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Preparation of PVA-Based Composites with the Addition of Zinc Oxide Nanoparticles

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Abstract
The paper presents the possibility of obtaining poly(vinyl alcohol)-based coatings containing zinc oxide nanoparticles. The research part has been divided into three steps. At the beginning, nanometric zinc oxide was produced by the hydrothermal method and its physicochemical properties were characterized. The second part of the research included the creation of a reference composition. Next, three independent variables were determined: the mixing temperature of composites, the concentration of glycerine and the concentration of nanometric zinc oxide that could affect the properties of products. In the last stage, the compositions were tested for physicochemical, utility and microbiological properties. Based on the conducted tests it was found that the composites have antimicrobial properties. Nanocrystalline zinc oxide is eluted from the composites in trace amounts and thus the products are safe for the environment. Among the independent variables, only the temperature affects utility properties of the obtained products. A product with the best functional properties is intended to be applied in a suspension form on the surface that is microbially infected and, after its solidification, it can be removed together with dead biological material.

Keywords Zinc oxide · PVA · Functional coatings · Antimicrobial effect · Solidification

1 Introduction

The development of science allows us to become better acquainted with the threats that microorganisms pose to human beings. Raising awareness about compliance with the principles of cleanliness helps to prevent the spread of diseases; however, the level of hygiene of many people still leaves much to be desired. In order to maintain cleanliness in public places, scientists are looking for new solutions that allow for the development of more effective cleaning products.

Pools, water parks, and public baths are places where high moisture levels persist and the temperature is a few degrees higher than room temperature. These are excellent

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conditions for the development of microorganisms, such as bacteria or fungi. The most common disease for athletes and people using the above-mentioned places is the "athlete's foot" [1].

Another example of problematic public places in which diseases can spread are gyms. The number of people using fitness centres increases year by year, which is a positive trend. Unfortunately, many people cannot adequately care for the cleanliness of exercise equipment, which is the cause of disease transmission. Surfaces in contact with human sweat are an ideal place for the development of microorganisms. The most common diseases that can be contracted are primarily skin diseases such as, for example, oedemas and tinea pedis [2].

With the development of nanotechnology, the influence of nanomaterials on bacteria and fungi is more and more often studied, considering them as an opportunity to raise the level of hygiene in public places [3]. Currently, research is being carried out on effective methods of destroying the habitats of microorganisms using materials containing nanoparticles of metals and metal oxides such as nanometer silver, titanium oxide or zinc oxide. The last of the mentioned ones is characterized by good electrical, photochemical, catalytic and optical properties. It is used, inter alia, as a component of biomimetic membranes. In addition, it can immobilize and modify proteins due to a rapid transfer of electrons between the enzyme and electrode sites. Zinc oxide has many advantages, one of which is a noticeable activity in the range of neutral pH 7–8; it is also non-toxic and stable under the influence of both UV radiation and high temperatures [4]. All this makes the nanometric ZnO a subject of research by scientists.

The interest in developing new organic–inorganic nanocomposites is growing year by year. The embedding of metallic oxide nanoparticles in the structure of polymeric matrix has a great importance due to novel properties derived from the developed material [5, 6]. For example, introducing the silica oxide nanoparticles to the structure of poly(2-aminophenyldisulfide) strongly influences the electrochemical activity of the resulting composite [7]. What is more, the addition of Al_2O_3 to polyaniline polymer makes the resulting composite exhibit enhanced thermal stability [8]. As found by Chouli et al. [9], nanocomposite containing titanium oxide nanoparticles may be used for commercial applications as ingredient of antistatic and anticorrosion coatings. Daikh et al. [10] concluded that thanks to good electrical properties, PANI/ZnO nanocomposites may be applied in microwave frequencies as absorbing and shielding materials.

This work concerns the development of functional composites based on poly(vinyl alcohol) with the addition of zinc oxide nanoparticles, which have bactericidal and fungicidal properties. It is expected that the product will be applied on flat surfaces infected by microorganisms such as floors in changing rooms or baths, or overflow grates at a pool. The assumption is to obtain a material which will solidify after its application and which will be possible to tear off together with dead biological film.

2 Materials and Methods

2.1 Materials

The following compounds were used in this study: poly(vinyl alcohol) (M = 72,000 g/mol, ≥ 99.0%), chitosan (M = 100,000–300,000 g/mol, high purity), gelatin (p.p.a.), xanthan gum (p.p.a.), glycerine (d = 1.26 g/cm^3, p.p.a.) methyl cellulose (viscosity = 400 cP, p.p.a), sucrose (≥ 99.5%), zinc nitrate hexahydrate (99.999%), sodium hydroxide (≥ 98.0%). All compounds were provided by Sigma Aldrich, Germany. In microbiological tests, the following compounds were used: peptone, yeast extract, saccharose (≥ 98.0%), agarose. All compounds were provided by Sigma Aldrich, Germany. The *Aspergillus niger* and *Saccharomyces cerevisiae* strains used in the study were provided by the National Collection of Yeast cultures, England. All solutions were prepared using deionized water, Polwater, 0.18 µS.

2.2 Methods

2.2.1 Preparation of Nanometric Zinc Oxide

Nanoparticles of zinc oxide were obtained in a two-stage process. In the first stage, zinc hydroxide was precipitated by the reaction of zinc nitrate with sodium hydroxide. At the beginning, aqueous solutions of zinc nitrate at a concentration of 0.2 mol/dm^3 and sodium hydroxide at a concentration of 0.4 mol/dm^3 were prepared. Thereafter, 160 cm^3 of zinc nitrate solution and 40 cm^3 of sodium hydroxide were mixed in a stainless steel vessel of Parr 4525 pressure reactor to give zinc hydroxide. The process of dehydration of zinc hydroxide to zinc oxide was carried out for 30 min at 180 °C. At the end of the process, the resulting nanometer zinc oxide was filtered under reduced pressure on Sartorius Stedim nitride-cellulose filters with a pore size of 0.45 µm. The sediment was washed several times with deionized water to wash out nitrate and sodium ions, and after the filtration was completed, the product was dried at 110 °C; after that it was triturated in an agate mortar. The obtained product was analyzed by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR) and X-ray diffraction method (XRD). The SEM analysis was performed using 1430 VP microscope by LEO Electron Microscopy Ltd. The FT-IR analysis was performed using Nicolet 380

spectrophotometer by Nicolet Co. The XRD analysis was performed using X-ray diffractometer X'Pert PW 1752/00 from Philips.

2.2.2 Preparation of PVA-Based Composites with the Addition of Zinc Oxide Nanoparticles

In the first step a reference composition was obtained. For this purpose aqueous solutions of individual components were prepared in accordance with Table 1.

In order to produce the reference composition, in a vessel with a capacity of 100 cm^3. 20 g of an aqueous solution of poly(vinyl alcohol) at a concentration of 13% was prepared. The operation was carried out in a water bath at 60 °C. The components were mixed using a mechanical stirrer (Model OS40-S, ChemLand) at a setting of 600 rpm. The PVA was introduced in portions every 10 s for 1 min. Then, the rest of ingredients was added according to the order given in Table 1. Table 1 also lists the final concentration of ingredients in the reference composition. After all the ingredients were introduced, the stirring speed was increased to 1000 rpm. The composition was mixed for 5 min from the time the first portion of PVA had been added. After stirring, the pH was checked and the consistency of the reference composition was evaluated.

The next step was to obtain compositions containing an active substance, which was a nanometric zinc oxide. In the studies the central-composition design was applied. It was generated in the Statistica® program, which is universal statistical software. The group of input parameters included: the process temperature, the concentration of glycerine and the concentration of zinc oxide nanoparticles in the final product. The ranges of variability of the process parameters were as follows:

- Temperature (°C): 40, 60 or 80,
- ZnO concentration (%): 1, 3 or 5,
- Glycerine concentration (%): 11, 14 or 17.

The concentrations were calculated into the mass of a pure ZnO added with accuracy to the hundredths and the volume of glycerine to the nearest decimal, remembering that its density is 1.26 g/cm^3. A complete list of individual parameters can be found in Table 2.

Each composition was obtained in the same way. As in the case of the reference composition, the processes were carried out in a water bath using a mechanical stirrer. One by one, all the ingredients were introduced in accordance with the order given in Table 1. The last addition was zinc oxide nanoparticles, after which the stirring speed was increased to 1000 rpm. The total mixing time was 5 min. After the process was completed, the compositions were applied to a flat polypropylene surface and allowed to dry for further testing. The obtained compositions were checked for physicochemical properties. The first test was density measurement. It was carried out using the weight method. Solid composites were also analyzed by scanning electron microscopy (SEM) with energy dispersion spectroscopy (EDS), which allowed to confirm the incorporation of zinc into the structure of composites. The XRD studies of the obtained products were performed as well. Rheological properties of the products were checked by determining flow curves and viscosity curves.

2.2.2.1 Study of Zinc Leaching from Composites

In order to check the elution of zinc oxide from the resulting compositions, its accumulation in water was assessed. For this purpose composites in a solid form were used. It was assumed that for every 0.5 g of the product, 20 cm^3 of deionized water which served as a washing medium was used. Table 2 shows individual quantities used in the research. In order to carry out the test, composites of known mass were placed in a 100 cm^3 polypropylene vessel, and a metered amount of deionized water was added to them. Next, they were placed in a water bath located on a magnetic stirrer. The test was carried out at 32 °C by mixing the whole for 2 h. After this time, all samples were filtered through a quantitative filter. To determine the concentration of the optionally released

Table 1 Ingredients of reference composition

Compound	Concentration in the applied solution (%)	Mass taken (g)	Mass of pure component (g)	Final concentration of the compound in the reference sample (%)
PVA	13	20	2.6000	7.811
Suchrose	2	2	0.0400	0.120
Methyl cellulose	0.1	1.5	0.0015	0.005
Xanthan gum	0.5	1	0.0050	0.015
Gelatin	1	2	0.0200	0.060
Chitosan	0.2	2	0.0040	0.012
Glycerine	100	4.788	4.7880	14.384
Solvent (summary value)	–	–	25.8295	77.594

Table 2 Parameters of the processes for the preparation of the composition with the addition of zinc oxide nanoparticles

Run	Input parameters			Output parameters		
	Temperature (°C)	Concentration of nano-ZnO (%)	Concentration of glycerine (%)	Density (g/cm^3)	Concentration of zinc eluted from composites (mg/dm^3)	Strength needed to tear off the composites (kPa)
C1	40	1	11	1.07	4.2	7.6
C2	40	1	17	1.07	4.1	79.1
C3	40	5	11	1.09	3.6	81.5
C4	40	5	17	1.10	2.3	48.7
C5	80	1	11	1.08	4.3	11.6
C6	80	1	17	1.08	3.7	43.9
C7	80	5	11	1.11	0.8	9.8
C8	80	5	17	1.12	0.6	42.8
C9	40	3	14	1.08	2.1	131.2
C10	80	3	14	1.11	1.8	111.6
C11	60	1	14	1.07	4.4	21.4
C12	60	5	14	1.11	1.3	12.6
C13	60	3	11	1.09	1.3	18.6
C14	60	3	17	1.09	1.9	147.3
C15	60	3	14	1.09	1.7	17.3
C16	60	3	14	1.10	2.2	20.4
Ref.				1.03	0.0	86.0

zinc, the filtrates were analyzed by means of inductively coupled atomic emission spectroscopy (ICP-OES).

2.2.2.2 Study of Zinc Penetration Through a Model Dermal Membrane According to the literature data, nanoparticle zinc oxide penetrates into the cells of organisms, which can be also dangerous for people. Tests were designed to check the amount of zinc released from composites and whether its penetration through the material imitating human skin was possible. The Strat-M® Membrane for Transdermal Diffusion Testing was used. Two research series were performed in which Ringer's solution and SBF solution played the role of acceptor fluids. They were prepared according to the literature data [11, 12]. The stand consisted of a magnetic stirrer with a heating plate, a water bath, a polypropylene vessel with a capacity of 100 cm^3, in which there was an acceptor liquid of appropriate volume and a plastic column with a diameter of 2.5 cm, at the end of which the membrane was mounted (Fig. 1).

Prior to the study, composites with a known surface area were prepared. Next, the amount of deionized water applied was calculated assuming that 1 cm^2 of the sample contacts with 3 cm^3 of deionized water and the amount of acceptor fluid was assessed, with the assumption that 1 cm^2 of the sample corresponds to 20 cm^3 of the accepting solution. The study was carried out according to a predetermined pattern. First, an appropriate amount of acceptor fluid with a mixing element was placed in a polypropylene container which was placed in a water bath at a constant temperature of 39 °C. Next, a column with the Strat-M® membrane in which the prepared composite had been placed was mounted. A metered amount of deionized water was introduced into the column and positioned so that the membrane touched the acceptor fluid surface. The system was mixed at 400 rpm for 20 min. After the test

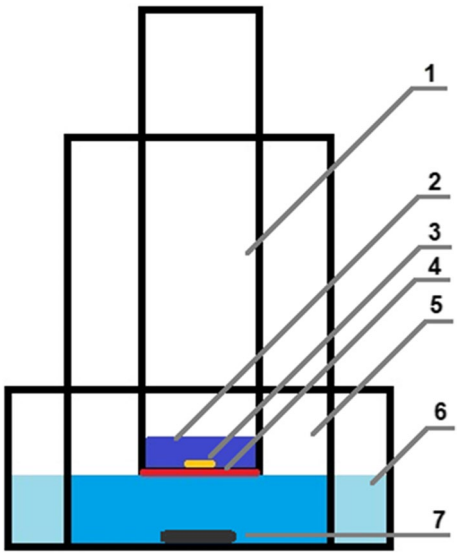

Fig. 1 Stand for testing the penetration of zinc oxide nanoparticles: 1—column, 2—deionized water, 3—tested composite, 4—model dermal membrane, 5—container with acceptor liquid, 6—water bath, 7—stirrer

the ICP-OES was used for the analysis of presence of all elements in the acceptor fluid.

2.2.2.3 Study of Adhesive Properties The obtained product is intended to be applied to surfaces infected by pathogenic microorganisms. After a few hours of application, the liquid composition solidifies and can be detached from the surface. In order to check which force should be applied to tear off the dried composite, the testing of adhesive properties was carried out.

At the beginning of the study, a structure was designed and constructed to examine the force needed to tear off the obtained composites from the polypropylene surface.

Composites in a form of suspension were applied onto a polypropylene surface, assuming that 0.5 cm^3 of the composition corresponds to 0.5 cm^2 of the surface. After solidification of the composite, a force needed to tear off the composite was measured using a Zwick 1445 testing machine.

2.2.2.4 Microbiological Studies The antifungal activity of nanoparticles in the prepared composites was studied in the course of microbiological tests against *Aspergillus niger*. This strain is commonly used in microbiological studies as a model species as it is one of the most intensively studied and known eukaryotic organisms [13]. The *A. niger* strain was cultured at 30 °C for 14 days in a Petri dish containing a growth medium. In the passaging stage, the cells were transferred to sterile 250 cm^3 flasks containing 50 cm^3 of fluid growth medium and 0.07 g of the obtained composites or reference composite which did not contain nanoparticles. The cultures were incubated in a rotary shaker at appropriate temperatures not exceeding 30 °C. Cell growth was studied by measuring the increasing optical density using a spectrophotometer at a wavelength of 540 nm. Measurements were performed consecutively for 48 h at the same time each day.

3 Results

3.1 Nanometric Zinc Oxide

Figure 2 shows results of the analysis of zinc oxide physicochemical properties.

The shape of ZnO nanoparticles can be seen in a micrograph (Fig. 2a) from scanning by electron microscopy. They have a diverse size ranging from several dozen to several 100 nm. Results of the XRD analysis (Fig. 2b) showed that pure zinc oxide was obtained, as evidenced by reflections at angles of $2\theta = 31.7°$, 34.4°, 36.2°, 47.5° and 56.5°. In Fig. 2c one may observe a characteristic peak at a wavenumber of approximately 400 cm^{-1}, corresponding to the Zn–O bond. In addition, the peak at a wavenumber of about 3500 cm^{-1} is derived from vibrations of the OH group. Probably there were residual amounts of zinc hydroxide in the sample.

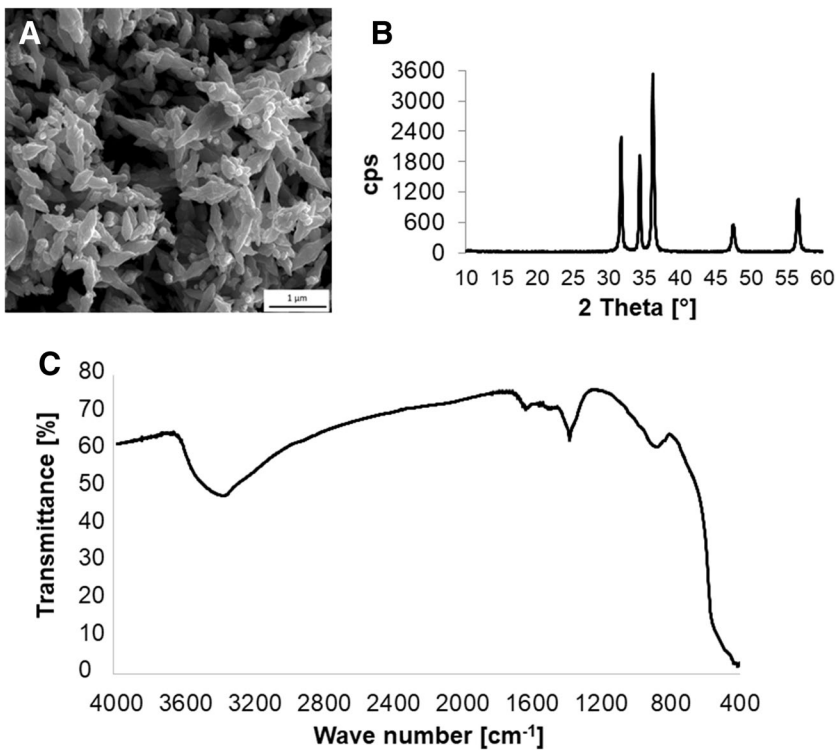

Fig. 2 **a** SEM microphotography, **b** XRD diffractogram, **c** FT-IR spectra of obtained zinc oxide

3.2 PVA-Based Composites with the Addition of Zinc Oxide Nanoparticles

White suspensions with undifferentiated density were obtained (Table 2). Basically, the greater amount of glycerine was used, the greater was the density of the obtained products.

Mappings of surfaces of the selected products are presented in Fig. 3 and results of the SEM–EDS analysis are provided in Fig. 4.

Thanks to the mapping and the SEM–EDS technique it was possible to determine the elemental composition and to visualize the surface of the selected materials. As expected, significant amounts of zinc oxide were identified in the selected samples of composites while in the reference sample mainly oxygen and carbon from other components were identified.

Figure 5 contains a collective plot of X-ray diffractometry analysis results. In all products, excluding the reference sample, the peaks characteristic for zinc oxide are visible at the angles between 30° and 60°. There is also a visible relationship between the intensity of counts and the percentage of ZnO. The highest peaks appeared in samples containing 5% of nanometric zinc oxide.

The selected samples were tested for rheological properties. Figure 6a shows viscosity curves, Fig. 6b shows flow curves. All composites exhibit similar properties. The addition of zinc oxide does not affect the rheological properties of the obtained products. This is desired due to their application properties.

3.2.1 Study of Zinc Leaching from Composites

The percentage share of zinc that is eluted from composites (Table 2) does not exceed 5%. This is a desired result since antimicrobial properties are not weakened due to the release of zinc. The results of this study were subjected to statistical analysis which aimed at indicating independent parameters significantly affecting the obtained data.

3.2.2 Zinc Penetration Through a Model Dermal Membrane

In all cases the concentration of zinc ions in acceptor liquids used in the study of the penetration of zinc through a model

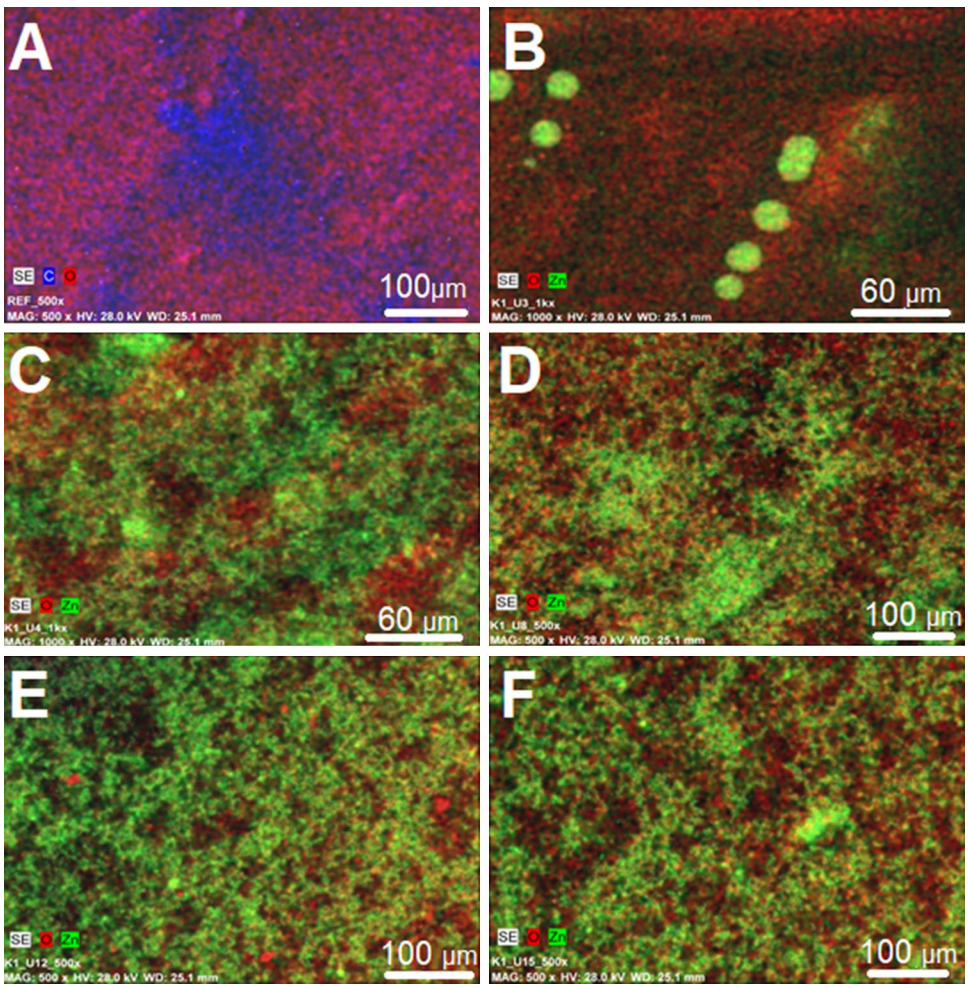

Fig. 3 Mappings of obtained composites: **a** C Ref., **b** C3, **c** C4, **d** C8, **e** C12, **f** C15

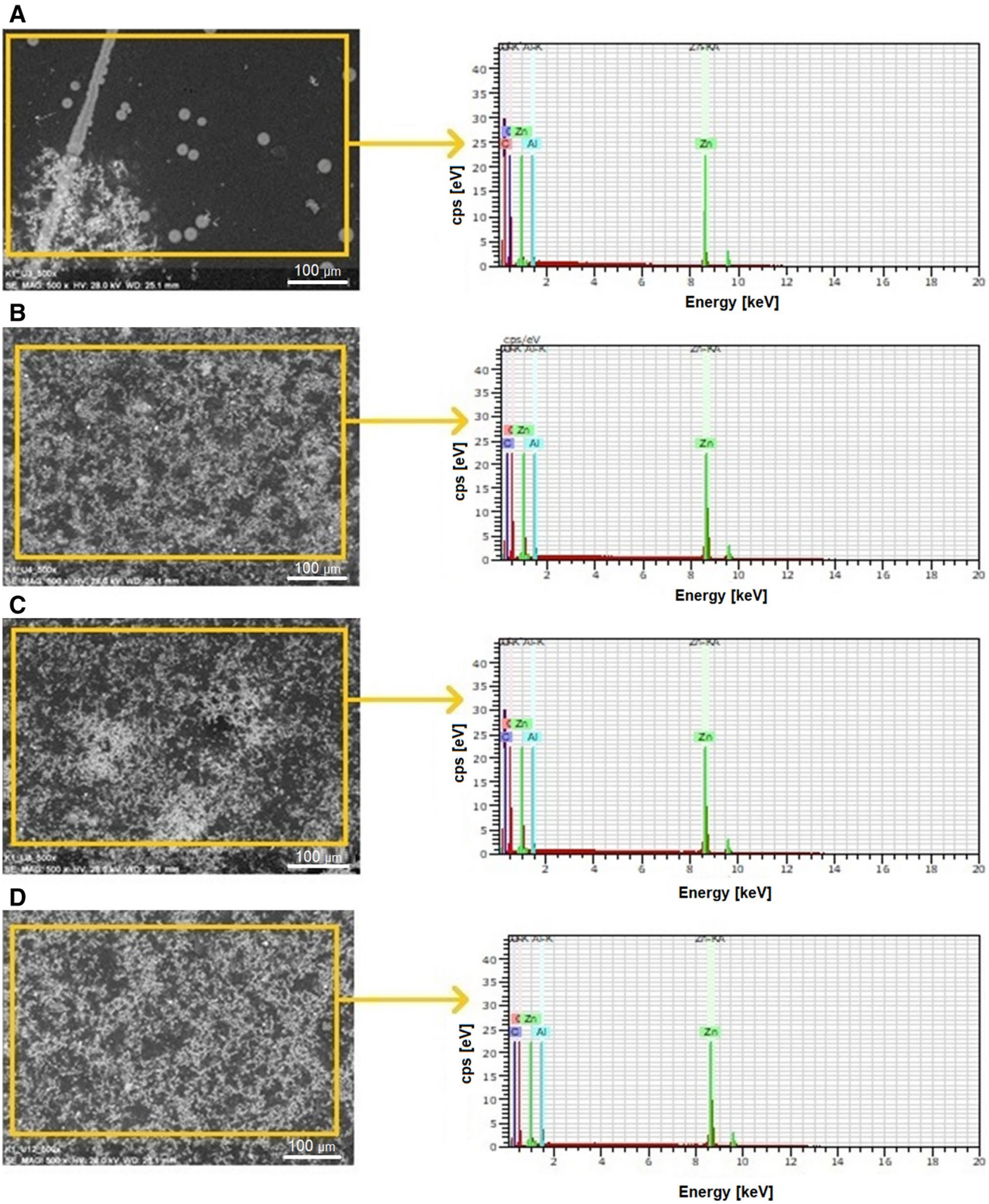

Fig. 4 Results of SEM–EDS analysis: **a** C3, **b** C4, **c** C8, **d** C12, **e** C15

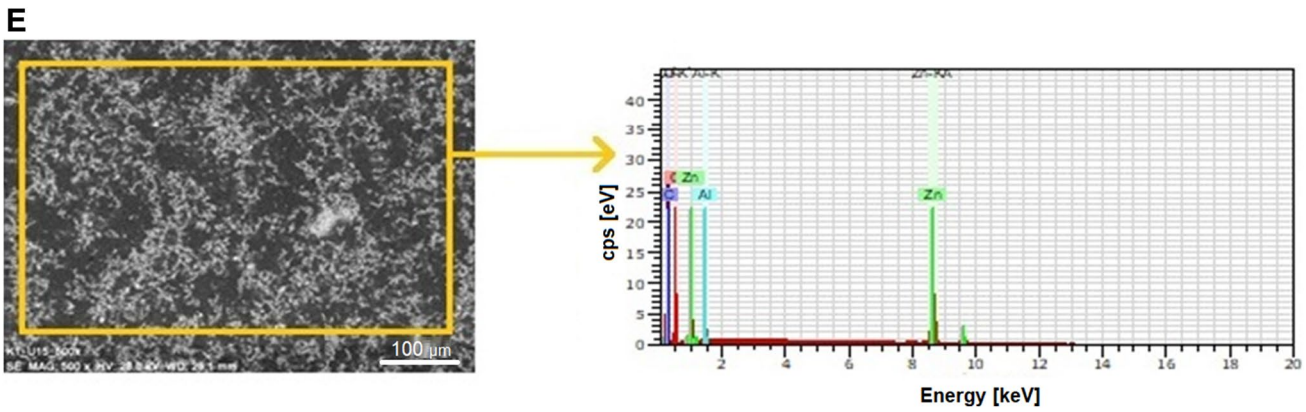

Fig. 4 (continued)

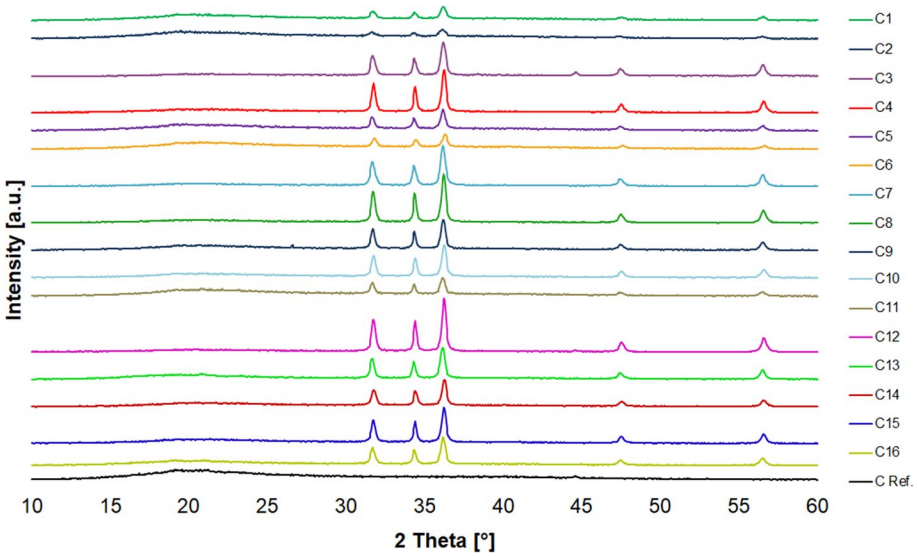

Fig. 5 Results of XRD analysis of all composites

dermal membrane was below the limit of quantification. That means that the active substance in a form of nanometric zinc oxide is not able to penetrate the skin of humans who have contact with the applied coatings.

3.2.3 Adhesive Properties

The study examined the strength that is needed to tear off the solidified composite coatings from a polypropylene surface. The results are included in Table 2. The influence of independent factors was checked during statistical analysis. The results indicate that the strength needed to tear off the composition is low. This is a beneficial situation because dried coatings could be removed easily.

3.2.4 Microbiological Properties

The results of optical density are presented in Fig. 7.

The addition of zinc oxide nanoparticles has a high impact on the viability and growth ability of the *A. niger* strain. It was revealed that all composites with zinc oxide nanoparticles inhibited the growth of the *A. niger* strain in the course of the analysis. The best results after 24 h were obtained in the case of C1, C2, C5 and C11 composites. The values of growth inhibition for these samples were: 94.8%, 92.0%, 91.7% and 91.4%, respectively. It was figured out that C8 and C6 exhibited the worst antifungal activity. The growth inhibition for them was equal to 0.3% and 38.6%. After 48 h the following growth inhibition values were obtained: 91.2% for C11, 83.0% for C10, 73% for C1 and 65.3% for C5. Samples C4 (7.2%) and C8 (15.8%) had a weaker antifungal activity. The difference in inhibition

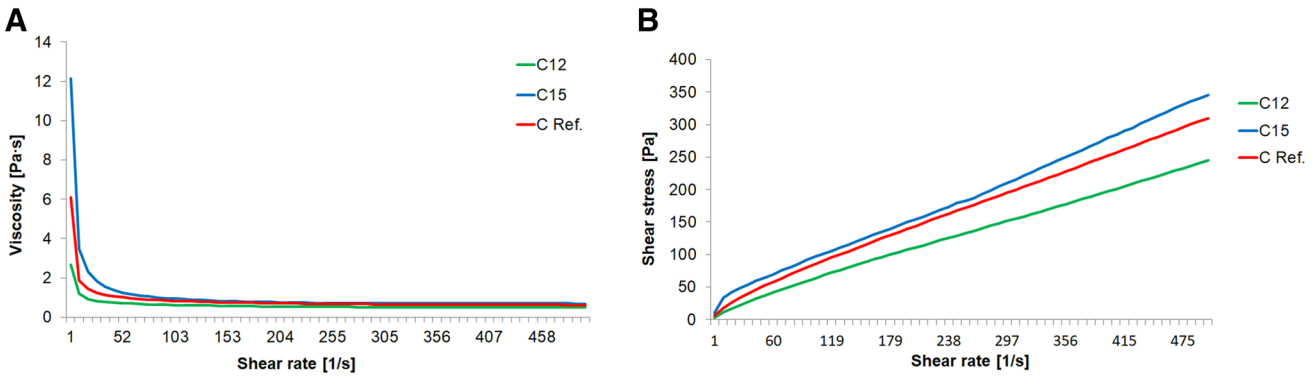

Fig. 6 Results of viscosity properties: **a** viscosity curves, **b** flow curves

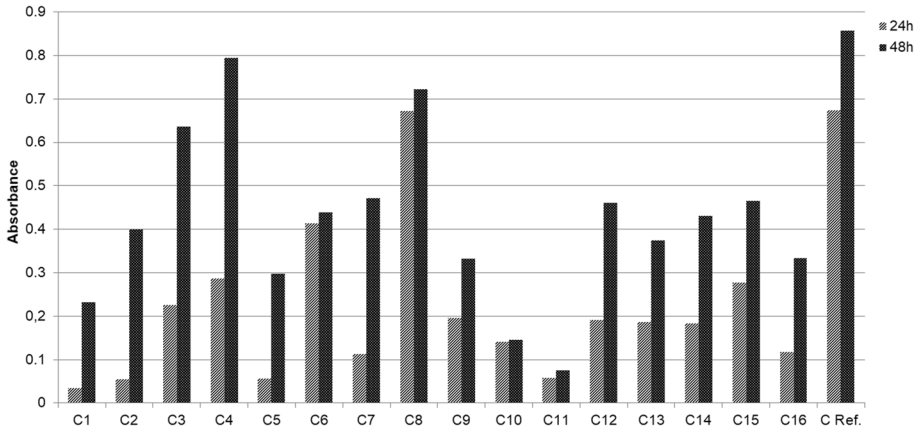

Fig. 7 Results of optical density measurements at $\lambda = 540$ nm

between samples is probably related to the ability of leaching of nanoparticles from composites to the culture medium. This is because the biological material was incubated in a liquid medium. To sum up, composite C8 was found as the best antifungal composition. It is directly related to the fact that the concentration of zinc eluted from this composite was equal to 4.4 (mg/dm^3) which was the highest value. The antimicrobial effect of PVA/ZnO nanocomposites was also confirmed by other scientists. Ahangar et al. [14] evaluated biocidal effect of such composites against the *E. coli* strain. The addition of zinc oxide nanoparticles to PVA resulted in the intensification of bacterial growth inhibition.

3.3 The Influence of Input Parameters on Properties of Obtained Composites

Statistical analysis was performed based on one-way analysis of variance (ANOVA). In order to evaluate the significance of the differences, an F-test was used. A value of $p < 0.05$ was established as significant in all cases. The profiles of the utility function with respect to certain independent parameters, thanks to which it was possible to determine changes in the dependent parameters when changing the values of independent parameters, were prepared.

The resulting approximation profiles allow us to provide specific values of input factors that ensure the most desirable (useful) estimated values of output factors. Approximated values are converted into a utility scale which includes the values of 0 (undesired effects) to 1 (desired effects). Thanks to the obtained approximation profiles, it was possible to optimize the usability of this product.

Figure 8 presents the Pareto charts for input parameters. Parameters which are statistically significant for the established p value ($p < 0.05$) are marked with a red line.

The concentration of glycerine in square function is the parameter which affects the elution of zinc from composites. As found by other researchers, the addition of metallic oxide nanoparticles to a polymer matrix has a great importance in creating their physicochemical and mechanical properties [15]. However, the force needed to tear off the composites from a polypropylene surface is dependent only on the temperature of samples prepared in linear function. The approximation profiles are presented in Fig. 9.

Based on an assessment of the approximation profiles, the influence of independent parameters on dependent variables

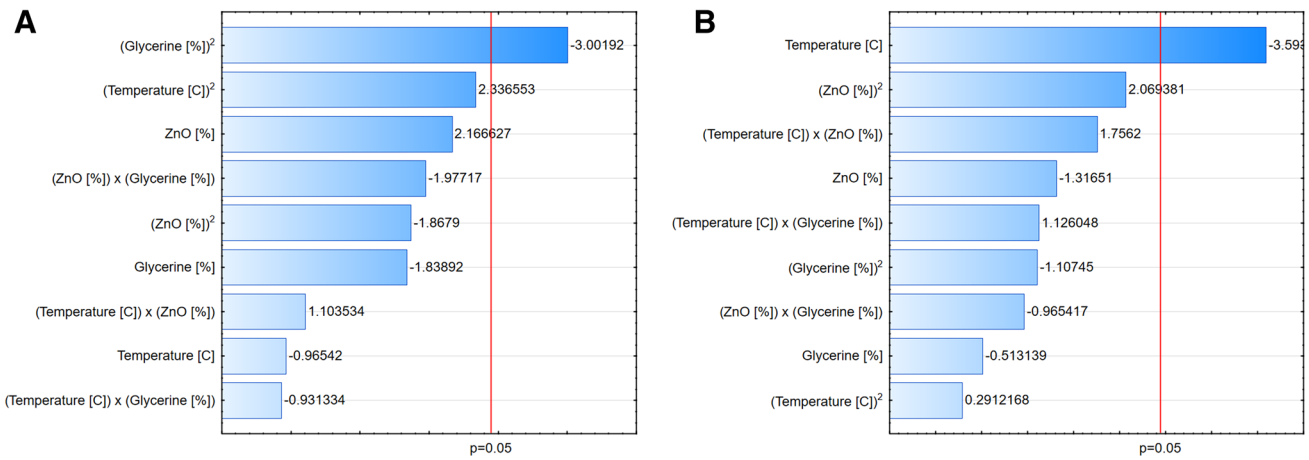

Fig. 8 Pareto charts for influence of input parameters on: **a** zinc leaching from composites, **b** strength needed to tear off composites

and determination of the specific values of input parameters ensure that reaching desired values of the output parameters is possible. Both the lower elution of zinc from composites and lower strength needed to tear off the composites are more desirable. When glycerine concentration influences the elution rate, one may observe an inflection point. Initially, when this value increases, the elution rate increases as well. After glycerine concentration reaches a value of 12.5, the elution rate begins to decay. Thus the most desired value of glycerine - in order to inhibit the release of zinc—among the tested values is equal to 17.0%. Therefore, the general conclusion is that the presence of glycerine favours the remaining zinc in composites. This may be due to the fact that glycerine which was used as thickening agent caused zinc to have a weaker ability to migrate from composites.

The influence of temperature on force needed to tear off the composites was as follows: a higher temperature caused decreasing of adhesive properties. This may be due to the fact that products obtained at a higher temperature were more flexible and thus the strength of their binding with the surface was weaker.

4 Discussion

The role of components in the prepared products was of crucial significance. Gelatin and guar gum swell in an aqueous medium, which leads to changes of suspension viscosity. By the addition of cellulose derivatives it was possible to form thixotropic gels that exhibited resistance to gravity. This feature is particularly desirable when it comes to coating, for example, ceilings. It is worth noting that the use of the substances mentioned above provided additional protection against agglomeration of dispersed zinc oxide nanoparticles [16, 17]. The adsorption of molecules of the said compounds on the surface of metal oxide nanoparticles gave them a surface charge that favours the electrostatic repulsion, which makes them kinetically stable. In order to increase the affinity of the resulting nanocomposite for a microbiological biofilm, it was necessary to add a substance for achieving the "hook effect". Extracellular polymers play a special role in the phenomenon of microbial adhesion to any surface. This group of compounds includes, inter alia, lipopolysaccharides and proteins. It is expected that the enrichment of the composition with compounds such as casein (protein), sucrose (carbohydrate) or chitosan (polysaccharide) will increase the adhesion of the biofilm to the applied material. It should be noted that the adhesion of microbial cells is a multistep process. It is affected by hydrodynamic forces, gravity, thermodynamic (Brownian motion) forces and van der Waals forces. The last ones favour efficient attraction of cells to the material surface. When the microbial cells are in a distance less than 1.5 nm from the material surface, then specific hydrogen bonding and covalent carbon–carbon bonds are formed. A chemical interaction of substances such as casein, sucrose, or chitosan with extracellular polymers that are produced by the microbial biofilm ensures better adhesion of the sprayed material [18–20].

Taking into consideration utility properties of the obtained products, the composition with best properties may be highlighted. This is composition C8 which was prepared at the highest temperature and when the concentrations of both glycerine and zinc oxide were the highest. However, this composite does not have the best antifungal properties. Taking into consideration all the desired properties, composite C10 may be highlighted as the best material.

5 Conclusion

At the beginning, nanometric zinc oxide was obtained by the hydrothermal method. The conducted analyses confirmed the purity of the obtained material. In the next part, the reference

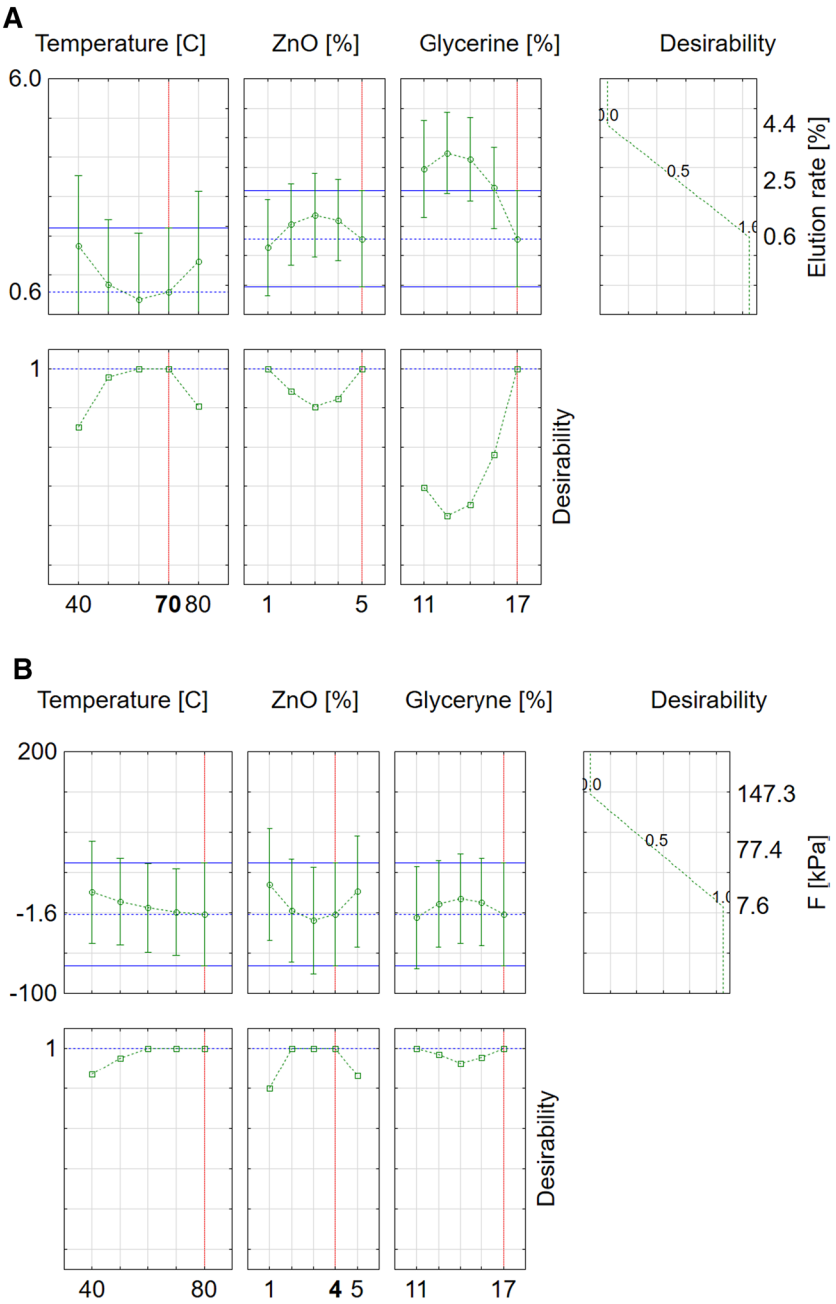

Fig. 9 Approximation profiles for influence of input parameters on: **a** zinc leaching from composites, **b** force needed to tear off composites

composition was developed, which was the basis for further research. The main ingredient was poly(vinyl alcohol), characterized by good solubility in water. The next step was to obtain 16 compositions containing the active substance that was previously prepared—zinc oxide nanoparticles. The adopted methodology allowed satisfactory incorporation of nanometric zinc oxide into the composite structure, as evidenced by the relatively low values of zinc concentration in the eluent solutions. In the last stage, samples of all compositions were analyzed for their physicochemical and utility properties. The penetration of zinc through model dermal membranes was also checked. In addition, microbiological tests were carried out for antifungal properties. The obtained composites have antimicrobial properties. After 24 and 48 h from application, a negative difference in the growth of *A. niger* was seen in comparison to the reference sample.

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Compliance with Ethical Standards

Conflict of interest The authors declare that there is no conflict of interests regarding the publication of this article.

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