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Possibilities of Manufacturing an Electrospun Web with Baltic Amber

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Abstract
In recent times, electrospinning has become a well known and widely investigated process used for manufacturing nano or/and micro fibres with electrostatic forces between two electrodes. Various additives such as silver, starch, copper, etc. are used in electrospinning to achieve specific properties. Amber is a natural material which has a positive influence on human health and wound healing. However, no information about the electrospinnig of amber particles has been found. In this paper, the possibility of electrospun nanofibrous web formation via electrospinning equipment (NanospiderTM) from poly(vinyl alcohol) solution with solid particles of Baltic amber is presented. It was determined that the maximum size of amber particles which can be transferred from the solution to the electrospun web is around 50 μm, while the probable optimal size of amber particles for electrospinning is below approximately 10 μm.

Key words: *nanofibres, electrospinning, poly(vinyl alcohol), amber.*

Introduction

Electrospinning is a well known process used for the formation of nano or/and micro fibres due to electrostatic forces between two electrodes. Nanofibres can be formed from polymer solution or melt, and their diameter is usually from 10 to 1000 nm [1]. Textiles for medical or health care application are one of the most important fields for electrospun nanofibres usage. For this purposes various additives are used which are characterized by having antibacterial or other kinds of properties important for health care. The majority of works published in various journals are about the use of silver nanoparticles [2 - 5]. Herewith some authors also analyse the possibility of manufacturing electrospun webs with copper nanoparticles, starch or other solid particles [6 - 10].

Some papers present investigations with different natural materials (proteins, hemp, olive leaves, fish scales and many others). Naturally the area of application of these materials depends on the additives which have been used while preparing the solution. Improved hygiene and health care standards have a great impact on the development of hygiene and health care products. The most promising antimicrobial compounds in modern times are metallic silver and fungicide copper nano-precipitates (SiO_2/Ag+Cu), silver nitrate, chitosan, zinc oxide, and others [11 - 13]. This antimicrobial protection can be done using different treatment techniques, one of which is antimicrobial web formation by electrospinning. It was estimated that PVA nanofibers containing silver nanoparticles showed very strong antimicrobial activity [2].

One of the additives which are used for healthcare and other medical applications are micro particles of amber. Amber as a natural material, which has some therapeutic properties, has been known from prehistoric times. Up to the present, amber has been very popular in Chinese medicine and in skin care products [14]. There are known investigations in which nano/micro particles of amber (in the size of 0.01 - 2000 μm) have been used for synthetic or natural fibres modification in order to obtain negative electrostatic charges [15, 16]. Yarns and fabrics have also been developed and manufactured on an industrial scale with the use of patented fibres. These products later won a Gold Award at the Brussel's fair. The particles of amber, according to patent [16], are incorporated mostly in the inside of fibres (size of amber particles was from 0.01 to 25 μm), while in accordance with patent [15] the majority of particles are outside the fibre structure (size of amber particles in this case was from 0.01 to 2000 μm). The possibilities to use particles of amber for filtration nonwoven products are also presented in [17], the technology of which is given in [18, 19]. However, in literature, we did not find any information about manufacturing electrospun nanofibres with amber particles. By electrospinning, it is possible to obtain such a variant of material where very small amber particles (even of a few μm) can be incorporated outside of the nanofibre material, and can have contact with the human skin under pressing, for example, which is a positive fact if we want to use amber for health care application.

The medical application of amber is a negotiable question, but some positive results of amber application in health care for wound healing stimulation are known. Some authors show that "…amber is a natural analgesic agent and possesses anti-inflammatory properties, so is often used to ease joint pain. It also acts as a natural antibiotic and, as we've seen, has an ages-old history of use in preventing and treating disease and healing wounds" [20]. This phenomenon is explained by the possibility of amber to produce negative ions, on which depends good health and healing. Authors [20] present "…that negative ions support the health of the autonomic nervous system, promote deep sleep, healthy digestion, affect the production of insulin, neutralize free radicals and enhance adrenal function". Furthermore some authors stated that succinic acid isolated from Baltic amber can bring about an increase in cultivated plants [21].

Hence the positive influence of amber on human health is not only well known, but investigations in this field have been carried out and very interesting information which enhances amber as a material in health care can be achieved. The considerations described above was an incentive for the authors to carry out investigations aimed at the incorporation of amber particles in an electrospun web, such as in a nonwoven structure, giving several advantages in comparison with other structures, as melt-blown, for example. Of course, we did not consider the use of electrospun webs as parts of clothing exposed to rough use, but for medical stationary applications. In this article, we did not want to confirm the assumed health features of an electrospun web with amber: The goal of our work presented was to show the possibility to manufacture electrospun webs from mikro or nanofibres with solid particles of natural Baltic amber. What should be here emphasized, is the selection by us of electrospinning with the use of an "Electrospider" device, which guarantees us much more effectivness than by using needles or other orifices. Further investigations of application attempts need to be carried out with the assistance of medical researchers, which will be one of the next steps of our work.

Materials and methods

A web from nanofibres was created using "Nanospider^{TM}" equipment (Elmarco, Czech Republic) with a uniform cylindrical, rotational electrode, by means of the electrospinning process, proceeded by stretching the polymeric solution from the rotational electrode (immersed in bath with a spinning solution) to the upper electrode (which was spunbond pp nonwoven) [22]. A solution of 8 wt.% concentration poly(vinyl alcohol) (PVA, ROTH, Germany, M = 72,000 g/mol) with 8 wt.% concentration of amber particles was prepared, electrospun and investigated. For preliminary trials PVA was chosen for easy formation, but experiments with other polymers e.g. PLA, PA6 will be conducted. Natural Baltic amber was used for investigations, milled with the use of a Laboratory Vibrating Disc Mill "pulverisette 9" (Fritsch GmbH, Germany) and next sifted with a Sonic Sifter Separator L3P (QAQC LAB, USA). A sieve of 63 μm size was used. The web was formed on polypropylene spunbond nonwoven (with an aerial mass of 21.5 g/m^2, and 20 μm diameter of the fibres). The speed of supporting the spunbond nonwoven material was 0.5 m/min. The distance between both electrodes was 13 cm, and the voltage applied - 70 kV. The temperature of the electrospinning environment was 20 ± 2 °C, and the air humidity 40 ± 2%. The parameters of electrospinning and of the materials supported were chosen on the basis of the results obtained in previous investigations, which show a good structure of the electrospun web manufactured. The process of electrospinning was not optimised at this step of the investigations, but a web was formed similar to that without amber, which does not mean that amber does not influence the structure of the web and the process of electrospinning itself; however, the variant of spinning amber presented did not have a critical influence.

The structure of the electrospun web received as well as the amber particle distribution were analysed by Scanning Electron Microscopy (SEM) with the use of Quanta 200 (FEI, Netherlands) by means of the LUCIA Image 5.0 programme. The size and distribution of amber particles before electrospinning were measured using a laser particle size and shape analyser CILAS 1090 LD (CILAS, France).

Results and discussions

Particles of Baltic amber were used in our investigations. Before preparing the spinning solution, the Baltic amber particles were milled and sieved out. A view of the milled amber particles is presented in ***Figure 1*** and their distribution by sizes in ***Figure 2***.

As is seen from ***Figure 1***, various particles by size and shape were obtained in the milled powder. It is necessary to note that the size of some particles in the milled powder is higher than that of the sieve (63 μm), which can be explained by the form of amber particle, i.e. if the one of dimensions of the particle is lower than the size of the sieve, the particle can transfer the sieve mesh despite a higher value of the dimension in other directions. Consequently in such cases it is possible to have particles whose average diameter is higher than the size of the sieve mesh. In the case presented

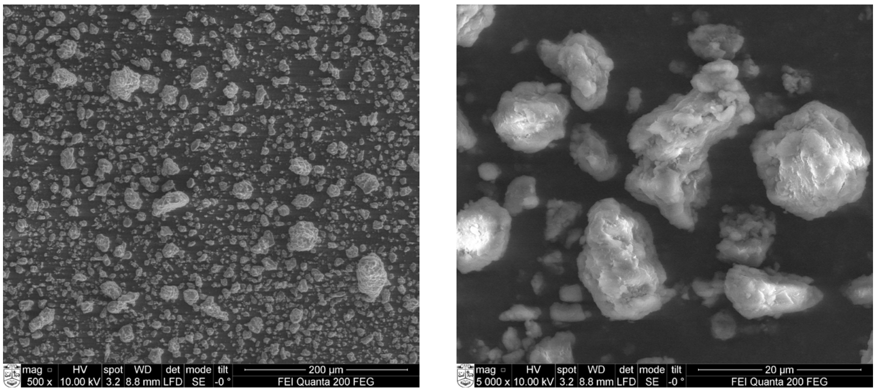

Figure 1. *SEM images of amber particles.*

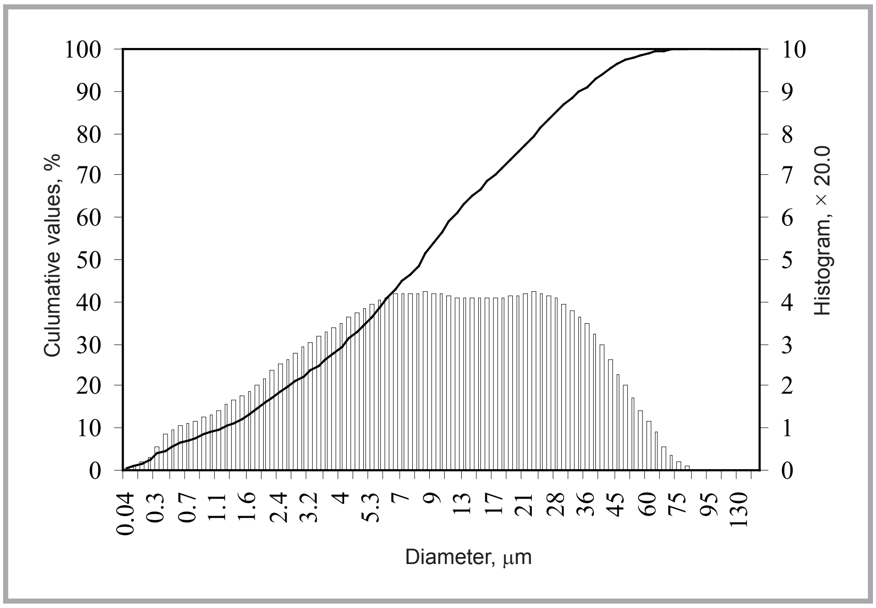

Figure 2. *Distribution of amber particles average size.*

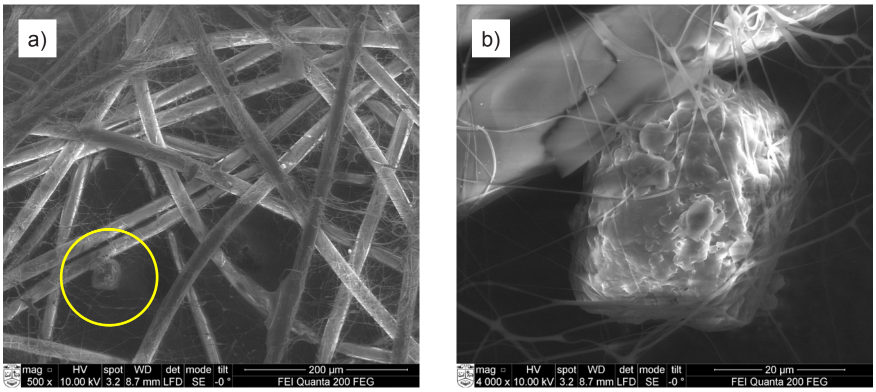

Figure 3. *SEM images of electrospun web with amber: a) panoramic view (resolution 200 µm), b) image of amber particle in panoramic view with higher resolution (20 µm).*

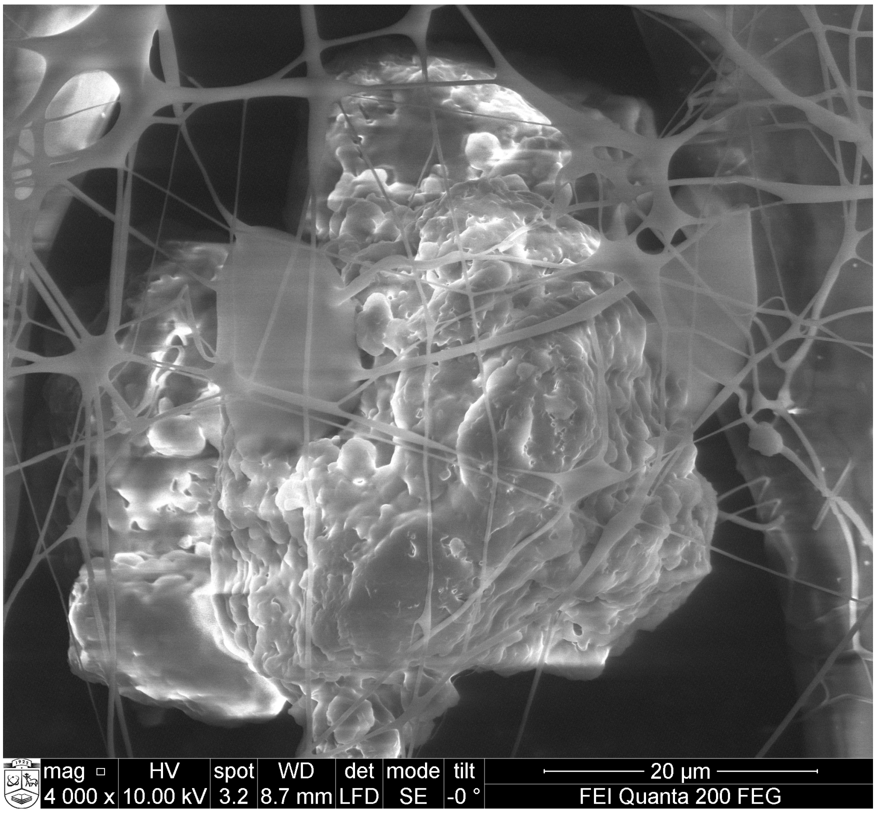

Figure 4. *SEM image of electrospun web with highest particle of amber.*

the size of around 2 % of all the particles was higher than that of the sieve, which means that the influence of the sieve size is also very important, and in the future maybe other sieves should be used.

A view of the electrospun web with amber particles is presented in ***Figure 3***.

As is seen from ***Figure 3***, various particles of amber were collected on the spunbond nonwoven. Analysis of various SEM images shows that the biggest particles of amber found on the electrospun web have a size at the level of 50 µm (see also ***Figure 4***), but the quantity of particles of such a size is very low. Only a few particles of such size have been found, while those with a size of around 40 µm can be found more offten (considering that more than 100 places of the electrospun web were analysed).

From ***Figure 3.b***, it can be seen that amber particles not only stuck to the polypropylene spunbond fibres by some poly(vinyl alcohol) formation but are also covered by nanofibres. It is a big advantage that the amber microparticles (with an approx. size of 40 × 25 µm) are additionally stiffened in the nanofibrous web. The same situation is seen in ***Figure 4***, which shows an amber particle of the biggest size found. Such a stiffening of amber particles on the surface by nanofibres strengthens the fastening of particles in the nanofibrous web.

Analysis of SEM images shows that the majority of amber particles have a size down to 10 µm; however, particles with a size even of 1 µm can be seen, but only in images of very high resolution (see ***Figure 5***).

After the analysis of SEM images of more than 100 various places of the electrospun web, it could be stated that the majority of amber particles with a size lower than 1 µm are not visible from panoramic images (made with a resolution of 200 or 100 µm). Such a size of amber particles is visible only in cases of higher resolution (starting from 20 µm). Herewith, as is well known that the diameter of PVA nanofibres varies from 100 nm up to 2 - 3 µm (the same results were achieved in our previous investigations), the smallest particles of amber possible are placed inside the PVA nanofibres and are not visible in the SEM images. Therefore the fact that we cannot find a high quantity of very small particles of amber does not mean that they were not transferred from the solution to the electrospun web. Hence a combined situation of amber incorporation into the web was achieved – some particles are inside the fibres and cannot contact with human skin, and also some particles are outside of the fibre structure and can contact with the skin. Once more, as is seen from ***Figures 3.b*** and ***4***, amber particles of a bigger size are not only stacked on the surface of the spunbond fibres or on the electrospun nanofibres but are also covered by a few nanofibres, being extra fasted to the surface of the electrospun web. Considering the preliminary results presented above, further investigations in this area are needed.

The analysis of the amber particle size distribution (see ***Figure 2***) shows that the number of amber particles with a size less than 1 µm compose around 7% of the total number of particles. The number of particles with a size from 1 to 10 µm compose around 45% of the total number of particles. The number of particles with a size from 10 to 50 µm (i.e. the highest size of amber particles which were found in the electrospun web) compose around 44%. and the number of particles with a higher size is around only 4% of all particles in the powder milled. The amber particles with a size bigger than

50 µm do not participate in the electrospinning process (we did not find them on the surface of the web). Herewith the number of particles with a size of 10 - 50 µm compose only a minority of all amber particles which were found in the electrospun web. It means that the size of amber particles used for electrospinning with PVA solution needs to be lower than 10 µm. In this case, the hypothesis about the possibility to transfer all particles of amber with a size less than 10 µm can be done. Of course, this presumption needs to be checked experimentally, but a preliminary conclusion can be made after our initial experiments.

Hence our work shows not only the possibility to create an electrospun nanofibrous web with micro particles of amber but also brings a lot of challenges for further investigations. The optimal technological and materials parameters have been not stated at this time, but the way how to obtain them is determined. For the development of an electrospun PVA nanoweb with amber nano/micro particles it is necessary to have amber particles with a size no bigger than 10 µm. On the other hand, the technological parameters of the electrospinning process (the distance between electrodes and voltage, as an example) could also influence the structure of the web and the quantity of amber particles on the electrospun nanoweb. Investigations in this field as well as cooperation with medics in the field of the usage of such materials for health care will be the topics of our further works.

Conclusions

- It was stated that it is possible to manufacture an electrospun web from poly(vinyl alcohol) nanofibres with micro particles of Baltic amber using needless equipment - Nanospider™ (Elmarco).
- The size of the biggest particle of amber transferred from the PVA solution to the electrospun web was around 50 µm; however the number of particles of such size is low, only a few of such particles were observed.
- The highest number of amber particles transferred was of a size up to 10 µm, while those with a size in the range of 10 - 50 µm was sometimes less.
- Probably the size of amber particles till 10 µm is an optimal value for manufacturing a PVA electrospun web with amber.

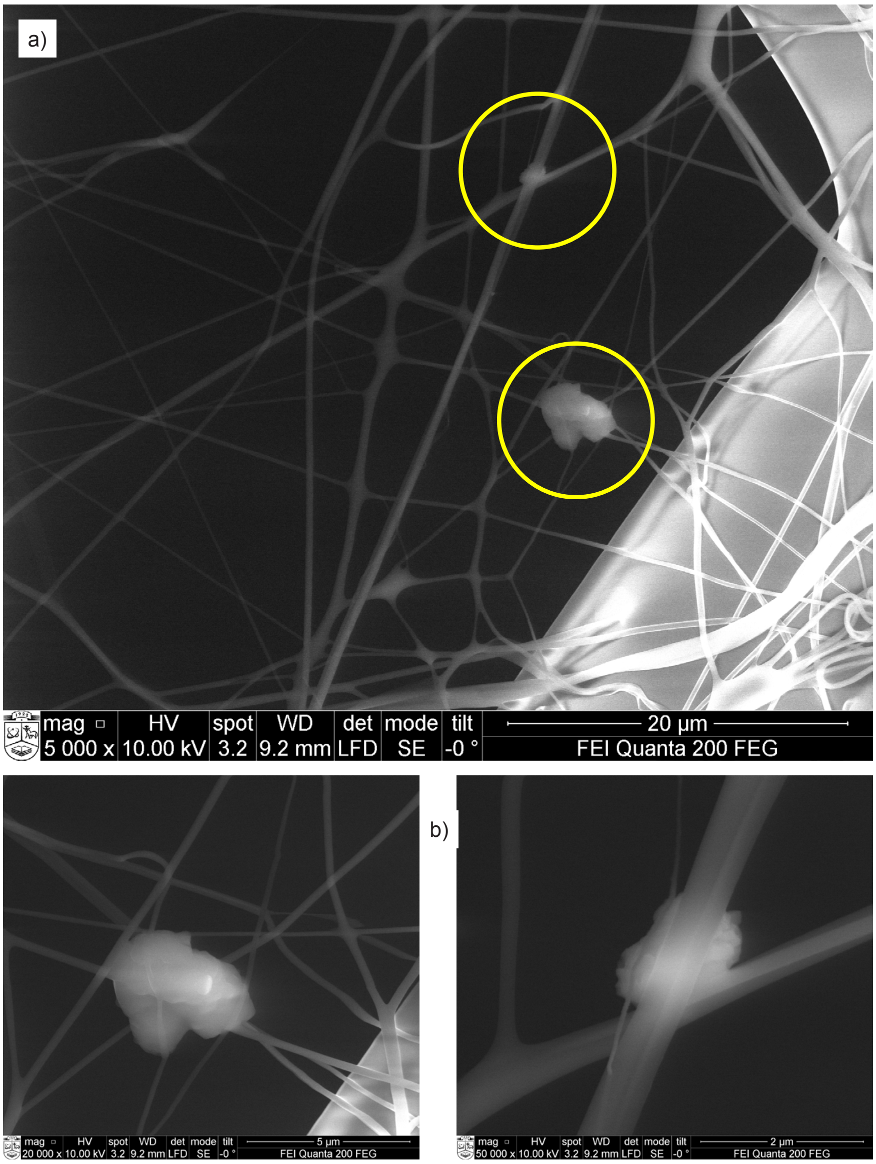

***Figure 5.** SEM images of electrospun web with small size of amber: a) image with resolution 20 µm, b) images with very high resolutions (5 and 2 µm).*

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- Hexachlorocyclohexane (lindane)
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- Phthalates
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