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Improving the Water-Repellent and Antifungal Properties of Electrospun Cellulose Acetate Materials by Decoration with ZnO Nanoparticles

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Abstract

Suitable conditions for the preparation of nano- and microstructured materials from cellulose acetate and cellulose acetate/ZnO from solutions/suspensions in aceton/water by electrospinning/electrospraying were found. The materials obtained were characterised by scanning electron microscopy (SEM), X-ray diffraction analysis (XRD) and contact angle measurements. The antifungal activity of the materials obtained against Phaeomoniella chlamydospora, which is one of the main species causing diseases in grapevines, was studied as well. It was found that electrospinning of CA solutions with a concentration of 10 wt% reproducibly resulted in the preparation of defect-free fibres with a mean fibre diameter of ~780 nm. The incorporation of ZnO nanoparticles resulted in the fabrication of hybrid materials with superhydrophobic properties (contact angle 152°). The materials decorated with ZnO possessed antifungal activity against P. chlamydospora. Thus, the fibrous materials of cellulose acetate decorated with ZnO particles obtained can be suitable candidates to find potential application in agriculture for plant protection.

Key words: *cellulose acetate, ZnO, electrospinning, electrospraying, superhydrophobicity, Phaeomoniella chlamydospora.*

Introduction

In recent years, electrospinning has been considered as one of the most effective technologies with great potential for the fabrication of continuous polymer fibres having micro- and nanoscale diameters and a length reaching several meters. In contrast to the conventional methods for fibre production, electrospinning uses an external electric field to accelerate and stretch a charged polymer jet. The electrospun materials possess an exceptionally large specific area and porous structure, and therefore find a variety of applications [1, 2].

The electrospinning process and the resultant morphology of the fibres obtained may be affected by the molecular weight and molecular weight distribution of the polymer(s), and solvent used, the polymer concentration, solution viscosity and conductivity, the electric field applied, the distance between the needle and collector, the flow rate, needle diameter, ambient temperature, as well as the atmospheric pressure and humidity. A systematic study of different polymer/solvent systems is required to determine the optimal conditions for a given electrospinning process.

In recent years, there has been a high demand for the development of innovative eco-friendly materials for agricultural crop protection. However, for modern agriculture, it is necessary not only to create new plant protection products with low toxicity to non-pathogenic microorganisms, but also to seek rational solutions and approaches to improve the existing ones. The use of electrospun nanofibres in agriculture especially for the protection of vineyards is an emerging field of interest.

Recently, the preparation of materials consisting of rayon membranes on which electrospun nanofibres of soy protein/polyvinyl alcohol and soy protein/polycaprolactone are deposited have been proposed for physically blocking fungal spore penetration [3]. It has been reported that physical blocking is insufficient and inclusion of an antifungal component has been proposed. Bandages of electrospun materials from poly(lactide-*co*-glycolide) and poly(butyleneadipate-*co*-terephthalate) with an antifungal agent incorporated – polyhexamethylene guanidine were prepared with the aim to block the penetration of *Phaeomoniella chlamydospora* spores [4]. The authors report, however, that further optimisation to find more efficient polymers and a more appropriate choice of antifungal additives are needed.

In our previous study we proposed a facile preparation of fibrous membranes containing an easily available and efficient antifungal compound – 8-hydroxyquinoline derivative for active protection against spore penetration and plant infection [5]. Moreover, we successfully obtained eco-friendly materials based on poly(3-hydroxybutyrate), nanosized TiO_2-anatase, and chitosan oligomers by the conjunction of electrospinning and electrospraying with antifungal activity for plant protection [6].

Cellulose acetate (CA) is one of the most important esters of cellulose [7]. The advantages of CA are its low cost, ease of solubility in solvents suitable for electro-

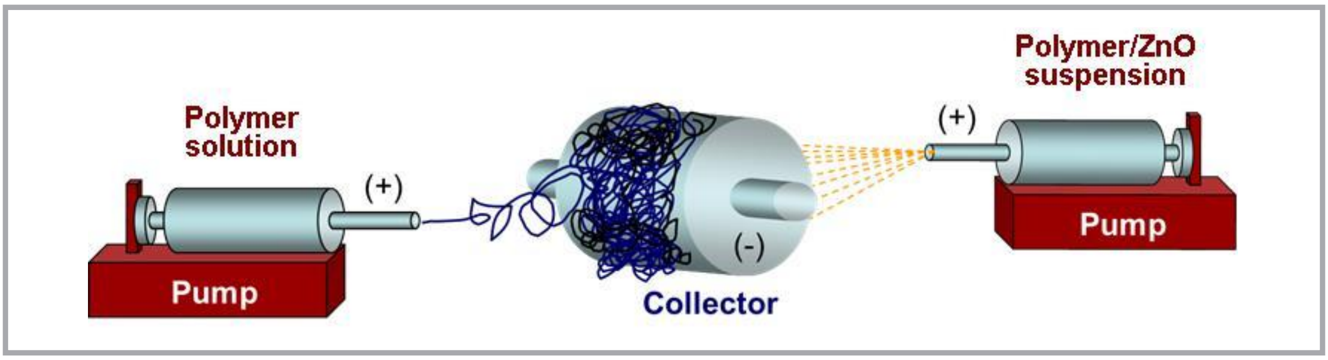


Figure 1. Schematic representation of the electrospinning/electrospraying set-up.

spinning, facile production, and a wide variety of applications [8].

ZnO is nontoxic and exhibits photochemical and antibacterial activity [9]. This is due to the fact that nanostructured ZnO is a very active material, since it can generate reactive oxygen species (ROS) and can release Zn^{2+} ions. ZnO-containing materials find many applications, such as in chemical sensors, luminescent devices, solar cells, medical and cosmetic products, etc. [10]. It has been demonstrated that there is a possibility to decorate fluorine-containing polymers with ZnO nanoparticles by applying electrospinning/electrospraying [11, 12]. It has also been shown that the hybrid fibrous mats obtained manifest antibacterial activity against the Gram-positive bacteria *Staphylococcus aureus*.

Recently, the potential of nanomaterials to improve the functionality and properties of polymers, especially of organic-inorganic hybrid materials, which exhibit a combined synergistic effect, has been investigated [13].

In the present study, the possibility to prepare electrospun materials (beads or fibres) from cellulose acetate or cellulose acetate and ZnO is shown. A series of studies were conducted in order to find optimal conditions for the electrospraying or electrospinning of cellulose acetate in acetone/water. The concentration of CA was varied, and the effect of including ZnO nanoparticles on morphology, wetting and antifungal activity against *P. chlamydospora* was assessed.

Materials and methods

Materials

Cellulose acetate (CA, Aldrich, St. Louis, MO, USA) with $\overline{M}_n$ = 30.000 g/mol and 39.8 wt% of degree of substitution in acetyl content and nanosized zinc oxide with a silanized surface Zano®20 Plus (Umicore Zinc Chemicals, Liège, Belgium) were used. Acetone (Sigma-Aldrich) of analytical grade of purity was also used. Potato dextrose agar medium was purchased from Merck, Darmstadt, Germany.

Preparation of fibrous mats of CA and CA/ZnO of design type "in" by one-pot electrospinning

First, cellulose acetate solutions with concentrations of 6, 8, 10 and 17 wt% in acetone/water (80/20 v/v) were prepared in order to find the optimal concentration for the electrospinning of defect-free fibres.

Nanosized ZnO was dispersed in cellulose acetate solution. The concentration of cellulose acetate was 10 wt%. ZnO was 30 wt% of the polymer weight. The suspensions were sonicated prior to being subjected to electrospinning (15 min in an ultrasonic bath – Bandelin Sonorex, 160/640 W, 35 kHz, Berlin, Germany).

The spinning solutions and suspensions were loaded in a 5 ml syringe equipped with a metal needle (gauge: 20GX1½″) connected to the positively charged electrode of a custom-made high-voltage power supply (up to 30 kV). Electrospinning was conducted at a constant applied voltage of 25 kV and constant tip-to-collector distance of 15 cm using a grounded rotating aluminum collector (1000 rpm). The spinning suspensions were delivered at a constant rate of 3 ml/h, enabled by the use of a pump Syringe Pump NE-300 (New Era Pump Systems, Inc., New York, USA). The electrospinning was performed under a room temperature of 21 °C and relative humidity of 50%.

Preparation of fibrous mats of CA/ZnO of design type "on" by the conjunction of electrospinning and electrospraying

ZnO-*on*-CA fibrous mats were prepared by simultaneous electrospinning of cellulose acetate and electrospraying of CA/ZnO suspension. A schematic representation of the set-up for the electrospinning/electrospraying is shown in ***Figure 1***. Mats of design type "*on*" were fabricated using two syringe pumps – NE-300 for delivering (i) CA solution (10 wt% in acetone/water (80/20 v/v)) for the electrospinning and (ii) CA/ZnO suspension (30% (w/v) in a solution of CA (0.5 wt%) in acetone/water (80/20 v/v)) for the electrospraying. The ZnO suspensions were sonicated prior to being subjected to electrospraying (15 min in an ultrasonic bath). The pumps for delivering the spinning solution and the suspension were placed at an angle of 180° with respect to the grounded rotating aluminium collector (1000 rpm). The spinning solutions and suspensions were delivered at a constant rate of 3 ml/h. Electrospinning and electrospraying were conducted at a constant tip-to-collector distance of 15 cm and at a constant applied voltage of 25 kV, provided by a custom-made high-voltage power supply.

Characterisation

The dynamic viscosity of the spinning solutions/suspensions was measured using a Brookfield DV-II+ Pro programmable viscometer with the cone/plate option, equipped with a sample thermostated cup and cone spindle CPE – 52, at 25 ± 0.1 °C.

The morphology of the materials was evaluated by scanning electron microscopy (SEM). The samples (1 cm^2) were vacuum-coated with gold and observed with a Jeol JSM-5510 (Jeol Ltd., Tokyo, Japan). The average fibre diameter was

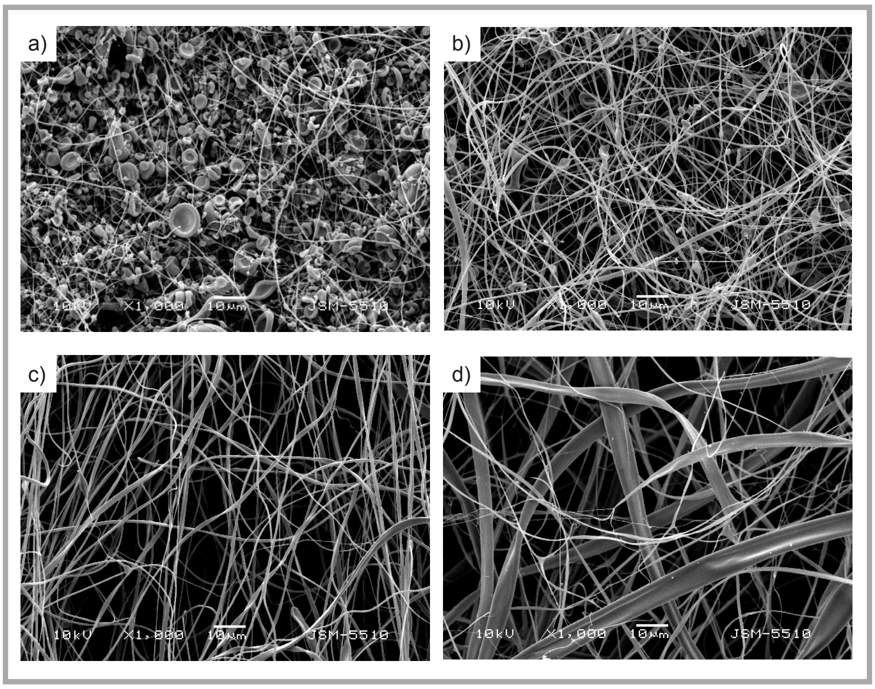


Figure 2. *SEM micrographs of electrospun fibrous materials of cellulose acetate prepared from solutions with the following concentrations: a) 6 wt%, b) 8 wt%, c) 10 wt% and d) 17 wt%.*

estimated with ImageJ software [14] by measuring at least 20 fibres from three different SEM micrographs for a total of 60 measurements, and their morphology was assessed, applying the criteria for the overall evaluation of electrospun materials as described in detail in [15].

Static contact angle measurements of the membranes were taken using an Easy Drop DSA20E Krüss GmbH drop shape analysis system (Hamburg, Germany) at 20 ± 0.2 °C. A sessile drop of deionized water with a volume of 10 µl, controlled by a computer dosing system, was deposited onto the fibrous materials (2 cm × 7 cm, cut in the direction of rotation of the collector). The contact angles were calculated by computer analysis of images of the droplet acquired. The data were averaged from 20 measurements for each sample.

X-ray diffraction (XRD) analyses were performed at room temperature using a computer-controlled D8 Bruker Advance ECO powder diffractometer with filtered Cu Kα radiation. Data were collected in the 2θ range from 10° to 60°, with a step of 0.02° and counting time of 1 s step^{-1}.

In vitro antifungal activity

Antifungal activity of the materials obtained was monitored against the fungi *P. chlamydospora* Centraalbureau voor Schimmelcultures (CBS) 239.74, purchased from the Westerdijk Fungal Biodiversity Institute, Utrecht, the Netherlands. In order to measure the zones of inhibition, *in vitro* studies were performed using potato dextrose agar medium (PDA, Merck, Darmstadt, Germany) for the fungal strain. The surface of the solid agar was inoculated with a suspension of fungi culture with a fungi concentration of 1×10^5 cells/ml, and on the surface of the agar in each Petri dish, one sample was placed. The Petri dishes were incubated for 96 h at 28 °C, and subsequently the zones of inhibition around the disks were measured.

Results and discussion

Cellulose acetate is soluble in solvents suitable for electrospinning. It was found that none of the solvents: acetone, acetic acid and dimethylacetamide alone enables continuous formation of cellulose acetate fibres [16]. By adding water, in which cellulose acetate is not soluble but which is miscible with acetone and acetic acid, the vapour pressure of the system is reduced, and this greatly improves the process of electrospinning [17].

Viscosity of the spinning solutions

Electrospraying results in the preparation of particles or beads, while electrospinning results in fibre formation. The lack of sufficient chain entanglements which stabilise the electrospinning jet by inhibiting jet breakup is the main reason for the transition from electrospinning to electrospraying [18]. The entanglements of polymer chains are crucial for the formation of fibres. The concentration of the spinning solution has to be higher than the critical concentration of chain entanglements in order to obtain defect-free fibres.

In the present study, solutions of cellulose acetate with different polymer concentrations in mixed solvent acetone/water were prepared. The values of the dynamic viscosity of the solutions prepared were measured. The viscosity of the CA solutions in acetone/water with concentrations 6, 8, 10 and 17 wt% was 20 cP, 52 cP, 122 and 1120 cP, respectively. It was found that by increasing the polymer concentration, the values of the solution viscosity increased. The increase in solution viscosity was attributed to the higher degree of chain entanglements.

Characterisation of the fibrous materials

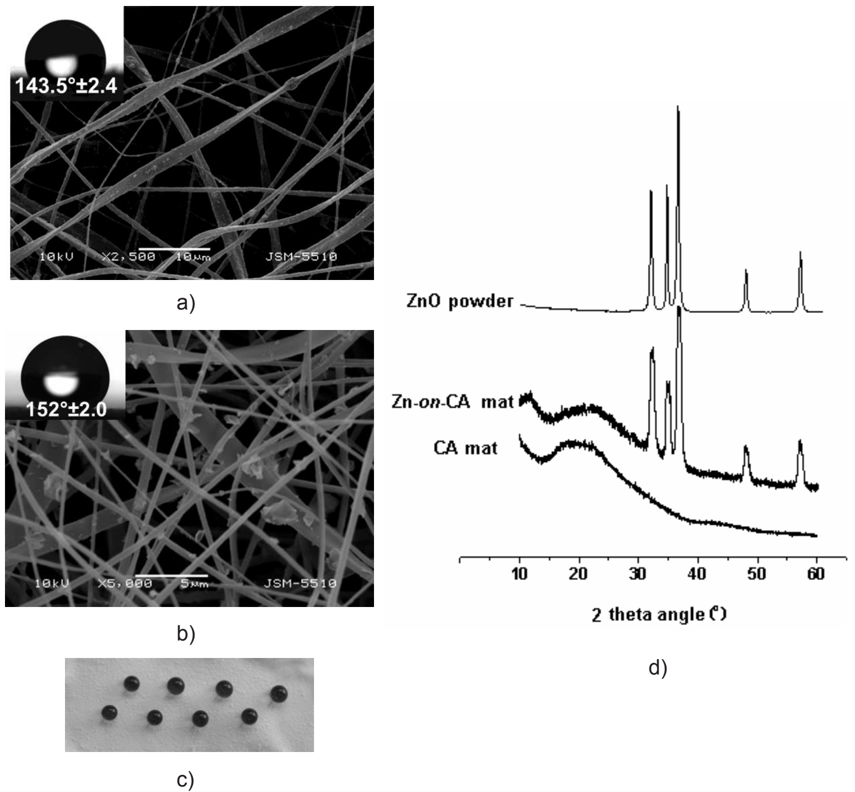
The morphology of the fibrous mats prepared was observed by scanning electron microscopy (SEM). Representative SEM images of the CA mats electrospun from solutions with concentration 6, 8, 10 and 17 wt% obtained are shown in ***Figure 2***. Electrospinning of a cellulose acetate solution with a concentration of 6 wt% and value of the solution viscosity of 20 cP resulted in the preparation mostly of microparticles connected to fine fibres (***Figure 2.a***).

A transition from the preparation of particles to the formation of fibres with defects was observed when a solution with a concentration of 8 wt% and viscosity of 52 cP was subjected to electrospinning (***Figure 2.b***). The mean fibre diameters of the cellulose acetate fibres prepared from solutions with concentrations if 6 and 8 wt% were 680 ± 119 nm and 780 ± 110 nm, respectively. By increasing the concentration of cellulose acetate, the number of defects decreased. It was found that the fibres prepared from the solution of cellulose acetate with a concentration of 10 wt% and values of the solution viscosity of 122 cP were uniform, defect-free and with a ribbon-like structure (***Figure 2.c***). The preparation of ribbon-like fibres by electrospinning of cellulose acetate is consistent with the literature data [16, 19]. The formation of ribbons is explained by the formation of a thin polymer skin on the jet. After the skin formed, the solvent inside escaped. Atmospheric pressure tended to collapse the tube formed by the skin as the solvent evaporated. The circular cross section became elliptical and then flat, forming a ribbon [20].

By a further increase in the concentration up to 17 wt%, however, the value of the solution viscosity increased to 1120 cP, which led to obstruction of the flow from the capillary and instability of the process, leading to the formation of non-uniform fibres (***Figure 2.d***). The mean fibre diameter of the thin fibres was 580 ± 180 nm and of the thicker ones – 5.9 ± 1.2 µm. It was found that the concentration of the cellulose acetate had a significant effect on the fibre morphology, while defect-free and uniform fibres were obtained by electrospinning of solutions of cellulose acetate with a concentration of 10 wt%.

Representative SEM images of the hybrid fibres of CA (10 wt%) and ZnO nanoparticles (30 wt%) of design type "*in*" (***Figure 3.a***) and "*on*" (***Figure 3.b***) obtained are shown in ***Figure 3***. The incorporation of ZnO (30 wt%) led to morphological changes in the fibres obtained and to an increase in the mean fibre diameter. The increase in fibre diameter was attributed to the increase in the viscosity of the CA/ZnO suspension (2010 cP). It is well known that an increase in the molecular weight of the polymer(s), polymer concentration and solution/suspension viscosity used results in an increase in the mean fibre diameter [21]. The mean fibre diameter of the hybrid ZnO-*in*-CA fibres was 1150 ± 285 nm. It was observed that the incorporation of ZnO nanoparticles resulted in the preparation of fibres with a rough surface in which zinc oxide was distributed mainly in the fibres' bulk; however, some ZnO aggregates were formed. It may be assumed that one of the possible reasons for the presence of aggregates in the fibres is the solvent evaporation during the flight of the jet from the nozzle to the collector.

SEM micrographs of fibrous mats of ZnO-*on*-CA are presented in ***Figure 3.b***. As can be seen, the ZnO particles are distributed uniformly onto the fibres in the form of small and large particles. This results in the decoration of CA fibres with ZnO particles.



a)

b)

c)

d)

Figure 3*. SEM micrographs of electrospun hybrid materials of ZnO-in-CA (a) and ZnO-on-CA (b) magnification x 5 000 images of a distilled water droplet (10 µl) on mats of ZnO-in-CA and ZnO-on-CA (inset), c) digital images of droplets coloured with reactive red and deposited on the ZnO-on-CA mat, d) XRD patterns of ZnO powder, ZnO-on-CA mat and CA mat.*

The static contact angle method is widely used in determining the contact angle, and it is well known that the value of the angle measured depends on the experimental conditions (droplet volume, contact time, ambient temperature, etc.) [22]. The water contact angle of the CA fibrous mats obtained was measured. It was found that the electrospun mats of CA were hydrophobic, with a water contact angle value of 120° ± 4°.

Effect of ZnO on the wettability of CA fibrous mats

The effect of ZnO particles on the wetting of cellulose acetate-based hybrid fibres was investigated. Images of the distilled water droplet (10 µl) deposited onto the surface of ZnO-*in*-CA and ZnO-*on*-CA mats are shown in ***Figure 3.a*** and ***3.b*** (inset). The incorporation of ZnO particles with the silanised surface resulted in the hydrophobisation of the CA fibrous mats. The mean value of the water contact angle of the ZnO-*in*-CA mat was 143.5° ± 2.4°. The preparation of novel fibrous hybrid materials based on CA and ZnO nanoparticles of design type "*on*" led to a further increase in the water contact angle and to the fabrication of materials with superhydrophobic properties with contact angles of 152° ± 2°. The decoration of CA fibres with ZnO particles led to the creation of materials with a rough structure and large specific surface area. These results show the effect of the material topology on the contact angle values and wetting.

Digital images of droplets deposited on the ZnO-*on*-CA mat (152°) are presented in ***Figure 3.c***. For ease of visualisation the water was coloured with reactive red. As can be clearly seen, the water droplets preserved their spherical and round shape and did not spread onto the surface, which is evidence of the superhydrophobic properties of the surface of the fibrous material.

X-ray diffraction

XRD patterns of ZnO powder and CA and ZnO-*on*-CA mats recorded in the 2θ range from 10 to 60° are presented in ***Figure 3.d***. The presence of main diffraction peaks of hexagonal wurtzite ZnO, (100) (002) (101) (102) and (110), located at 2θ = 34.5°, 36.3°, 47.7° and 56.7°, was found [23, 24]. Two broad peaks at 2θ = 10.3° and 21.7° were pres-

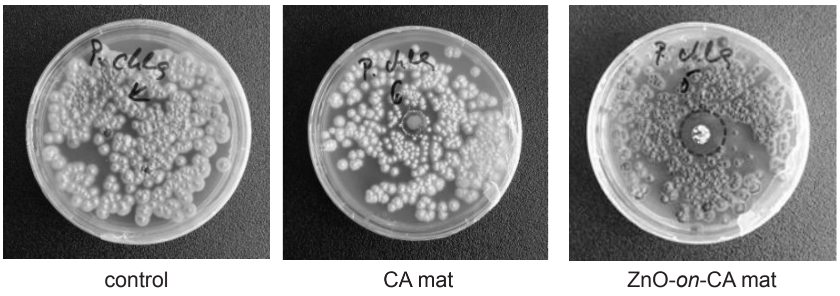

control CA mat ZnO-*on*-CA mat

***Figure 4.** Digital images of the zones of inhibition against P. chlamydospora after contact of the fibrous materials with fungal cells.*

ent in the XRD pattern of the CA mat, which reveals that the CA mat was in an amorphous state. This result was in accordance with the literature data [25]. In the hybrid fibrous materials based on CA and ZnO materials, the XRD analysis revealed the presence of two broad peaks characteristic for CA and sharp peaks characteristic for ZnO. This confirms that all the hybrid mats contained CA and ZnO as well.

Antifungal activity of the fibrous materials

It is known that the esca disease of grapevines is caused mainly by the species *P. chlamydospora* and *P. aleophilum* [26]. Recently, we proposed a novel fibrous membrane loaded with 5-chloro-8-hydroxyquinoline and demonstrated that 5-Cl8Q is an efficient and sustainable antifungal agent against *P. chlamydospora* and *P. aleophilum* [27].

In the present study, the antifungal activity of the electrospun mats based on CA and CA/ZnO was assessed by performing tests against *P. chlamydospora*. The results obtained by determination of the zones of inhibition after contact of the fibrous materials with the fungal cells are shown in ***Figure 4***.

The fibrous CA mats did not alter the fungal growth nor exhibit any antifungal activity. The ZnO-*in*-CA mat showed an insignificant inhibitory effect. The decoration of the surface of CA fibres with ZnO particles led to inhibition of the growth of the fungi and the formation of an inhibition zone (***Figure 4.c***). The diameter of the zone of inhibition was 16 mm. The observation of a zone of inhibition around the ZnO-*on*-CA mat is evidence that the ZnO deposited onto the fibre surface imparts antifungal activity to the novel hybrid mats prepared.

Conclusions

In the present study CA fibrous materials and CA/ZnO hybrid materials were successfully prepared by the conjunction of electrospinning and electrospraying techniques. It was found that the concentration of the spinning solutions/suspensions influenced the their viscosity and the morphology of the particles/fibres obtained. Furthermore, an increase in the polymer concentration resulted in transition from a regime of electrospraying to that of electrospinning. The incorporation of ZnO nanoparticles with the silanised surface resulted in a change in the morphology and structure of the type "*in*" and "*on*" hybrid fibres obtained and imparted superhydrophobic and antifungal properties to the ZnO-*on*-CA mats. These features indicate that fibrous materials based on cellulose or cellulose derivatives decorated with ZnO could find application in agriculture for plant protection against the adhesion and growth of pathogenic fungi.

Author contributions

I.R. and N.M. conceived the original concept. M.S. and N.N. conducted the experiments and characterised the fibrous materials. M.N. performed microbiological assessments of the membranes obtained. M.S., N.M. and I.R. wrote the manuscript. M.S, N.M., I.R. and M.N. revised the manuscript.

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Conflicts of interest

The authors declare no conflict of interest.

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