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Needleless electrospun nanofibers containing microcapsules: a methodology for self-supported microcontainers

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ABSTRACT
The present paper investigates the facile production of electrospun polyvinyl alcohol (PVA) nanofibers containing either micro-sized polymer or hybrid capsules, using a needleless electrospinning system. Oil-containing microcapsules with diameters of around 3 or 10 µm, respectively, were produced via an oil-in-water miniemulsion and mixed with a PVA solution. Appropriate adjustment of electrospinning parameters enabled a controlled assembly of PVA nanofibers into a network containing microcapsules, without damaging their integrity. The PVA nanofibers have diameters in a range of 200-300 nm and showed good homogeneity. The introduction of microcapsules caused an increase in the PVA nanofiber diameters probably due to an increase in the solution viscosity. The production of such self-supported and loaded microcontainers could be of high interest for various applications.
Keywords: Electrospinning, hybrid, microcapsule, nanofiber, polymer

I. INTRODUCTION

Electrospinning is a convenient and versatile technique to prepare continuous fibers with diameters ranging from tens of nanometers to several micrometers [1]. A basic electrospinning setup normally comprises a high voltage power supply, a syringe needle connected to power supply and a counter electrode. Unfortunately, and in spite of wide interests and applications, this technique runs at low production rate, which hinders further commercialization. Needleless electrospinning system is a new and scalable process that shows considerable improvement in the production rate. Particularly, the so-called Nanospider© technology is a unique method which has been industrially used to produce nanofibers continuously. In this case, Taylor cones (the nucleation of nanofibers) are created on the surface of a metallic wire electrode, continuously impregnated with droplets of a polymer solution. This is a simple and versatile method for production of ultrathin fibers from a variety of materials [2].

Various types of nanomaterials have been introduced in polymer blends for electrospinning: encapsulated hydrophobic liquids [3,4,5,6], cellulose nanofibrils [7], dye [8] and nanoparticles [9]. On the other hand, the introduction of micron-size particles in electrospun blends is new and potentially of high interest, and only a very limited amount of work can be found in the literature. For instance Bansal *et al*. studied water-stable microparticles with size up to 1.2 µm in polyethyleneoxide (PEO) nanofibers for pheromone release [10]. Salalha *et al*. worked on the encapsulation of bacteria and viruses with typical size of 1 x 2 µm in electrospun nanofibres and proved a relatively high viability [11]. Brettman *et al*. investigated the spinability of polystyrene beads in polyvinylpyrrolidone (PVP) nanofibers [12]. Their work probably opened the route for electrospinning of larger or more complex geometries by electrospinning microparticles up to a diameter of 10 µm.

However, to the best of our knowledge, this paper is the first report on the preparation of electrospun nanofibers containing microcapsules using a needleless electrospinning process. This fabrication method is considered as a key enabling technology, a generic principle that can be made available for many different applications. We choose here to demonstrate the feasibility of this process by using polyurea (PU) based microcapsules containing an oil in an electrospun PVA nanofiber network. PVA is a highly hydrophilic, nontoxic and biocompatible polymer with excellent properties such as strength, water solubility, gas permeability and thermal characteristics [13] and applied in many fields especially biomedical, i.e. effective biodegradable polymer carriers for drug delivery.

II. EXPERIMENTAL

Materials: All chemicals were analytical grade: 87-90% hydrolyzed polyvinyl alcohol (PVA, average mol. wt. 30 000 - 70 000, Sigma Aldrich), polyethylene glycol (PEG, M_w 2000), oil (Mereta 49, Statoil), Diphenyl methane diisocyanate

(Desmodur VL, Covestro), isophorone diisocyanate (IPDI, Fluka), diethylenetriamine (DETA, Sigma Aldrich), Diazabicyclo[2.2.2]octane (DABCO, Sigma Aldrich), guanidine carbonate (MERCK) and concentrated phosphoric acid were used without further purification. Amine-POSS, a hybrid organic/inorganic polyhedral oligomeric silsesquioxanes (POSS), has been prepared by a sol–gel process as reported previously by our group [14].

Preparation of microcapsules: Oil-filled polyurea-based microcapsules were synthesized based on a modified experimental procedure previously published [15]. *Polymeric capsules*: Briefly, an oil-in-water miniemulsion was prepared by emulsifying an oil phase (Mereta 49, IPDI) in an aqueous phase (1% PVA) using a homogenizer (3x400kg/m^2). A saturated solution of guanidine carbonate in water was added dropwise to the emulsion while stirring. The reaction was conducted at 70°C for 16h. *Hybrid capsules*: Briefly, an oil-in-water miniemulsion was prepared by emulsifying an oil phase (Mereta 49, Desmodur) in an aqueous phase (PVA 2%) using an ultraturrax (9500 rpm, 2 x 1 min). A mixture of DETA, DABCO, amine-POSS and distilled water was then added dropwise to the emulsified solution. The reaction was conducted at 40°C for 4h.

Electrospinning solutions: In parallel, a 11wt% PVA solution was prepared by dissolving PVA powder in distilled water at 90°C. A 5% PEG solution was prepared the same way. After cooling to room temperature, both solutions were mixed at a volume ratio of PVA/PEG 80:20. To facilitate the electrospinning, a small amount (0,5 %wt) of concentrated phosphoric acid was added. Finally, 20 mL of the microcapsule suspension was then added to 80 mL of the prepared PVA solution, and gently stirred for 30 min before electrospinning. The final concentration of capsules in PVA was ca. 1.8 wt%.

Electrospinning: PVA-based nanofibers were electrospun using a NS-LAB Nanospider^{TM} laboratory instrument (Elmarco, Czech Republic). The electrospinning substrate was a non-woven polypropylene (PP) antistatic material (Pegatex S, 30 g/m^2) provided by Elmarco. The polymer mixture was charged in a carriage reservoir and delivered to the spinning electrode wire at a speed of 100 mm/s. Electrospun fibers were produced at a voltage of 70 kV, at a fixed distance of 20 cm, and the PP substrate speed was fixed at 10 mm/min. *Note*: This equipment is based on the new generation of electrospinner fabricated by Elmarco, where the electrospinning electrode does not consist of a rotating cylinder immersed in the spinning solution as previously reported in several papers but as a thin wire constantly coated with a solution using a moving applicator reservoir.

Characterizations: Conductivity of solutions before electrospinning was measured using a FG-3 FiveGo^{TM} from Mettler Toledo. Optical microscope images were taken using a Leica M420 equipped with a digital camera. The morphology of the electrospun nanofibers was observed using a FEI Nova NanoSEM 650 field emission gun scanning electron microscope (FEG-SEM). Prior to SEM imaging, all samples were carbon coated.

III. RESULTS

Microcontainers used in this report were synthesized by interfacial polymerization from an oil-in-water emulsion using the miniemulsion polymerization method. Different average sizes could be produced depending on the experimental parameters controlled during the procedure, but we choose here to use only one size of hybrid and polymer capsules for demonstration. Optical microscope images are shown in figure 1 and have been analyzed using ImageJ software for particle size distribution analysis. The results showed a rather large capsule size distribution ranging from 1 to 40 µm, but with high frequency sizes centered at 3 and 10 µm for polymer and hybrid microcapsules, respectively, which is in agreement with our previous work [15]. Further microscopic investigations showed well defined round shapes and shell surface configuration of microcapsules, as well as a high encapsulation yield (>90%).

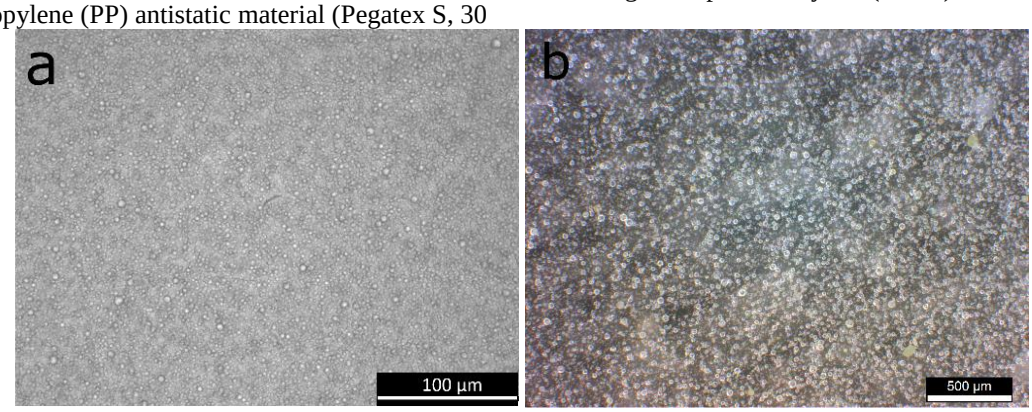


Figure 1: Optical image of a) synthesized polymer microcapsules, b) synthesized hybrid microcapsules.

Samples	Average capsule size	Conductivity	Voltage electrospinning	Distance between electrodes	Average fiber diameter (±10 nm)
PVA	-	10,3 mS/cm	70 kV	20 cm	150 nm
PVA + polymer capsules	3 µm	7,5 mS/cm	70 kV	20 cm	210 nm
PVA + hybrid capsules	10 µm	7,2 mS/cm	70 kV	20 cm	220 nm

Table 1: Parameters of the different prepared samples.

Suspensions of PVA and PVA containing microcapsules have been electrospun and look visually similar, like a white thin layer on the blue nonwoven PP support. Macroscopically, the effective width of electrospun samples is up to 50 cm, and the length of the produced samples varies from 40 to 80 cm, depending on how long the roll-to-roll electrospinning process is performed. After electrospinning, optical microscopy of a sample of PVA containing hybrid microcapsules at a magnification of 35x (Figure 2) clearly showed the distribution of microcapsules in the electrospun fiber web spread on the surface of the PP support.

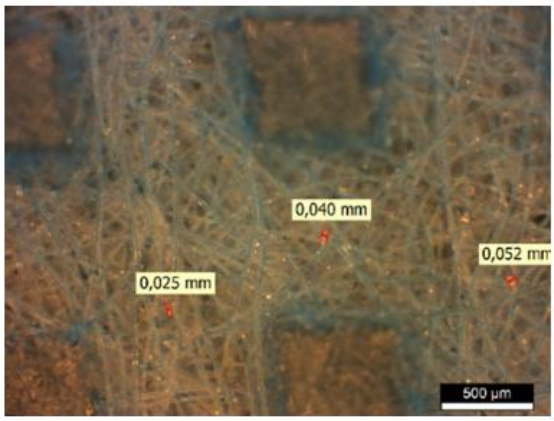
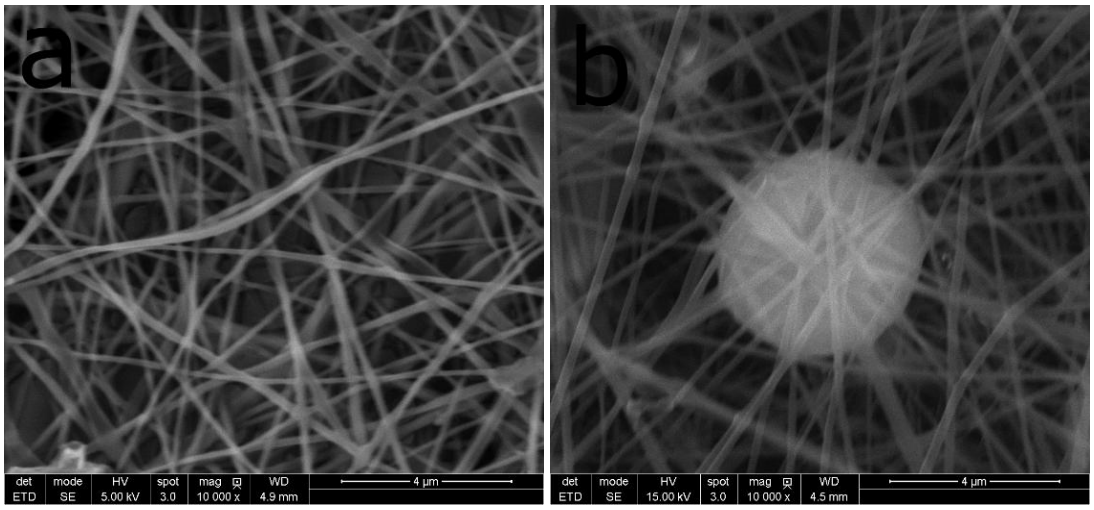


Figure 2: Optical image of electrospun PVA nanofibers comtaining hybrid microcapsules (the square patterns in the background image come from the underneath PP substrate machining)



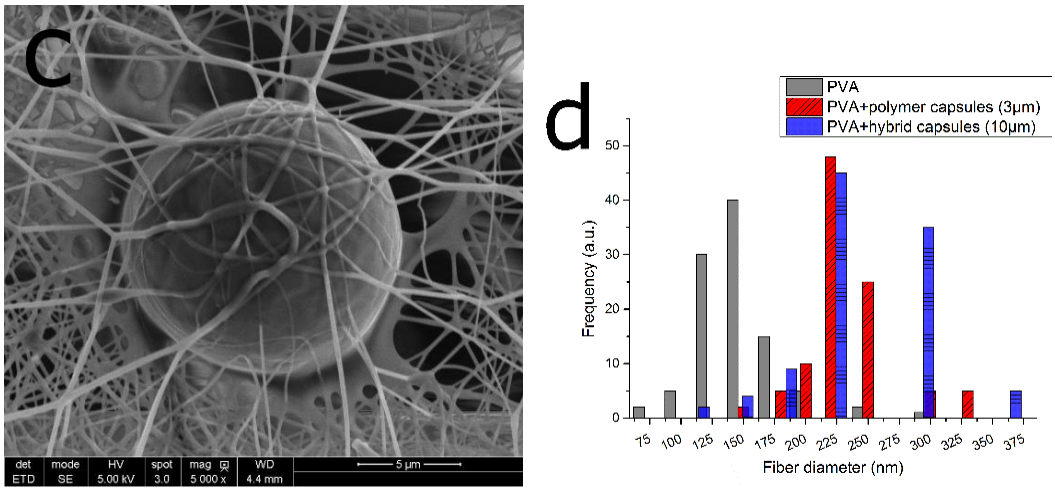


Figure 3: SEM pictures of a) PVA nanofibers, b) PVA nanofibers + polymer capsules with an average size of 3 µm, c) PVA nanofibers + hybrid capsules with an average size of 10µm; d) fiber diameter distribution

Figure 3a shows a SEM image of electrospun neat PVA nanofibers (without microcapsules). The as-prepared PVA nanofibers are randomly distributed to form a non-woven fibrous mat characteristic of needleless electrospun samples. Fiber diameters have been measured on a relevant number of SEM images between 30 and 300 nm with high frequency centered at 150 nm. The surface of nanofibers is smooth and only a very small amount of beads and imperfections were observed.

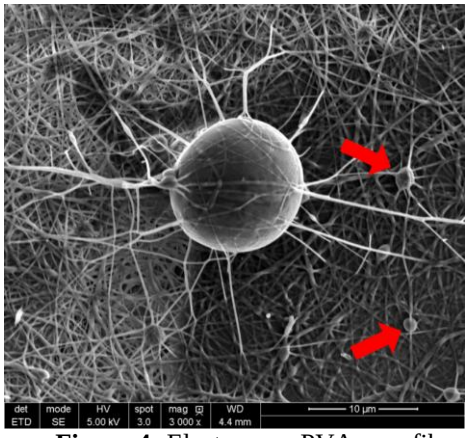


Figure 4: Electrospun PVA nanofibers containing hybrid microcapsules; red arrows show some beads along the nanofibers

The SEM images of the electrospun PVA network containing both types of microcapsules in figure 3b and 3c show that fibers are continuous with an average diameter higher compared to pure PVA nanofibers, between 120 and 370 nm with high frequency centered between 220 and 230 nm (figure 3d). The polymeric network showed good homogeneity and fibers appeared with low defects on all produced samples, even though we observed more droplets on the surface as well as several beads on some fibers (figure 4), compared to neat PVA. Individual fibers had a very high aspect ratio and appeared with a visually smooth and uniform surface. We could not observe significant changes in the size or shape of the microcapsules in the nanofiber web, indicating that the electrospinning process did not alter or damage the microcapsules. A contrario to previous work [12], we could observe a slight change in nanofiber diameters when capsules are added in the polymeric solution. This difference could be explained by both the viscosity of the solutions and the solvent-polymer-capsule interactions.

IV. CONCLUSION

For the first time, a material with microcapsules entrapped in a nanofiber network has been successfully produced using a one-pot solution and needleless electrospinning. After electrospinning, we observed that the addition of either polymer or hybrid microcapsules increased the average nanofiber diameters. Especially, the hybrid capsules may give new opportunities to produce high-performance materials, due to their superior mechanical strength and diverse functionalities, compared to polymeric capsules. The introduction of microcapsules with an active component into electrospun nanofibers is new, bringing opportunities to develop self-supported micronized containers and therefore is believed to bring new insights in several applications.

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