plasticizer loss; values fall into the standard range (values higher than 300%),

- **Residual elongation** increases proportionally to the addition of nanometric reinforcing agent. The higher the percentage of reinforcing agent in the form

of nanoparticles, the higher the residual elongation, and after accelerated ageing, the values of residual elongation decrease by approximately 2-3% compared to values of specimens in normal state (due to plasticizer loss),

- **Tear strength** in normal state improves with the increased amount of reinforcing agent (19.5 – 28 N/mm), and after accelerated ageing it decreases, with values ranging between 17 N/mm and 18.5 N/mm.

3.2. Resistance to solvents

Mixtures were immersed in various working media - ethyl alcohol (70% alcohol dilution), distilled water, vegetable fat (sunflower seed oil), for 24 hours at room temperature in brown-colored recipients and sealed, and their behaviour was analyzed, with results presented in table 3 (rheological analysis showed that a higher PD percentage does not influence the vulcanization degree, and therefore control sample CS_2 was excluded).

Table 3

Immersions of mixtures based on silicone rubber

Mixture	CS_1		CSZ_1		CSZ_2		CSZ_3	
	ΔM	ΔV	ΔM	ΔV	ΔM	ΔV	ΔM	ΔV
Ethyl alcohol (70%)	-0.76	-1.11	-0.69	-0.94	-0.62	-0.49	-0.45	-0.84
Distilled water	0.17	0.69	0.24	0.34	0.18	0.53	0.17	0.86
Cooking oil (sunflower seed oil)	-1.23	-1.65	-1.74	-2.15	-1.19	-1.13	-1.04	-1.05

After 22-hour immersion, the following results were obtained:

- in distilled water, good behaviour, below 1%, is noticed for mass variation (ΔM), including for volumetric variation (ΔV), which shows very low swelling in this immersion medium,
- in ethyl alcohol and vegetable fat (cooking oil) variations are negative for both media, below $\pm$ 2.5%. The values indicate that extraction of a substance such as stearin takes place in these media,
- mass and volumetric variation are significantly influenced by adding ZnO as reinforcing agent (from 0.24 to 0.86 in the case of volumetric variation).
- the concentration of nanometric reinforcing agent, ZnO, influences the mass variation (ΔM) and volume variation (ΔV), which decrease proportionally to the percentage of nano ZnO, added in the resulting compounds.

After immersion of samples in these working media, formulations do not undergo changes in appearance of surface by colour change, cracking or swelling. This indicates that the technologies used and processing parameters are optimal.

3.3. Biological characterization

Samples were also tested biologically, analyzing the antimicrobial activity of the surfaces treated with ZnO and TiO_2 nanoparticles for 24 h, on the following

strains: *Staphylococcus aureus* ATCC 25923; *Escherichia coli* ATCC 25992; *Candida albicans* ATCC 1023, Figs. 4-6.

Samples with ZnO nanoparticles - CSZ_2, CSZ_3 and the sample with TiO_2 nanoparticles - CSZT were found to be effective against the analyzed bacterial strains, inhibiting the adherence of bacteria to the substrate. CSZ_1 sample did not show antimicrobial activity against any of the two strains; seemingly a small amount of ZnO rather favours bacterial adherence.
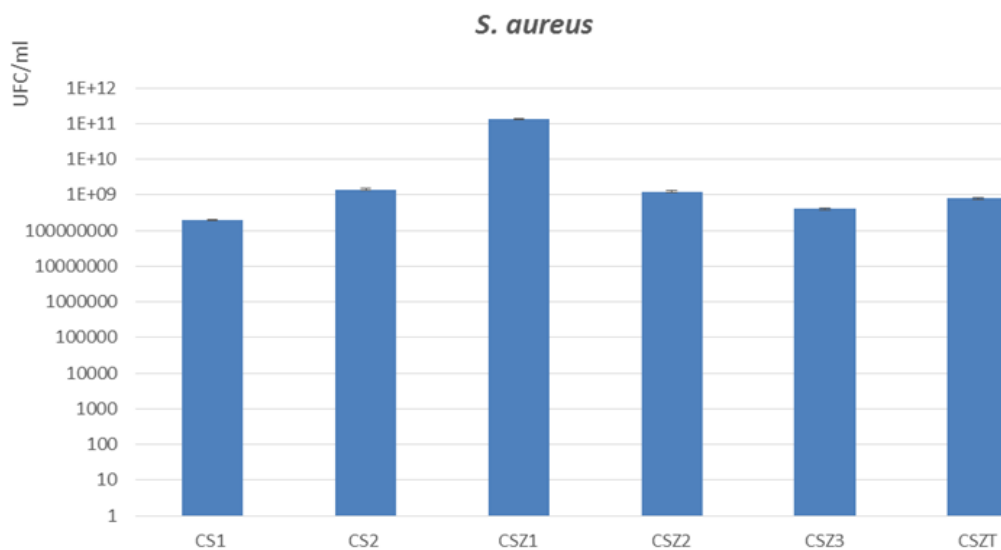

Fig. 4. Biological characterization of samples with ZnO and TiO_2 nanoparticles on Staphylococcus aureus ATCC 25923 strains
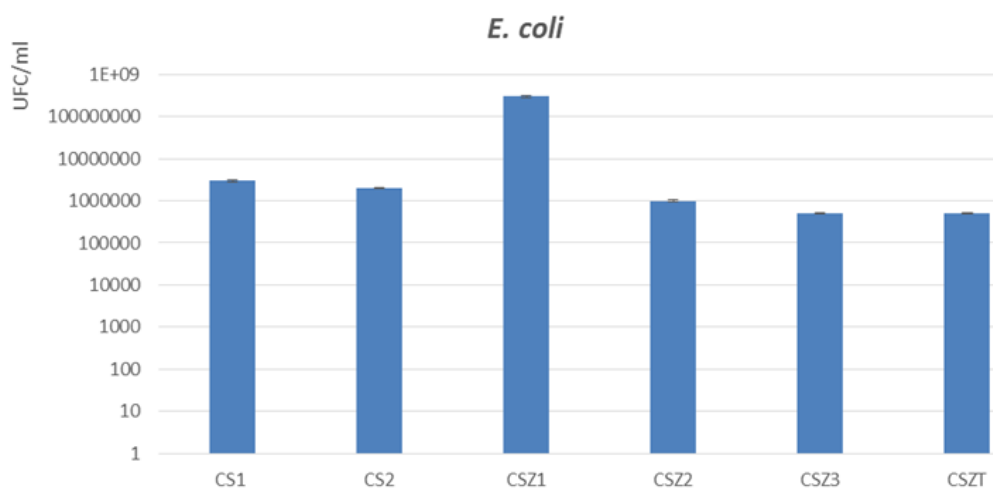

Fig. 5. Biological characterization of samples with ZnO and TiO_2 nanoparticles on Escherichia coli ATCC 25992 strains

In the case of the fungal strain, the analyzed samples did not prove to be effective, as the UFC values are higher compared to the two control samples.
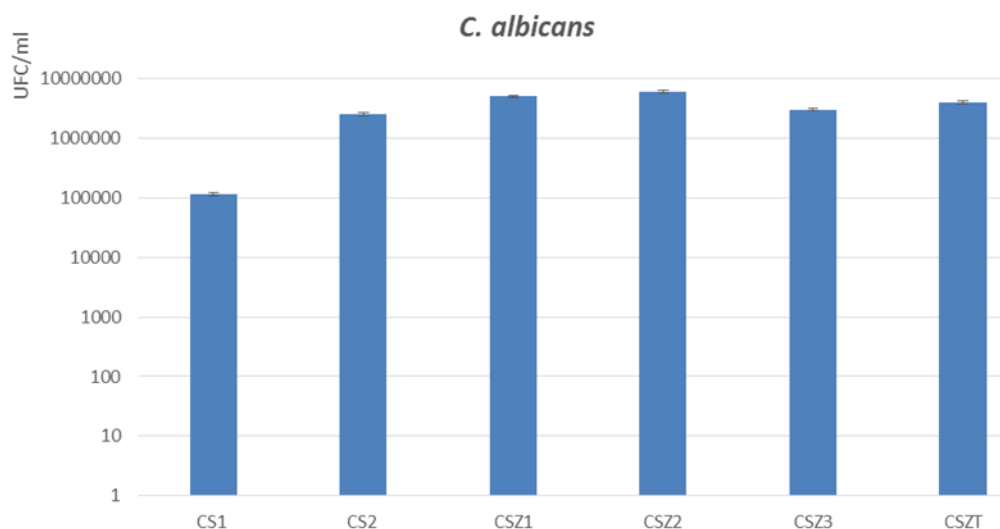

Fig. 6. Biological characterization of samples with ZnO and TiO$_2$ nanoparticles on Candida albicans ATCC 10231 strains

In conclusion, sample CSZ$_3$ proved to have the highest antibacterial activity, while samples with TiO$_2$ nanoparticles proved more active against fungi.

4. Conclusions

The rheological analysis of polymer nanocomposites shows that the addition of ZnO and TiO$_2$ nanoparticles does not influence the vulcanization degree. Immersion in specific working media shows that polymer nanocomposites based on silicone rubber reinforced with TiO$_2$ and ZnO nanoparticles do not undergo changes in the surface appearance by colour change, cracking and swelling. Formulations containing ZnO nanoparticles showed the highest antibacterial activity, while samples containing TiO$_2$ nanoparticles proved more active against fungi. As a result of analyses, it is found that the obtained polymer nanocomposites based on silicone rubber, reinforced with nanoparticles have potential application in food industry, medical, pharmaceutical industry and consumer goods.

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