Antimicrobial functionalization of Ca alginate-coconut oil latent heat storing microcapsules by Ag nanoparticles

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Summary
Latent heat storage by phase change materials (PCM) is a promising way of thermal energy storage for equilibrating the daily fluctuation of temperature in office- and home buildings. Bio-originated compounds have got great importance to evade further plastic contamination all over the world. Durability of biodegradable natural materials by means of environmentally friendly agents is an exciting challenge. In this study Ca alginate-coconut oil eco-friendly core-shell PCM microcapsules were functionalized with Ag nanoparticles, following their synthesis using harmless reducing agents. Throughout the preparation of the PCM microcapsules by repeated interfacial coacervation/crosslinking procedure, the Ag nanoparticles were homogeneously dispersed in the Ca alginate shell. High coconut oil content was achieved in the Ag nanoparticle-loaded microcapsules, which was not influenced by the Ag nanoparticle content. The high PCM content resulted in correspondingly high latent heat storing capability. The freezing and melting heat storing capacities were in the range of 83.6 and 85.6 J/g, as well as 89.7 to 92.6 J/g, respectively, matching to the extremely high PCM content in the range of 82.7% to 84.8% (m/m). Leaking of the heat storing microcapsules was not observed after 200 heating-cooling cycles. The Ag nanoparticle content did not influence the PCM ratio of the microcapsules, although as expected their antimicrobial potential was significantly enhanced by it. The highest Ag nanoparticle loading, that was 1.3% (m/m) related to the total mass of microcapsules, exerted excellent antibacterial and antifungal impact.

KEYWORDS
Ag nanoparticles, antimicrobial effect, calcium alginate, coconut oil, eco-friendly microcapsules, energy storage, phase change materials

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1 | INTRODUCTION

Energy storing systems have got crucial importance due to the enormously increased population and energy demand, which led to the steeply growing carbon dioxide concentration in the atmosphere and climate change. Phase change materials (PCM) are capable to store and release latent heat, which enables higher thermal storing capacity and—density compared to sensible heat as well as low temperature swing. They have been widely studied for renewable energy utilization in buildings and solar cells, waste heat recovery, thermal comfort in textiles, preservation of biological substances, thermal regulation and management in photovoltaic-thermoelectric systems, pharmaceutical or biological products and protection of electronics from undercooling. PCMs have substantially higher thermal energy-storage densities related to sensible heat-storing materials, moreover, they can improve the energy efficiency by harmonizing the energy demand and availability, hence decreasing the waste of energy. Organic PCMs, such as fatty acids and paraffins are commonly used latent heat storing materials because of their versatile phase change temperature, and thus, potential wide range of use. Although they have some limitations, including low thermal conductivity, supercooling, phase segregation, and volume change during the phase change. To overcome these disadvantages and widen their application, microencapsulation provides important benefits such as increased heat transfer area, decreased supercooling, controlled volume change during melting and freezing, reactivity reduction and leakage prevention. Coacervation, emulsion-solvent evaporation, polymerization, spray drying, sol-gel methods and coating techniques have been widely used for the microencapsulation of PCMs.

The common PCM entrapment strategies using durable but non-recyclable and non-degradable polymers require waste processing at additional cost after use. In the food or pharmaceutical thermal control processes, the use of biocompatible materials takes important role, for example, Unal et al. entrapped octanoic acid PCM by polystyrene to thermally control food products. According to the author’s aim, the polystyrene was chosen because of its human compatible nature. Nevertheless, a biocompatible and biodegradable polymer can have additional benefit considering the sustainable technologies. Bio-originated compounds should be favored against non-degradable materials to repel the accumulating waste all over the world. Coconut oil composed of mostly fatty acids freezes and melts around room temperature. It is characterized by high latent heat capacity, non-toxicity and non-corrosivity, thus, it is a promising biocompatible PCM which was found to be suitable for form-stabilization or microencapsulation. Coconut oil showed better oxidative properties than other vegetable oils, because it contains saturated fatty acids, though oxidation and microorganisms can cause deterioration. Alginate is a renewable resource that is gained from brown algae. Due to its non-toxicity, biocompatibility and suitability for matrix- or shell formation, it is widely used in numerous microencapsulation applications especially in drug delivery and environmental decontamination.

In our group a novel method was developed to use Ca alginate to entrap paraffin PCM in order to obtain core-shell microcapsules with high heat storing capacity. Recently, entirely eco-friendly microparticles were prepared by a scaled-up procedure using the same shell material, however, encapsulating coconut oil. These fully bio-originated microcapsules possessed high PCM content (81.1% m/m) together with compact shell. Ca alginate is supposed to have antimicrobial effect, however, we experienced that subjecting it to water, our microcapsules were infected by mildew within some weeks. Therefore, to increase the lifetime of Ca alginate microcomposites, it is essential to supply them with an effective antimicrobial agent. Antimicrobial protection of PCM-loaded microcapsules have got various mode of action, for example, enhancement of photocatalytic activity by TiO2 or ZnO or application of antibacterial silver. Silver (Ag) nanoparticles are widely examined metallic nanoparticles against both gram-positive and gram-negative bacteria, which have been mostly utilized in the biomedical and pharmaceutical industry and food packaging. Ag nanoparticles perform improved antimicrobial effect owing to their large surface area, thermal stability, and sustained Ag release. Numerous physical, chemical, and biological methods have been used to prepare Ag nanoparticles. Chemical reduction in the presence of a stabilizing agent is the most common method for the synthesis of Ag nanoparticles, since it is a simple and efficient method for the industrial production and does not require expensive equipment. However, many reducing agents with high reactivity, such as hydrazine and N,N-dimethylformamide may exhibit potential toxicity to the environment and organisms. Ag nanoparticles can be synthesized by “green chemistry” with an eco-friendly solvent medium and a natural reducing agent to decrease the toxic effects of the procedure. Dimitrijević et al. developed a variety of wet-chemical methods to prepare Ag nanoparticles from silver nitrate solution with hydrazine hydrate and ascorbic acid as reducing agents.

In some work Ag is used to crosslink alginate to prepare particles or beads for theranostic and catalytic
purposes. More frequently, Ag nanoparticles are adsorbed or encapsulated by Ca alginate composites, for example, for catalytic,\textsuperscript{28} food packaging\textsuperscript{29} or water disinfection\textsuperscript{30} activity. However, to our knowledge Ag nanoparticles have not been used so far in PCM capsules entrapped by Ca alginate.

Since bio-originated PCM-loaded microcapsules have importance in some applications, such as thermal control of food or pharmaceuticals, we aimed at the functionalization of our recently developed eco-friendly coconut oil-loaded Ca alginate microcapsules to meet the requirements of these industries. The biodegradable character can also be a drawback of the bio-originated materials. Hence, in the present work we aimed at the antimicrobial functionalization of these microcapsules to enable their long term use. The loading of microcapsules with Ag nanoparticles prepared with an environmentally friendly process, supply the microparticles with antimicrobial functionality and can broaden their usability. The main novelty of these latent heat storing microcapsules is the eco-friendly formation throughout the whole process involving also the antimicrobial functionalization.

2 | MATERIALS AND METHODS

2.1 | Materials

Sodium alginate (viscosity at 25°C, concentration 2 w/v %: 950 mPas) was bought from Cargill (Wayzata, Minnesota). Nitric acid (Suprapur 65%), Hoechst 33342 stain, propidium iodide, CaCl\textsubscript{2}7H\textsubscript{2}O, MgSO\textsubscript{4}7H\textsubscript{2}O, CuSO\textsubscript{4}5H\textsubscript{2}O, ZnSO\textsubscript{4}7H\textsubscript{2}O were purchased from VWR International Kft. (Debrecen, Hungary). Agar-agar was produced by Scharlau Chemie S.A. (Spain), sucrose, yeast extract and 2,3,5-triphenyl-tetrazolium chloride (TTC) were purchased from Sigma-Aldrich (St. Louis, Missouri). Coconut oil was obtained from Soya Group Ltd. (Győr, Hungary). Petroleum ether (boiling temperature 60°C-62°C) was purchased from Lach-Ner s.r.o (Nereticev, Czech Republic). AgNO\textsubscript{3}, sodium citrate and sodium nitrate were also from VWR International Kft. (Debrecen, Hungary). All chemicals were of analytical grade and were used as purchased. For preparation of all aqueous solutions distilled water was used.

The applied three fungal strains belong to the species suggested by the Hungarian standard MSZ EN 60068-2-10:2005/A1:2018:
- Penicillium funiculosum NCAIM F 00689.
- Paecilomyces variotii NCAIM F 00862.
- Trichoderma viride NCAIM F 00795.

YES-05 medium (Table 1) was used for the growing of the fungi.

| Table 1 | YES-05 medium |
|---------|---------------|
| Yeast extract | 10 g |
| Sucrose | 75 g |
| MgSO\textsubscript{4}7H\textsubscript{2}O | 0.25 g |
| CuSO\textsubscript{4}5H\textsubscript{2}O | 0.0025 g |
| ZnSO\textsubscript{4}7H\textsubscript{2}O | 0.0005 g |
| Agar-agar | 10 g |
| Distilled water | 1000 ml |
| Sterilization | 121°C, 15 minutes |

2.2 | Ag nanoparticle preparation

Solution “A”:
- 880 ml MilliQ water.
- 50 ml 0.2 M sodium citrate.
- 20 ml 0.2 M AgNO\textsubscript{3}.

Solution “B”:
- 30 ml MilliQ water.
- 20 ml 0.2 M sodium ascorbate.

Solution “A” was poured into solution “B” (1000 rpm) in a beaker under stirring at 1000 rpm (IKA XY [IKA, Staufen, Germany] equipped with a propeller stirrer), and the mixing was continued for 1 hour. Then, the dispersion was added into a measuring cylinder and sedimented overnight. The clear supernatant was removed by a peristaltic pump, and the rest was centrifuged with 8500 rpm at 24°C for 30 minutes by a Sorvall Discovery 90SE ultracentrifuge (Thermo Scientific, Waltham, Massachusetts). After the removal of the supernatant, the particles were resuspended in 20 ml MilliQ water and centrifuged with a Sorvall Discovery 90SE ultracentrifuge (Thermo Scientific) with 70 000 rpm at 21°C for 20 minutes. The supernatant was removed and the particles were redispersed in MilliQ water resulting in 27 ml suspension that was sonicated by a Sonics Vibra Cell VCX 130 (Sonics & Materials Inc., Newtown, Connecticut) for 3 x 30 seconds at a power of 40%.

2.3 | Ag nanoparticle analysis by X-ray photoelectron spectroscopy

The washed Ag nanoparticles were dried at 60°C in an oven, and X-ray photoelectron spectroscopy (XPS) study was performed by an EA 125 electron spectrometer (Omicron Nanotechnology GmbH, Germany) with non-monochromatic MgK\textalpha (1253.6 eV) excitation to analyze the composition. The powder sample was suspended in isopropanol and drops of this suspension were dried onto a standard stainless steel sample plate. The measured
spectra were evaluated using the CasaXPS and the XPS MultiQuant software packages.

2.4 | Formation of calcium alginate-coconut oil microcapsules

The microcapsules were prepared by the repeated interfacial coacervation/crosslinking method that was described in detail by Németh et al. The preparation method can be seen in Figure 1.

2.4.1 | Formation of the core particles

Twenty-two grams 2% (m/m) sodium alginate solution in MilliQ water (AG0) was mixed with 8 g coconut oil at 30°C then homogenized by a Sonics Vibra Cell VCX 130 (Sonics & Materials Inc., Newtown, Connecticut) for 3 × 30 seconds at a power of 40%. The formed emulsion was pipetted dropwise to 4% (m/m) CaCl₂ solution under magnetic stirring (200 rpm) and stirred further 30 minutes. The prepared core particles were filtered, and air dried.

2.4.2 | Formation of the blank microcapsules (without Ag nanoparticles)

The core particles were placed in 1.3% (m/m) sodium alginate solution for 10 minutes, then the particles were separated by filtration and poured into 4% (m/m) CaCl₂ solution and stirred for 30 minutes using mild magnetic stirring (200 rpm). The microcapsules were filtered and washed with distilled water, then, dried in a fluidized bed dryer at 120°C for 15 minutes.

2.5 | Formation of Ag-loaded calcium alginate-coconut oil microcapsules

The compositions of the Ag nanoparticle dispersions for Ca alginate shell formation are shown in Table 2. Ag nanoparticle dispersions were prepared as follows: 25 g 2.5% (m/m) sodium alginate solution in MilliQ water was added to 25 ml AG1, AG5 or AG10 dispersions (Table 2) under magnetic stirring and the mixtures were sonicated by a Sonics Vibra Cell VCX 130 (Sonics & Materials Inc.) for 3 × 30 seconds at a power of 40%. The obtained dispersions contain 1%, 5% and 10% Ag.
respectively. The formed cores described in Section 2.4.1. were added to the Ag nanoparticle dispersion containing sodium alginate solutions and stirred for 10 minutes, then, after filtration the particles were poured to 4% (m/m) CaCl$_2$ solution and stirred for 30 minutes using mild magnetic stirring (200 rpm). The microcapsules were filtered and washed with distilled water, then, dried in a fluidized bed dryer at 120°C for 15 minutes.

2.6 Analysis of yield, coconut oil content, size, morphology and chemical structure of microcapsules

The yield of microcapsules was determined by gravimetry (Equation 1). For the determination of PCM content 0.15 g of each type of microcapsules was ground with a micro-ball mill (Narva Vibrating mill, Knoxfield, Australia), then, the coconut oil content was extracted by 20 ml petroleum ether and vacuum filtered. The organic solvent was evaporated in vacuum (Heidolph Laborota 4001) and the remaining coconut oil was weighed (Equation 2).

\[
\text{Yield (\%) = \frac{\text{microcapsule mass (g)}}{\text{mass of alginate (g) + coconut oil (g) + CaCl}_2 (g) + \text{Ag nanoparticle in the preparation process}}} \times 100
\]

\[
\text{Coconut oil content in microcapsules (\%) = \frac{\text{coconut oil mass extracted from microcapsules (g)}}{\text{total mass of microcapsules (g)}}
\]

The size of the Ag nanoparticles was measured using a Zetasizer Nano ZS (Malvern Instruments, Malvern, UK) based on photon correlation spectroscopy. The size of Ag-loaded calcium alginate-coconut oil microcapsules was investigated by an optical microscope (Carl Zeiss, Oberkochen, Germany). Fifty particles per sample were measured, and the average values and standard deviations were calculated.

The morphology of microcapsules was imaged with FEI Apreo scanning electron microscope (SEM; Thermo-fisher) at 20 kV acceleration voltage.

FTIR measurements were recorded on a Jasco FT/IR-4600 (Japan) system, equipped with a Jasco ATR Pro One single reflection diamond ATR accessory (incident angle 45°), and a DLATGS detector operating in the 4000 to 400 cm$^{-1}$ interval. A resolution of 4 cm$^{-1}$ and co-addition of 64 individual spectra were applied. Prior to the evaluation, an ATR correction (Jasco Spectra Manager version 2, Spectra analysis module version 2.15.11) was performed on the raw spectra. The capsules were ground in an agate mortar and the resulting paste (containing both the shell and the inner PCM material) was placed on the crystal.

2.7 Thermal analysis of microcapsules

The heat storing properties of the microcapsules were determined by a Setaram μDSC3evo (Lyon, France) differential scanning calorimeter (DSC). Each sample was weighed directly into the calorimeter’s batch vessel and was cycled three times in the temperature range of −10°C to +45°C, first time by a scanning speed of 0.4°C/min, followed by two cycles with a rate of 0.2°C/min. The results were processed by using Calisto Processing software (ver. 2.05), corresponding melting/freezing enthalpies, and the extrapolated onset temperatures were determined using the baseline integration method (Tangential sigmoid baseline type used).

Thermogravimetric analysis was performed on a LabsysEvo (Setaram, Lyon, France) TG-DSC system, in flowing, high purity synthetic air (20 v/v % oxygen, 80 v/v % nitrogen, flow rate 90 ml/min). The samples were weighed into 100 μL alumina crucibles and were analyzed in 25°C to 1000°C temperature range, with a heating rate of 10°C/min. A 300 μm hole was drilled into the shell of the microcapsules in order to avoid their jump out from the crucible due to the vaporization and sudden pressure release of the inner coconut oil content. The obtained data was baseline corrected and further processed with the thermoanalyzer’s processing software (Calisto Processing, ver. 2.06). The thermal analyzer (both the temperature scale and calorimetric sensitivity) was calibrated by a multipoint calibration method, in which seven different certified reference materials were used to cover the thermal analyzer’s entire operating temperature range.

Cyclic thermal tests were done following the method of Sari and Karaipekli in a testing setup composed of a

| Table 2 Composition of the Ag nanoparticle (AgNP) dispersions for Ca alginate shell formation |
|---------------------------------|--------------------------------|--------------------------------|
| Ag dispersions | V$_{\text{AgNP}}$ (ml) | V$_{\text{MilliQ}}$ (ml) |
| Ag1 | 0.7 | 24.3 |
| Ag5 | 3.5 | 21.5 |
| Ag10 | 7.0 | 18.0 |
metal sample holder with trays for the PCM microcapsules. A thermoelectric Peltier unit heated and cooled the samples, which was controlled by a PC. About 0.15 to 0.20 g per sample was placed into the holder, and 200 heating/cooling cycles between 3°C and 43°C were carried out corresponding to 9 hours test duration. After the thermal cycling test, DSC measurements have been done to compare the melting/freezing enthalpies with the original values in order to investigate the potential leakage of the microcapsules.

2.8 Determination of Ag content with ICP-MS

About 0.4 ml high purity concentrated nitric acid was added to the samples (0.1 ml solutions) to digest the organic material. After 24 hours the sample solutions were completed up to 5 ml with ultrapure water (Elga Purelab, 18.2 MΩ cm⁻¹) into analytical flasks (5 ml) and diluted 10-fold for the measurements with a Thermo Scientific iCAP Q ICP-MS (Thermo Scientific) instrument with quadrupole mass filter in KED mode (Kinetic Energy Discrimination) with helium gas. Three blank samples were prepared as follows: 0.4 ml Suprapur nitric acid was filled with ultrapure water up to 5 ml in analytical flask and diluted 10-fold for the ICP-MS measurement.

2.9 Antibacterial assay

Antibacterial efficiency of nanoparticles was tested on the flagellin deficient Salmonella serovar Typhimurium strain SJW2536 containing the ampicillin (Amp) resistant pKOT-1 plasmid (pKOT-1/SJW2536) to enable the control of the exclusive growing of this particular bacteria on Amp containing culture medium. A 3 ml Luria Broth (LB) medium containing 100 µg/l Amp was inoculated with pKOT-1/SJW2536 from a freshly prepared LB/Amp plate and grown overnight at 37°C with vigorous shaking (285 rpm). Three milliliters LB/Amp fresh medium was inoculated with 3, 6 and 15 µl starter culture, respectively, and grown at 37°C and 285 rpm. After 3 hours, optical density of the cultures at 600 nm (OD600) was measured and found to be 0.11, 0.22 and 0.45 for the 3 (A), 6 (B) and 15 (C) µl induced cultures, respectively. Flow cytometry was used to determine the cell number. The cells were stained with Hoechst 33342 and propidium iodide. Flow cytometry was performed on a Beckman Coulter Gallios Flow Cytometer (Brea, California) at Ex/Em wavelengths of 488/620 nm for propidium iodide and 405/450 nm for Hoechst 33342. LB medium was removed by the centrifugation of 1 ml culture for 5 minutes at 6000 g to avoid further bacteria growing and the cell pellets were resuspended in 1 ml MilliQ water. This step was repeated once more. The cell suspensions were diluted to get cell numbers of 2 × 10⁵/ml, 4 × 10⁵/ml, 2 × 10⁶/ml and 4 × 10⁶/ml by the addition of MilliQ water. About 28.5 ± 0.9 mg microcapsules prepared using 0%, 1%, 5% and 10% Ag, respectively, were placed into 2 ml Cliklok microcentrifuge tubes with conical bottom (Simport, Beloeil, Canada) and 1 ml of each cell suspension was pipetted onto them, resulting in all together 16 samples. As negative control, bacterial dilutions without microcapsules were also incubated. The microcentrifuge tubes with the cell suspensions were gently rotated on a Bio RS-24 Mini-Rotator (BioSan, Riga, Latvia) at room temperature. In order to check the survival of the cells after 6 and 24 hours, 100 µl sample from every tube was added to 900 µl LB/Amp media and grown for 16 to 20 hours at 37°C with vigorous shaking (285 rpm). Presence of cells was detected visually by the change of turbidity of the overnight cultures. Another 100 µl of the 6 and 24 hours rotated samples, respectively, were collected for Ag analysis using ICP-MS.

2.10 Antifungal assay

Calcium alginate-coconut oil beads with or without Ag were dip-coated for 20 seconds with fungus suspensions with concentration 10⁶ spores/ml and stored on filter paper at 25°C for 3 hours. Then, one infected microcapsule was put into 4 ml YES-05 medium in a test tube, and incubated at 25°C for 4 days. Finally, the mycelium diameter was recorded and calculated to the volume of the mold colony.

3 RESULTS AND DISCUSSION

3.1 Nanoparticle composition

The composition and the oxidation state of the silver nanomaterial were checked by XPS. The identification of the photoelectron features, the amount and the probable chemical state of the components of the sample are summarized in Table 3. XPS indicated the presence of silver in the sample, along with carbon and oxygen, which may be assigned both to remnants of the compounds used for synthesis or to adsorbates collected during exposure to atmospheric ambient, so their presence is not surprising. No other contaminants were detected in quantities exceeding the detection limit of XPS (0.1-1 at%).
The carbon content may arise from both the organic moieties of the synthesis mixture, which were incompletely removed from the silver particles after washing, and the naturally developing adventitious hydrocarbon contamination layer collected from the ambient. The dominant hydrocarbon peak accompanied by significantly weaker contributions from more or less oxidized carbon species is a general feature of both types of carbonaceous contamination. Nevertheless, the relatively high carbon content suggests that carbonaceous species from both sources are present on the surface of the silver particles.

The spectral features of silver (the binding energy of the Ag 3d_{5/2} peak, the kinetic energy of the Ag MNN Auger peak, the shape of the valence band and the MNN Auger region and the presence of the Fermi edge) indicate that the sample is almost exclusively metallic. Only a marginal component observed at the high binding energy side of the Ag 3d_{5/2} peak suggests that the sample may contain some ionic silver. It must be noted that distinction between the different oxidation states of silver based on the Ag 3d_{5/2} binding energy is difficult as peak positions from Ag, Ag_{2}O and AgO almost completely overlap. The line shape and peak position of the Ag MNN Auger transitions show a much more pronounced variation with the oxidation state, however, if the sample contains only a small amount of oxidized silver, ionic contributions to the Auger spectra can still be masked by the dominant metallic features.

The oxygen content of the sample arises from two distinct sources. The more intense contribution to the O 1 second spectrum around 533 eV binding energy can be assigned to oxygen in the carbonaceous contamination layer. However, a weaker peak at 530.8 eV conclusively points to silver-bound oxygen species. Taking this into account, the tiny high binding energy Ag 3d_{5/2} contribution can most probably be assigned to a satellite of the peak of AgO, which is not masked by the strong metallic signal.\textsuperscript{35} Both of this Ag-oxide contribution and the peak of the silver-bound oxygen rapidly decreased during the XPS experiment, indicating the fast decomposition of the oxide fraction.

Considering these observations, it can be stated that the silver material is predominantly metallic with a few percent of oxide content which is presumably located on the surface of the air-exposed particles.

### 3.2 Physical and chemical characterization of microcapsules

Ag nanoparticle size was investigated by photon correlation spectroscopy. The aggregation of Ag nanoparticles had to be avoided in the microcapsule product, hence, it was studied whether the high Ag nanomaterial content (5% and 10% related to the sodium alginate mass) caused agglomeration in its solution. The synthesized nanoparticles had a mean size of 131.6 ± 5.3 nm accompanied with a wide size distribution. Although aggregation was observed using 5% and 10% Ag nanoparticles in sodium alginate solution, their size remained in the submicron size range (Figure 2).
The Fourier transform infrared (FTIR) spectra of the calcium alginate, coconut oil and control, silver non-containing capsule are presented on Figure 3. In the spectra of the calcium alginate, stretching vibrations of the O–H bonds ($\nu_{O-H}$) as a wide absorption band appears between 3000 and 3500 cm$^{-1}$. This strong absorption band can be attributed to the high water content of the sample, which is also confirmed by the thermal measurement results. The small shoulder at 2935 cm$^{-1}$ corresponds to the stretching vibrations of aliphatic hydrocarbon bonds ($\nu_{C-H}$) present in the polysaccharide structure. The absorption band at 1592 cm$^{-1}$ can be assigned to the asymmetric ($\nu_a$), while the band at 1415 cm$^{-1}$ to the symmetric ($\nu_s$) stretching vibrations of the COO$^-$. The band at 1078 cm$^{-1}$ corresponds to the C–O stretching vibration of the pyranosyl ring, while the band at 1019 cm$^{-1}$ correspond also to the vibrations of C–O–C and C–C bonds ($\nu_{C-O}$, $\nu_{C-C}$). In the spectra of coconut oil, three more or less overlapped, strong absorption bands (2954, 2920 and 2851 cm$^{-1}$) can be seen in the 2800 to 3000 cm$^{-1}$ region, which can be attributed to the asymmetric C-H vibrations in methyl, asymmetric vibrations of methylene and symmetric vibrations of methylene. The strong and sharp absorption band at 1741 cm$^{-1}$ corresponds to the C=O stretching in the triacylglycerols. Vibrations in the lower wavenumber region characteristic to the C–O stretching, symmetric and asymmetric deformation stretching of hydrocarbon chains are also observable. The spectra of control sample (containing no silver) looks like a superposition of the two previously described spectra, with a dominance of the absorption bands specific to the coconut oil.

The FTIR spectra of the different silver containing capsules (Figure 4), similarly to the results obtained from thermal measurements, strongly resembles to the spectra of the control microcapsules. It can also be noticed that many absorption bands (eg, C=O, C–O) are shifted to lower wavenumber regions, which proves the chelation with Ca$^{2+}$ ions. The presence of silver does not have any influence on the spectrum of the Ag containing samples compared to that of the control sample.

The DSC measurements of coconut oil showed $108.2 \pm 1.3$ J/g melting and $101.4 \pm 1.2$ J/g freezing enthalpy changes, while $92.6 \pm 0.9$ J/g and $85.1 \pm 0.6$ J/g, respectively, for unloaded Ca-alginate-coconut oil microcapsules (Figure 5). The Ag nanoparticle content did not have any substantial effect on heat storing capacity, neither on the heat conductivity, since $91.0 \pm 0.6$ J/g and $85.6 \pm 1.0$ J/g for 1% (m/v) Ag, $89.7 \pm 0.7$ J/g and $83.6 \pm 0.8$ J/g for 5% (m/v) Ag, and $90.8 \pm 1.0$ J/g and $84.6 \pm 1.2$ J/g for 10% (m/v) Ag were found for the melting and freezing enthalpies, respectively. These high latent storing enthalpies are very similar to those found by Konuklu and Erzin very recently for pentadecane-loaded...
poly(melamine-urea-formaldehyde) microcapsules, although pentadecane has significantly higher energy storing capacity. The lower thermal performance of coconut oil was compensated by the extremely high PCM content in our microcapsules.

The yield of the PCM-loaded microcapsule formation was calculated considering all of the used chemicals in the process (Table 3). The weight loss of the procedure derived mostly from the excess of CaCl₂ and partly from the washed alginate. The yield of Ag nanoparticle synthesis took also a tiny part of the yield, since it displayed 68.1% ± 3.8%. The coconut oil content of the latent heat storing microcapsules was measured by gravimetry after extraction with petroleum ether, and it can be calculated also from the DSC results by comparing and proportioning the melting and freezing enthalpies of the microcapsuled samples to the corresponding values of pure coconut oil (Figure 5). The two methods resulted in very similar coconut oil content in the microcapsules (Table 4). Moreover, the Ag nanoparticles did not influence the coconut oil loading, since their ratio compared to the total mass of microcapsules was almost negligible, even in the case of higher Ag concentration, because they are present only in the shell material, which is around 15% of the total capsule mass. This means approximately 1.3% (m/m) Ag concentration in relation with the total capsule mass in the case of the highest Ag loading.

The Ag content in the microcapsules was measured by ICP-MS. The Ag concentration in the shell of micro-particles was lower than the initial one in the shell solution (Table 5), which is the consequence of the fact that during the core preparation, the emulsion also contained alginate solution, though Ag nanoparticles were not added to it. The alginate in the core was substantially lower in weight than the shell forming alginate loaded by Ag nanoparticles. The core-forming alginate decreases the Ag ratio of the Ca alginate shell, since it is also included in the calculation of the Ag content, however, it could be dispersed in the core or partly coalesced with the shell.

The size of Ca alginate microcapsules was neither affected by the Ag nanoparticle loading (Table 6) similarly to the coconut oil content of the microspheres also due to the low ratio of Ag nanomaterials. Optical and scanning electron microscopy was performed for morphological analysis of the microcapsules. Optical microscopy showed spherical microcapsules, though smaller and deeper roughness and dents could be observed on their surface (Figures 6). Nevertheless, breaking of the capsules was not detected with this imaging method. By increasing the Ag content, the roughness of the microcapsule surface was enhanced. The thickness of microcapsule shell was typically 20 to 40 μm (Figure 7B,F). In reflection mode, the increasing amount
FIGURE 5  DSC traces of coconut oil, A, as well as Ca alginate-coconut oil microcapsules prepared using 0%, B, 1%, C, 5%, D, and 10% (m/v), E, Ag nanoparticles [Colour figure can be viewed at wileyonlinelibrary.com]

TABLE 4  Yield and coconut oil content of microcapsules prepared using different concentration of Ag nanoparticles calculated from gravimetric and DSC analyses

| Initial Ag content in sodium alginate solution (% m/v) | Yield (%) | Coconut oil content in microcapsules (%) |
|------------------------------------------------------|-----------|----------------------------------------|
|                                                      |           | Gravimetry | DSC         |
| 0.0 (control)                                        | 72.2 ± 6.4| 85.0 ± 3.8 | 84.8 ± 3.6  |
| 1.0                                                  | 73.0 ± 4.6| 83.9 ± 3.9 | 84.3 ± 2.7  |
| 5.0                                                  | 72.4 ± 4.9| 83.2 ± 3.2 | 82.7 ± 2.3  |
| 10.0                                                 | 70.9 ± 5.4| 84.2 ± 3.9 | 83.7 ± 3.1  |

TABLE 5  Ag content of Ca alginate microcapsules by varying initial concentration in the sodium alginate solution

| Initial Ag content in sodium alginate solution (% m/v) | Ag concentration related to Ca alginate content in microcapsules (% m/m) |
|-------------------------------------------------------|-------------------------------------------------|
|                                                      | 0.82 ± 0.08                                     |
| 1.0                                                  | 3.69 ± 0.17                                     |
| 10.0                                                 | 8.38 ± 0.88                                     |

TABLE 6  Size of Ca alginate microcapsules as a function of Ag nanoparticle concentration

| Initial Ag content in sodium alginate solution (% m/v) | Size (mm) |
|-------------------------------------------------------|-----------|
| 0.0                                                  | 2.59 ± 0.14|
| 1.0                                                  | 2.61 ± 0.11|
| 5.0                                                  | 2.60 ± 0.12|
| 10.0                                                 | 2.58 ± 0.12|
of Ag nanoparticles can be seen on the surface of the microcapsules as white dots (Figures 4E and 7C,G). The Ag nanoparticles are distributed homogeneously throughout the shell as can be seen in the cross section of a microcapsule (Figure 7D). The observable size of Ag nanoparticles on the surface of the Ca alginate-coconut oil microcapsules in the SEM images (Figure 7D,H) was in good agreement with the result of laser diffraction size analysis (Figure 2), which indicated further nanoparticle agglomeration did not occur during the formation and solidification of the microcapsules.

3.3 Thermal stability

The thermal behavior of the two main components (calcium alginate and coconut oil) of the prepared capsules and the control capsules without silver nanoparticles are presented in Figure 8. On the mass loss curve of the calcium alginate it can be seen that the material starts to lose weight starting at quite low temperatures. The mass loss of 30.2% up to 185°C accompanied by an endotherm is due to the release of physically bound and most probably structural water too.43 The chemical degradation of the polysaccharide rings takes place in the next two mass loss steps (185°C-258°C Δm –9.2% and 258°C-368°C Δm –10.9%), while the oxidative burning of the remaining organic material takes place in another two-step process, between 368°C and 557°C (Δm –10.6%) and 557°C and 668°C (Δm –2.5%). This oxidative degradation/burning step is also confirmed by series of overlapped exothermic peaks.44,45 The small mass loss step above 668.39°C (Δm –1.2%) corresponds to the degradation of the calcium carbonate, which was formed previously during the oxidative degradations of the calcium alginate. From thermal point of view, coconut oil is a little bit more stable, compared to the calcium alginate. From the beginning of the measurement up to 278°C, a small fraction (Δm –2.9%) of moisture is lost. Above this temperature, three mass loss steps can be observed: the largest one, between 278°C and 419°C, with a mass loss of 78.9% is followed by a much smaller step (between 419°C and 535°C, mass loss 16.7%). Both mass losses are accompanied by two large exothermic peaks proving the oxidative degradation of the saturated and polyunsaturated oils and fatty acids from the coconut oil. This is in agreement with the findings of Jayadas et al.46,47 The small mass loss between 535°C and 700°C (Δm –0.8%), accompanied by a small endotherm could be the result of decomposition and volatilization of some high molecular weight organic components. The
FIGURE 7  Scanning electron microscopic images of Ca alginate-coconut oil microcapsules without Ag nanoparticles, A and B, as well as prepared with 1% (m/v), C and D, 5% (m/v), E and F, and 10% (m/v), G and H, Ag nanoparticles (scale bar: A, C, E, G: 500 μm, B: 200 μm, D: 2 μm, F: 50 μm, H: 2 μm) [Colour figure can be viewed at wileyonlinelibrary.com]
TGA trace of the control microcapsules is very similar to the mass loss curve of the coconut oil, indicating that its degradation behavior dominates over the degradation of the calcium alginate shell material. The higher mass loss observable between 550°C and 710°C in the case of the control sample is the consequence of the previously described decomposition of calcium carbonate.

The thermal behavior of the Ag containing microcapsules (TG—Figure 9A and DSC—Figure 9B) in oxidative atmosphere is very similar to the trace of the control sample, which means, that the silver content has no influence on the thermal degradation of the capsules. The increasing content of silver is reflected in the increasing amount of residues.

**Figure 8** Mass loss /TG/, A, and heat flow /DSC/ curves, B, of the capsule’s components and control capsules

**Figure 9** Mass loss /TG/, A, and heat flow /DSC/ curves, B, of the different silver containing capsules
The PCM-loaded microcapsules should withstand numerous cycles of heating and cooling without any leakage in their life period. Thus, thermal cycling of microcapsules was performed by heating them up to 43°C and cooling down to 3°C periodically. After 200 cycles the heat storing property of the microcapsules was measured by DSC to study whether any decrease can be found, which would indicate leakage of the PCM from the microcapsules. Table 7 shows that no significant change occurred during the thermal cycling, which proves that the shell can resist the volume change throughout several phase change cycles.

### 3.4 Antimicrobial effect of microcapsules

The antibacterial influence of the microcapsules was tested using *Salmonella serovar Typhimurium* (pKOT-1/SJW2536) at a cell number range of $2 \times 10^5$ to $4 \times 10^6$ cells/ml. In this study concentration dependent bactericide impact was found at both of the incubation period, however, the incubation time also had substantial effect (Table 8). After 6 hours incubation, all of the Ag-loaded samples inhibited the bacterial growth up to $4 \times 10^6$ cells/ml concentration, moreover, the microcapsules prepared using 5% and 10% (m/v) Ag nanoparticles was also efficient in bacteria elimination at a concentration of $2 \times 10^6$ cells/ml. After 24 hours incubation, the bacteria were impeded by all of the Ag-loaded samples up to $2 \times 10^6$ cells/ml concentration, while the microcapsules prepared by 5% and 10% (m/v) hampered the cultivation of bacterial cells at the highest cell concentration ($4 \times 10^6$/ml) as well.

The dissolved Ag content of the samples in the antimicrobial study was also analyzed by ICP-MS to correlate it with the bactericide effect. After 6 hours incubation the Ag dissolution was under the detection limit in all of the samples, however, after 24 hours the Ag concentration was $0.23 \pm 0.12$ mg/L and $0.47 \pm 0.25$ mg/L in the presence of bacteria and Ag-loaded microcapsules prepared by 5% and 10% (m/v) Ag nanoparticles, respectively. This result correlates with the findings of antibacterial test. From the bacterial tests, on an average 0.12% (m/m) and 0.13% (m/m) of leached Ag ion ratios can be calculated from the microcapsules formed using 5% and 10% (m/v) Ag nanoparticles, respectively.

Significant antifungal effect was found also with the microcapsules prepared using 5% and 10% (m/v) Ag nanoparticle (Figure 10). *Paecilomyces variotii* and *Trichoderma viride* species were completely eliminated, while *Penicillium funiculosum* was inhibited to 25% of the initial mycelium volume by the highest Ag-loaded microcapsules. Significant mycelium inhibition was found by the microcapsules prepared with 5% (m/v) Ag nanoparticles. 56%, 36% and 88% related to the control mycelium volume was grown for *Paecilomyces variotii*, *Trichoderma viride* and *Penicillium funiculosum*, respectively. Microcapsules prepared with 1% (m/v) Ag nanoparticles inhibited only *Trichoderma viride* fungi by 28%, while the other two species were slightly stimulated at the lowest Ag nanoparticle concentration.

Use of Ag nanoparticles for the enhancement of thermal conductivity is more common than their application for antimicrobial purposes. Zhang et al. prepared silver/silica double-layered shell n-eicosane PCM-loaded microcapsules for improving both the conductivity and the antibacterial feature of the heat storing microparticles. Similar structured n-octadecane-loaded microcapsules were prepared and included in polyvinyl alcohol gel to reach the mentioned two purposes. These studies also collected relevant available information on the antibacterial mechanism of Ag nanoparticles. For achieving antifungal effect in latent heat storing microparticles, generally essential oils have been used so far. However, to our knowledge antifungal effect of Ag nanoparticle in PCM capsules have not been investigated, yet, thus, it can be considered as a novel area of tests, which can be further improved.

### Table 7 DSC results of Ca alginate-coconut oil microcapsules by varying initial concentration in the sodium alginate solution

| Initial Ag content in sodium alginate solution (%, m/v) | Before thermal cycling | After thermal cycling |
|--------------------------------------------------------|------------------------|-----------------------|
|                                                        | Melting ΔH (J/g) | Freezing ΔH (J/g)   | Melting ΔH (J/g) | Freezing ΔH (J/g)   |
| 0.0 (control)                                          | 92.6 ± 0.9           | 85.1 ± 0.6           | 92.5 ± 0.9       | 84.4 ± 1.9           |
| 1.0                                                    | 91.0 ± 0.6           | 85.6 ± 1.0           | 91.6 ± 0.4       | 85.7 ± 1.0           |
| 5.0                                                    | 89.7 ± 0.7           | 83.6 ± 0.8           | 90.5 ± 0.2       | 83.7 ± 0.8           |
| 10.0                                                   | 90.8 ± 1.0           | 84.6 ± 1.2           | 91.7 ± 0.9       | 84.9 ± 1.3           |
CONCLUSIONS

Ca alginate-coconut oil PCM microcapsules were prepared by repeated interfacial coacervation/crosslinking procedure. The shell of fully bio-originated Ca alginate-coconut oil PCM microcapsules were loaded with Ag nanoparticles following their preparation by mild reduction of silver nitrate. The Ag nanoparticles were composed mostly of metallic Ag with a small amount of oxides showed by XPS measurements. The extremely high coconut oil content (85%) of the microcapsules proved by both gravimetric and DSC analysis could be reached also in the presence of Ag nanoparticles. The corresponding high freezing and melting heat storing capacities were in the range of 83.6 to 85.6 J/g, as well as 89.7 to 92.6 J/g, respectively. The heat storing capability of the microcapsules did not change after 200 heating and cooling cycles, which indicates their shell is capable to resist the volume change during numerous phase change processes. The involvement of Ag nanoparticles did not decrease the PCM content of the microcapsules. The Ag nanoparticle-loaded microcapsules represented concentration-dependent oligodynamic effect both on bacteria and fungi. The highest Ag concentration (1.3% related to the total capsule weight) exerted effective inhibition effect against Salmonella serovar Typhimurium and the three investigated fungal strains.

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### TABLE 8

Antibacterial effect of Ag nanoparticle-loaded and blank microcapsules with Salmonella serovar Typhimurium (pKOT-1/SJW2536) vs cell number at 6 and 24 hours incubation

| Cell concentration | Negative control | Ca alginate-coconut oil (0% Ag) | Ca alginate-coconut oil (1% Ag) | Ca alginate-coconut oil (5% Ag) | Ca alginate-coconut oil (10% Ag) |
|--------------------|------------------|-------------------------------|-------------------------------|-------------------------------|----------------------------------|
| 6 hours            |                  |                               |                               |                               |                                  |
| 2 × 10⁵/ml         | +                | +                             | −                             | −                             | −                                |
| 4 × 10⁵/ml         | +                | +                             | −                             | −                             | −                                |
| 2 × 10⁶/ml         | +                | +                             | +                             | −                             | −                                |
| 4 × 10⁶/ml         | +                | +                             | +                             | +                             | +                                |
| 24 hours           |                  |                               |                               |                               |                                  |
| 2 × 10⁵/ml         | −                | −                             | −                             | −                             | −                                |
| 4 × 10⁵/ml         | +                | +                             | −                             | −                             | −                                |
| 2 × 10⁶/ml         | +                | +                             | −                             | −                             | −                                |
| 4 × 10⁶/ml         | +                | +                             | +                             | +                             | +                                |

Note: Negative control was bacteria culture without microcapsules.

### FIGURE 10

Antifungal effect of Ca alginate microcapsules by varying initial Ag nanoparticle concentration
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