

ANTIBACTERIAL COMPOUND BASED ON SILICONE RUBBER AND ZnO AND TiO₂ NANOPARTICLES FOR THE FOOD AND PHARMACEUTIC INDUSTRIES. PART I – OBTAINING AND CHARACTERISATION

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ANTIBACTERIAL COMPOUND BASED ON SILICONE RUBBER AND ZnO AND TiO₂ NANOPARTICLES FOR THE FOOD AND PHARMACEUTIC INDUSTRIES. PART I – OBTAINING AND CHARACTERISATION

ABSTRACT. Taking into account the progress in science and technology, it has been and is still necessary to develop new innovative and high-performance materials. Globally, obtaining new advanced polymeric structures based on nanopowder-reinforced elastomers, with high-performance properties, offers possibilities for developing new materials and expanding their field of application. At present, polymeric materials occupy a very important place in all areas of human activity, being part more and more of everyday life. The need to develop new materials with high-performance properties led to this paper, which describes the obtaining and characterization of a compound with antibacterial properties based on silicone rubber (silicone elastomer - ELASTOSIL) reinforced with nanoparticles with antifungal, antibacterial and antimicrobial properties (ZnO and TiO₂). The dispersion of nanoparticles in the mass of the elastomeric compound has a decisive role in influencing its antimicrobial and antibacterial sterilization properties. The elastomeric compound based on silicone rubber with antibacterial and antimicrobial properties is obtained by vulcanization, and is characterized from a physical-mechanical, chemical and structural point of view, according to the standards in force. The antibacterial elastomeric compound reinforced with nanoparticles has potential uses in the food and pharmaceutical fields.

KEY WORDS: antibacterial compound, curing, silicone rubber, TiO₂, ZnO

COMPOUND ANTIBACTERIAN PE BAZĂ DE ELASTOMER SILICONIC ȘI NANOPARTICULE DE ZnO ȘI TiO₂ PENTRU DOMENIUL ALIMENTAR ȘI FARMACEUTIC. PARTEA I – OBTINERE ȘI CARACTERIZARE

REZUMAT. Ținându-se cont de progresul în știință și tehnologie a fost și este necesară dezvoltarea de noi materiale inovative și performante. La nivel mondial, obținerea de noi structuri polimerice avansate pe bază de elastomeri ranforșați cu nanopulberi, cu proprietăți performante, oferă posibilități de obținere a unor noi materiale și de extindere a domeniului de aplicații ale acestora. În prezent, materialele polimerice ocupă un loc foarte important în toate domeniile activității umane, luând parte din ce în ce mai mult la viața de zi cu zi. Necesitatea dezvoltării de noi materiale cu proprietăți performante a condus la prezenta lucrare, ce descrie obținerea și caracterizarea unui compound cu proprietăți antibacteriene pe bază de cauciuc siliconic (elastomer siliconic - ELASTOSIL) ranforsat cu nanoparticule cu proprietăți antifungice, antibacteriene și antimicrobiene (ZnO și TiO₂). Dispersia nanoparticulelor în masa compoundului elastomeric are rol determinant în influențarea proprietăților de sterilizare antimicrobiană și antibacteriană a acestuia. Compoundul elastomeric pe bază de cauciuc siliconic cu proprietăți antibacteriene și antimicrobiene este obținut prin vulcanizare, urmând a fi caracterizat din punct de vedere fizico-mecanic, chimic și structural, conform standardelor în vigoare. Compoundul elastomeric antibacterian ranforsat cu nanoparticule are potențiale utilizări în domeniul alimentar și farmaceutic.

CUVINTE CHEIE: compound antibacterian, vulcanizare, cauciuc siliconic, TiO₂, ZnO

COMPOSÉ ANTIBACTÉRIEN À BASE D'ÉLASTOMÈRE DE SILICONE ET DE NANOPARTICULES DE ZnO ET TiO₂ POUR LE DOMAINE ALIMENTAIRE ET PHARMACEUTIQUE. PARTIE I - OBTENTION ET CARACTÉRISATION

RÉSUMÉ. Compte tenu des progrès de la science et de la technologie, il a été et est encore nécessaire de développer de nouveaux matériaux innovants et performants. A l'échelle mondiale, l'obtention de nouvelles structures polymériques avancées à base d'élastomères renforcés par des nanopoudres, aux propriétés performantes, offre des possibilités pour le développement de nouveaux matériaux et d'élargissement de leur domaine d'application. Actuellement, les matériaux polymères occupent une place très importante dans tous les domaines de l'activité humaine, participant de plus en plus à la vie quotidienne. La nécessité de développer de nouveaux matériaux aux propriétés performantes a conduit à cet article qui présente l'obtention et la caractérisation d'un composé aux propriétés antibactériennes à base de caoutchouc silicone (élastomère silicone - ELASTOSIL) renforcé de nanoparticules aux propriétés antifongiques, antibactériennes et antimicrobiennes (ZnO et TiO₂). La dispersion des nanoparticules dans la masse du composé élastomère joue un rôle déterminant pour influencer ses propriétés de stérilisation antimicrobienne et antibactérienne. Le composé élastomère à base de caoutchouc silicone aux propriétés antibactériennes et antimicrobiennes est obtenu par vulcanisation, et sera caractérisé d'un point de vue physico-mécanique, chimique et structurel, selon les normes en vigueur. Le composé élastomère antibactérien renforcé de nanoparticules a des utilisations potentielles dans les domaines alimentaire et pharmaceutique.

MOTS CLÉS : composé antibactérien, vulcanisation, caoutchouc silicone, TiO₂, ZnO

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INTRODUCTION

Vulcanization of elastomers (silicone) is a main step that has a major impact on the final properties of the products [1, 2]. Both the quantity and the type of vulcanizing agent, the time, temperature and pressure of vulcanization, are important factors that control the degree of crosslinking, the properties of the finished product, thus leading to obtaining advanced compounds. These advanced materials based on silicone elastomers (silicone rubber), reinforced with nanopowders that have antibacterial, antifungal and antimicrobial properties, contribute to improving product quality, environmental protection and of course human health [3-7]. The dispersion of nanoparticles in the obtained mixture (elastomeric compound) has the decisive role in influencing its antimicrobial and antibacterial sterilization properties [8, 9].

Silicone elastomers - silicone rubber is generally preferred in the food and pharmaceutical fields because it does not contain substances that are not toxicologically acceptable (nitrile, styrene, chlorine, antioxidants and other restricted ingredients), and has characteristics such as high resistance to temperatures from -100°C to above +300°C. Higher temperatures than +300°C are specific to sterilization and therefore silicone elastomers are preferred by the above mentioned fields [10-15].

The aim of this work was to obtain an antibacterial compound based on silicone rubber - Elastosil R701/70-OH, filled with chalk, crosslinked with PD (dicumyl peroxide), stearin as plasticizer and reinforced with two types of nanoparticles - zinc oxide and titanium dioxide, made by mixing on an electric roller between its rollers (the rollers were cooled with water) [16-19]. The obtained antibacterial compound was characterized in terms of physical-mechanical properties (hardness, residual elongation, tear strength), chemically by immersion in various media (three different immersion environments) and by FT-IR spectrometry, all according to standards in force.

EXPERIMENTAL

Materials

The following materials were used to make the antibacterial compound based on siliconic rubber and nanometric particles: (1) Elastosil R701/70-OH – silicone rubber: polydimethylsiloxane with vinyl groups, dynamic viscosity over 9.000.000 mPa*s, in the form of paste, density – 1.32 g/cm³, colour – opaque; (2) stearin, white flakes, moisture - 0.5% max, ash – 0.025 % max; (3) ZnO – zinc oxide microparticles: precipitate 93-95%, in the form of white powder, density – 5.5 g/cm³, specific surface – 45-55 m²/g; (4) ZnO – zinc oxide nanoparticles: white powder, 99.99% trace metals basis; (5) TiO₂ - titanium dioxide nanoparticles: white nanopowder, assay ≥ 99.5 % trace metals basis; (6) chalk: CaCO₃ precipitate – white powder, molecular weight 100.09; (7) PD – di(tert-butylperoxyisopropyl) benzene: powder 40% with calcium carbonate and silica – Perkadox 14-40B (1.65 g/cm³ density, 3.8% active oxygen content, pH 7, assay: 39.0-41.0%).

Methods

Preparation of Antibacterial Compound and Characterization Methods

The antibacterial compound based on silicone rubber – Elastosil R701/70-OH, reinforced with nanometric particles TiO₂ and ZnO, filled with chalk - CaCO₃, plasticized with stearin and crosslinked with dicumyl peroxide - PD was developed by electric laboratory roll mill mixing, the rolls were water-cooled. The Elastosil R701/70-OH was plasticized between the rolls for approximately 2.5-3 minutes, then the stearin was added and mixing continued for approximately 2 minutes. After the ZnO microparticle was added and embedded into the mixture until homogenisation, for maximum 2 minutes, the nanoparticles of TiO₂ and ZnO were added, continuing to mix for 3 minutes until the nanometric component was embedded. Mixing continued for 3 minutes while adding the filler - CaCO₃ and the dicumyl peroxide – PD

(last ingredient) was embedded for 2 minutes. The mixture is homogenized on the roll mill for maximum 2 minutes and taken off in the form

of a 3-4 mm thick sheet. The order of adding ingredients was strictly observed, according to Table 1.

Table 1: Formulations of antibacterial compounds based on silicone rubber reinforced with TiO₂ and ZnO nanoparticles

Symbol	MU [g]	CS ₁ (control)	Sample 2	Sample 3	Sample 4
Silicone rubber (Elastosil R701/70-OH)	g	150	150	150	150
Stearin (FLAKES)	g	7.5	7.5	7.5	7.5
Zinc oxide (active powder)	g	6	4.5	3	1.5
Zinc oxide (nanoparticles)	g	-	1.5	3	4.5
Titanium dioxide (nanoparticles)	g	-	1.5	3	4.5
Chalk (CaCO ₃ - powder)	g	15	15	15	15
Dicumyl peroxide (PD– 40% - on silica and CaCO ₃ powder substrate)	g	11.25	11.25	11.25	11.25

The resulting antibacterial compound was subjected to rheological determinations (using a Monsanto rheometer – Figure 1), to establish the optimal curing time in the electrical press.

From the rheological analysis made by comparing the samples it is found that the introduction of nanometric reinforcing agent - ZnO and TiO₂ (with antiseptic, antifungal, antimicrobial role), does not influence the degree of vulcanization of the compound obtained. The samples obtained are similar to each other, compared to the control sample - CS₁. Control sample CS₁ does not contain nanometric reinforcing agent – Figure 2.



Figure 1. Monsanto rheometer used in rheological determination

Sarja:	ML (dNm):	MH (dNm):	ts2 (min):	t50 (min):	t90 (min):
CS1 Martor.rho	5.7	19	1	1.6	2.7
3.rho	6.2	24.4	1.1	2.1	17.8
4.rho	6.3	22.3	0.9	1.7	17.4

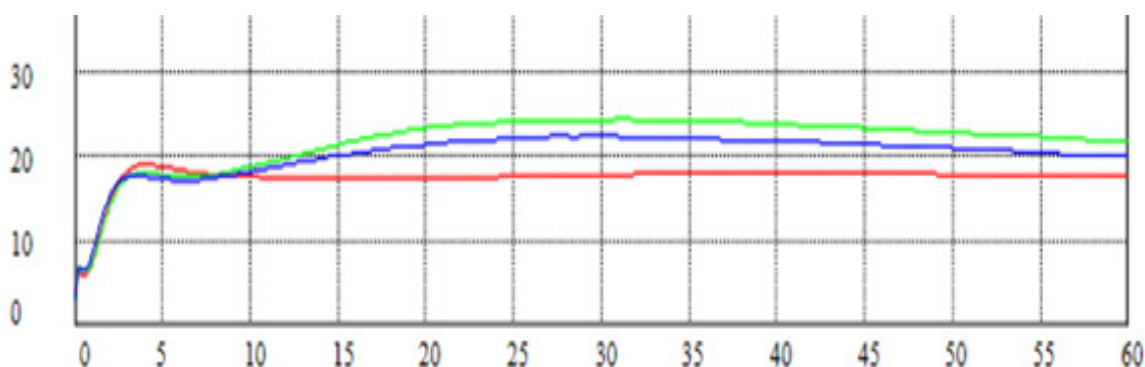


Figure 2. Rheological analysis of samples – CS1 (control), sample 3, sample 4

The specimens were made in an electric press (TP 600) between its plates, by the compression method (by pressing) at the preset parameters: temperature of 170°C, 2 minutes pressing at a pressure of 300 KN, 10 minutes cooling time (Figure 3).

The specimens obtained in the electric press after a stabilization of 24 hours at ambient temperature are then characterized, in compliance with the physical-mechanical standards:

- physically-mechanically (normal state and accelerated aging at 70°C for 168 h,

SR ISO 188-2010): hardness (°ShA-SR ISO 7619: 2011), residual elongation (100% - SR ISO 37-2012), tear strength (N/mm -SR ISO 37-2012);

- chemically (immersion in average media for 24 hours): ISO 1817: 2015, following both the volume variation (ΔV) and the mass variation (ΔM).
- structurally: double beam molecular absorption IR spectrometer in, in the range 4000-600 cm^{-1} , using the Able Jasco 4200 FT-IR device equipped with ATR with diamond crystal.

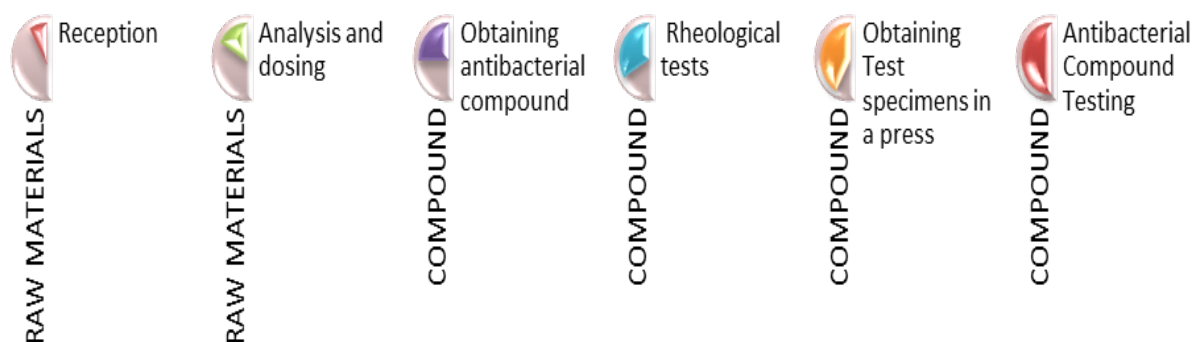


Figure 3. Technological process of obtaining the antibacterial compound reinforced with ZnO and TiO_2 nanoparticles

RESULTS AND DISCUSSIONS

Physical-Mechanical Characterization of Antibacterial Compounds

The antibacterial compounds were tested from a physical-mechanical point of view after

a stabilization for 24 h at room temperature, according to the standards in force (normal state and accelerated aging at 70°C and 168 h).

As a result of the physical-mechanical analysis performed according to Figures 4, 5 and 6, the following are found:

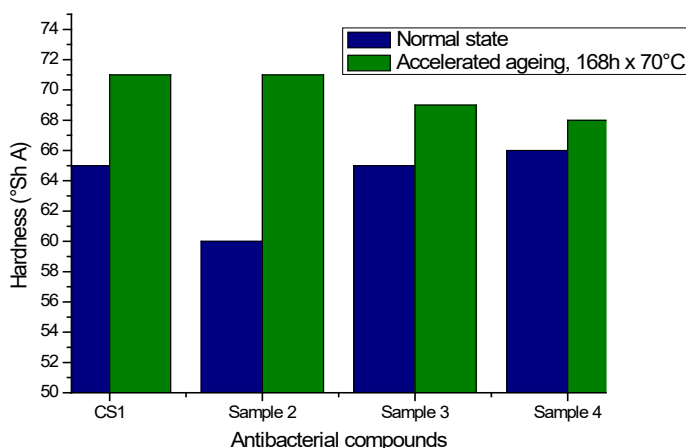


Figure 4. Hardness for antibacterial compounds reinforced with ZnO and TiO_2 nanoparticles

• The **hardness** (Figure 4) of antibacterial compounds based on silicone elastomer in normal state, increases slightly compared to the control sample CS₁. Increasing the amount of nanoparticles (ZnO and TiO₂) added in the mass of the elastomeric compound, it is observed that

the hardness values increase slightly. Due to the loss of plasticizer, the hardness of the samples decreased compared to the control sample, after they were subjected to the accelerated aging process at 70°C for 168h.

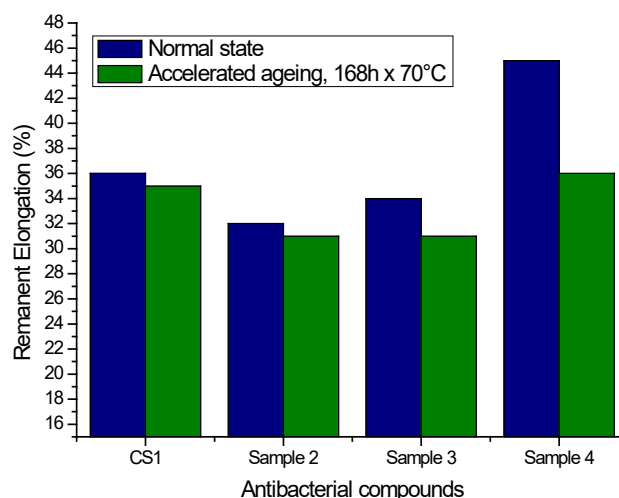


Figure 5. Residual elongation for antibacterial compounds reinforced with ZnO and TiO₂ nanoparticles

• For **residual elongation** (Figure 5), the higher the percentage of reinforcing agent in the form of nanoparticles, the higher the residual elongation, thus demonstrating that the processing parameters are optimal. Similar to hardness, after subjecting the specimens to the

accelerated aging process at 70°C for 168 hours, the values of the residual elongation decrease. Due to the loss of plasticizer, the values decrease by approximately 2.5% compared to the values of the specimens in the normal state.

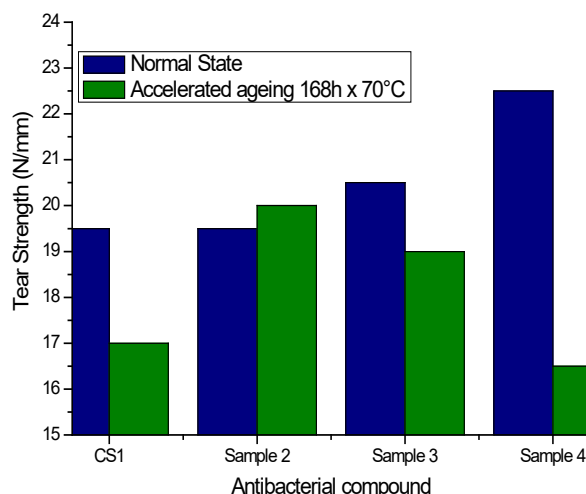


Figure 6. Tear strength for antibacterial compounds reinforced with ZnO and TiO₂ nanoparticles

• **Tear strength** (Figure 6) in the normal state increases in proportion to the amount of reinforcing agent added. The values obtained in the normal state are between 19.5-22.5 N/mm, while after subjecting the specimens to the accelerated aging process, the values of tear resistance decrease, presenting values between 16.5 and 20 N/mm.

Chemical Characterization of Antibacterial Compounds

The chemical characterization of antibacterial compounds was performed

by immersing them in various working environments: ethyl alcohol concentration 70%, distilled water and sunflower oil, for 24 hours at room temperature, in dark containers (brown, black), tightly closed (samples are completely covered by the work environment used and are immersed at a relatively equal distance from each other without them coming into contact with each other).

Mass variation – ΔM and volumetric mass – ΔV , after immersion in environments specific to the food, pharmaceutical and food fields are presented in Table 2.

Table 2: Mass variation (ΔM) and volumetric mass (ΔV) of antibacterial compounds reinforced with TiO_2 and ZnO nanoparticles, in various environments

Material	CS ₁ (control)		Sample 2		Sample 3		Sample 4	
	ΔM	ΔV	ΔM	ΔV	ΔM	ΔV	ΔM	ΔV
Ethyl alcohol – 70%	-0,75	-1,11	-1,2	-2,72	-1,19	-1,77	-1,34	-1,66
Distilled water	0,16	0,68	0,15	0,38	0,18	0,44	0,72	0,53
Sunflower oil	-1,24	-1,59	-2,23	-3,54	-2,1	-3,26	-1,73	-1,85

The immersion of samples of mixtures based on silicone elastomer reinforced with nanopowders (ZnO and TiO_2) in different specific media, presents the following results:

1. in ethyl alcohol, both the mass variation, ΔM , and the volumetric one, ΔV , present negative values, below $\pm 2.8\%$. These values indicate the extraction of substances – stearin and chalk – that take place in this work environment;
2. for both ΔM (mass variation) and ΔV (volumetric variation) the values calculated after a 24-hour immersion in distilled water are below 0.8%, which indicates an insignificant swelling of the tested specimens;
3. in the vegetable oil environment, the values recorded for the mass and volumetric variation are negative, below $\pm 3.6\%$, indicating, as in the case of specimens immersed in the ethyl alcohol, the extraction of substances such as unreacted crosslinking agent;
4. after immersing the samples in the media listed above, it is observed that their surface does not alter, they do not show color change (the color of the

samples being gray) and do not swell, and no cracks or other non-conformities of the specimens are observed on their surface (taking into account that they do not come into contact with each other).

FT-IR Spectrometric Analysis

Samples were tested spectroscopically through FT-IR spectroscopy, using an Able Jasco 4200 FT-IR device coupled with ATR with diamond crystal and sapphire head and all the samples had as reference the spectrum recorded for the principal component – Elastosil R701/70-OH (elastomeric rubber).

The IR frequencies (cm^{-1}) and vibration attributions for the silicone rubber sample – Elastosil R701/70-OH are given in Table 3 and Figure 7.

Table 3: IR frequencies and vibration attributions for the silicone rubber sample

Frequency	Vibration attributions
696	$\nu \text{Si}(\text{CH}_3)_3$
787.271	$\nu \text{Si}(\text{CH}_3)$
866.338	$\text{Si}(\text{CH}_3)_2(r)$
1007.12	$\text{Si}(-\text{CH}_3=\text{CH}_2)$
1258.78	δSiCH_3

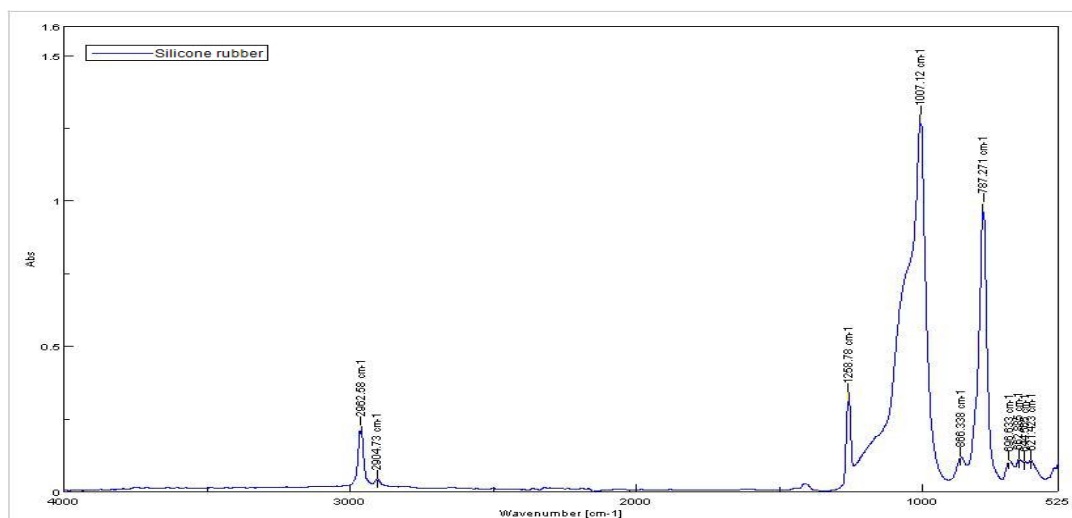


Figure 7. IR spectrum recorded for Elastosil R701/70-OH (silicone rubber)

Control sample, CS₁, has the following IR frequencies (cm⁻¹) and vibration attributions – Table 4, and the IR recorded spectrum – Figure 8.

Table 4: IR frequencies and vibration attributions for the control sample – CS₁

Frequency	Vibration attributions
697.141	ν Si(CH ₃) ₃
786.815	ν Si(CH ₃)
871.667	Si(CH ₃) ₃ + Si(CH ₂) ₂
1006.66	Si(-CH ₃ =CH ₂)
1258.32	δ SiCH ₃
1451.17	ν CH ₃ (CH ₂) ₁₆ -CO- (stearic acid)
2849.31	Si-O-C
3361.32	ν (OH) linked

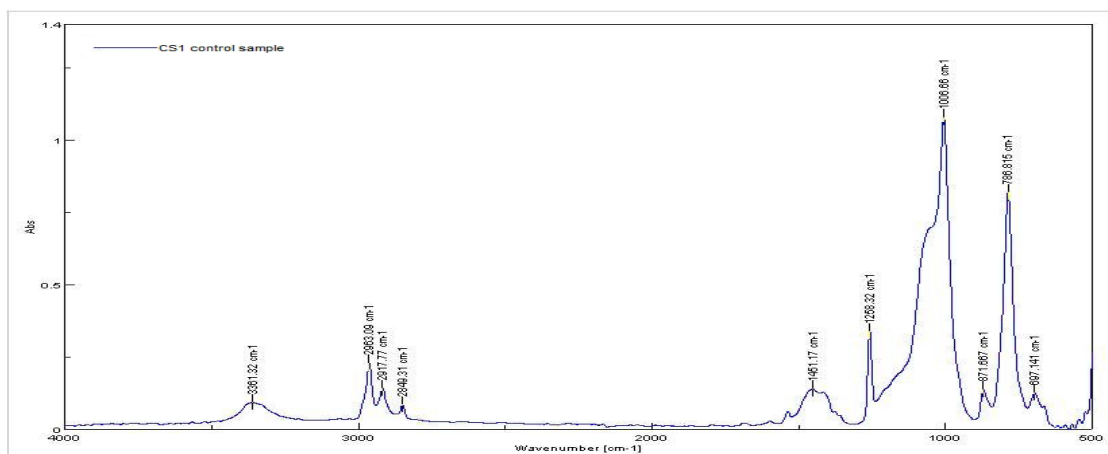


Figure 8. IR spectrum recorded for CS₁ (control sample)

All the samples were tested from the point of view of FT-IR spectroscopy (Figure 9 – A and B) and overlapped spectra confirm the presence of the silicone elastomer Elastosil R701/70-OH by the intensity of the characteristic peaks, this being the main material. The silicone elastomer

– Elastosil R701/70-OH represents the dispersed phase (in the largest quantity), the material in which the other ingredients are incorporated, and from the overlapping spectra, the presence of silicone groups is observed from the intensity of the characteristic peaks.

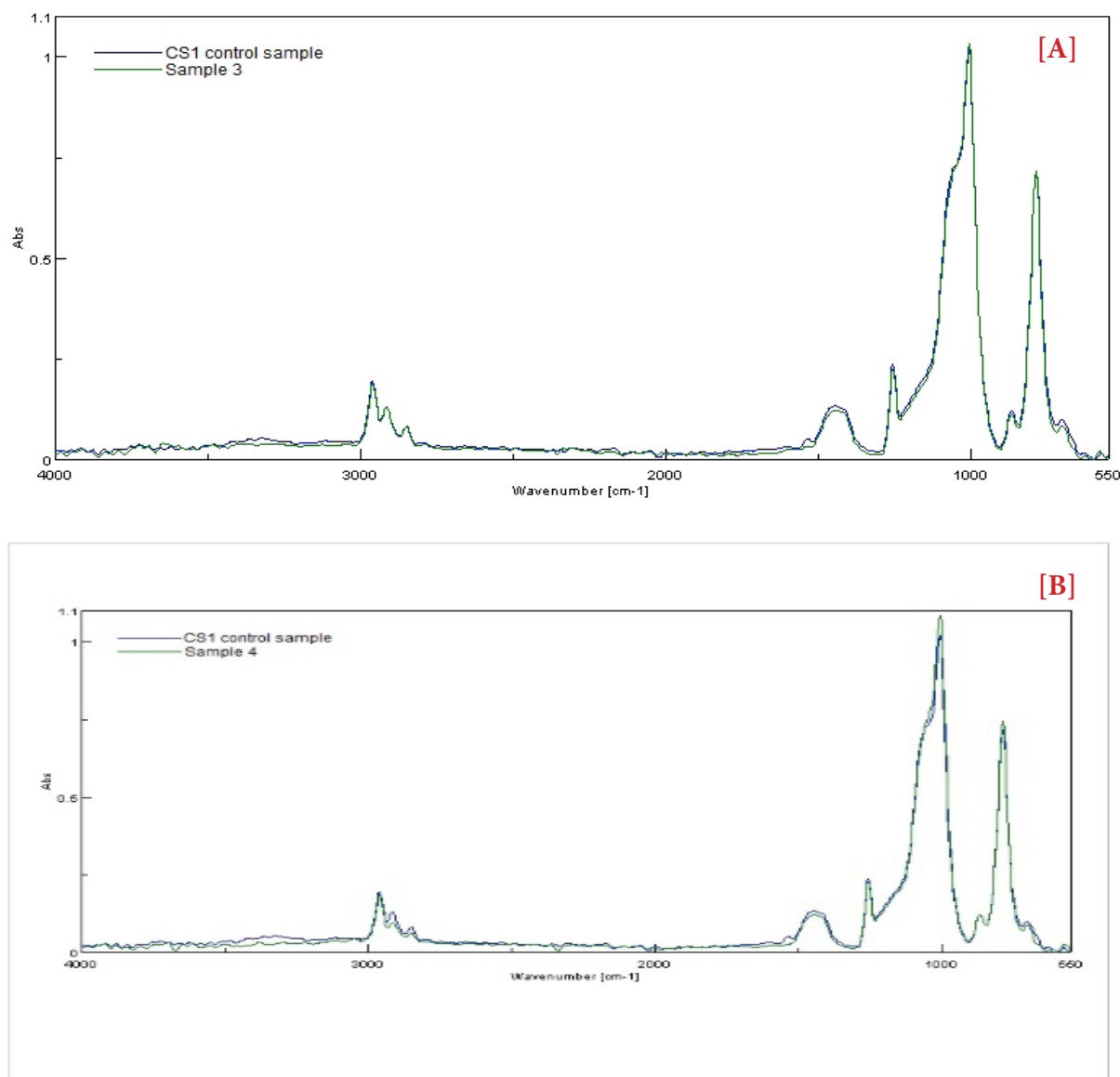


Figure 9. Overlapping spectra recorded for sample 3 [A] and sample 4 [B]

CONCLUSION

The article presents the technology for developing antibacterial compounds based on elastomeric rubber - Elastosil R701/70-OH, reinforced with two types of nanoparticles, ZnO and TiO₂, according to standards in force.

The physical-mechanical characterization after a stabilization for 24 h at room temperature, according to the standards in force, in normal state and after accelerated aging at 70°C and 168 h, confirms the fact that the processing parameters are optimal. After the immersion process, it is observed that the samples do not undergo surface changes, do not show color change and do not swell, and on the surface they

do not show cracks or other non-conformities. FT-IR spectroscopy, by superimposing the spectra of each sample separately with the control sample CS₁, confirms the presence of Elastosil R701/70-OH silicone rubber, by the intensity of its characteristic peaks, this being the material in which the other ingredients are incorporated.

As a result of physical-mechanical, chemical and characteristics of FT-IR frequencies (cm⁻¹) and vibration attributions of antibacterial compounds based on silicone elastomer, we can say that they have potential applications in the food and pharmaceutical field.

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