Published in Proceedings of the 12th International Conference Nanomaterials: Applications & Properties (NAP), Krakow, Poland, 11-16 september 2022, which should be cited to refer to this work.
DOI: 10.1109/NAP55339.2022.9934136

Large Area Fabrication of Bio-Sourced Polymer Nanofibers for Food Packaging Applications

Silvia Schintke
Laboratory of Applied Nanosciences
Department of Industrial Technologies
HEIG-VD//HES-SO University of Applied Sciences Western Switzerland
Yverdon-les-Bains, Switzerland
silvia.schintke@heig-vd.ch

Léonard Troesch
Laboratory of Applied Nanosciences
Department of Industrial Technologies
HEIG-VD//HES-SO University of Applied Sciences Western Switzerland
Yverdon-les-Bains, Switzerland
leonard.troesch@heig-vd.ch

Stefan del Rossi
Laboratory of Applied Nanosciences
Department of Industrial Technologies
HEIG-VD//HES-SO University of Applied Sciences Western Switzerland
Yverdon-les-Bains, Switzerland
stefan.delrossi@heig-vd.ch

Eleonora Frau
Laboratory of Applied Nanosciences
Department of Industrial Technologies
HEIG-VD//HES-SO University of Applied Sciences Western Switzerland
Yverdon-les-Bains, Switzerland
eleonora.frau@heig-vd.ch

***Abstract*— Electrospinning of two bio-sourced polymers, suitable for edible food packaging applications, chitosan, as well as pullulan, is investigated in view of large area fiber mat production. The fiber shape and dimensions were measured using scanning electron microscopy and atomic force microscopy, for various process parameters using rotating disc electrodes. An electrospinning pilot production system was designed for the fabrication of large area nanofiber and microfiber mats, using a drum collector electrode together with controllable lateral needle motion. System tests were performed using polyethylene oxide. Finally, large area fiber mats of pullulan were produced. The system is promising for the development of edible, bio-sourced packaging applications.**

Keywords—nanofibers, electrospinning, system design, edible polymers, food packaging, large area coating

I. Introduction

Nanofiber and microfiber mats of edible or bio-sourced polymers are promising materials for advanced food packaging applications [1-3]. Biopolymers and edible polymers have gained special attention in research on active packaging, aroma encapsulation, and their microbial properties in order to replace conventional plastics of packaging materials or to increase shelf life by coating conventional packaging materials. A recent comprehensive review on food packaging perspectives of electrospun nanofibers can be found in [4], in particular, chitosan and pullulan have gained attention in this context.

Chitosan is one of the leading polysaccharides on the polymer market [5]. Electrospinning of chitosan needs a carrier polymer [4], chitosan nanofibers have e.g. been studied for dry-aging of beef [6]. Another prominent example is the bio-polymer pullulan, widely used as a food additive [7], which is also studied for active food packaging applications [4,7].

Nano- and microfibers have the advantage of large surface area compared to flat thin films, when it comes to oxygen scavenging or release of antimicrobial compounds in active packaging applications. Therefore, up-scalable and reproducible large area nanofiber mat fabrication is needed in research and development towards the use of electrospinning in industrially relevant packaging applications.

In this study, we have thus investigated the examples of chitosan and pullulan, and nanofiber mat production to identify a stable and reproducible parameter range for electrospinning. Finally, we have designed and constructed an electrospinning set-up that allows for large area fiber mat production, being compatible with up-scalable roll-to-roll manufacturing. Machine testing with pullulan allows for large area fabrication of nanofiber mats.

II. Experimental

A. Formulation of polymer suspensions for electrospinning

Chitosan (Sigma Aldrich) was dispersed together with gelatin (gelatin from bovine skin, Sigma Aldrich) in acetic acid (AC) (aq, M60.05, Sigma Aldrich). The formulation was inspired by a method presented by Ebrahimi et al. [1]. Gelatin was dissolved by magnetic stirring at ambient temperature in an aqueous acetic acid solution (AC) (60% v/v) to obtain a solution of 14.4% wt/v. Chitosan powder was dissolved in AC (60% v/v) at a concentration of 3.6% wt/v. The chitosan and gelatin solutions were mixed in a ratio of 1:4 and magnetically stirred for 24h at room temperature before usage.

Pullulan (kindly provided by Hayashibara Co, Japan) was dispersed together with with cyclodextrin (β-CD, Fischer scientific) in a solution of limonen-cyclodextrin (aq); the formulation was inspired by a method presented by Fuenmayor et al. [2]. An aqueous solution of pullulan (20% wt/wt) was prepared by magnetic stirring for 4 hours at room temperature, then cyclodextrin (β-CD, 25% of the mass of pullulan) was added. A solution of R-(+)-Limonen (Fischer scientific) was then prepared, R-(+)-Limonen/β-CD (90:10), 10% wt of the previous solution, and added. For emulsifying, a micro-centrifuge (Argos Flexifuge, Cole-Parmer Instruments Company Ltd, UK) was used at 9200 rpm for 6 min.

The obtained viscosity of the emulsions was measured using a micro-viscometer (μVISC, Rheosens Inc, Tracomme, Switzerland).

Furthermore, a test solution of polyethylene oxide (PEO, Sigma Aldrich) was prepared by dissolving PEO in acetonitrile (60 mg/ml) by magnetic stirring at room temperature; the PEO solution was used for validation tests of the electrospinning system.

B. *Electrospinning*

Electrospinning was first performed onto a rotating circular disc electrode (diameter 26 mm) made of brass. For large area electrospinning of pullulan, a system with a rotating cylinder (drum collector) electrode was used; the system design is presented in section III).

The parameters for electrospinning were adjusted to the following values (unless differently stated): (i) for the chitosan-gelatin solution: inner needle diameter di=0.61 mm (0.40 mm), volume flow rate dV/dt=0.1 ml/h, needle-collector distance d=20.0 cm (15.0 cm, 25.0 cm), high voltage HV= 19.0 kV (17.0 kV, 21.0 kV), deposition time t=30 s (1 min, 2 min, 5 min); (ii) for the pullulan solution: inner needle diameter di=0.61 mm (0.40 mm, 0.84 mm), volume flow rate dV/dt=0.1 ml/h (0.05 ml/h, 0.2 ml/h), needle-collector distance d=17.0 cm (12.0 cm, 23.0 cm), high voltage HV= 15.0 kV (12.5 kV,17.5 kV), deposition time t=30 s (1 min, 2 min); for the PEO solution: inner needle diameter di=0.40 mm, volume flow rate dV/dt=50 μl/min, needle-collector distance d=12 cm, high voltage HV=15.9 kV.

C. *Nano – and microfiber characterization*

The fiber shape and dimensions were measured using scanning electron microscopy (SEM) (EVO 15, ZEISS, Germany) and atomic force microscopy (AFM) (XE-7, Park Systems, Germany). The diameters of the electrospun fibers were investigated based on SEM images, measuring at least 100 fibers for each parameter variation; for each analysis, SEM images of at least three different sample regions were considered.

III. Electrospinning System Design and Validation

To produce large area nano- and microfiber mats, electrospinning systems using a drum collector electrode was designed and constructed. The drum collector (diameter 60 mm, length 33 mm) of the electrospinning system (Fig.1), is powered by an electric DC motor (Transmotec).

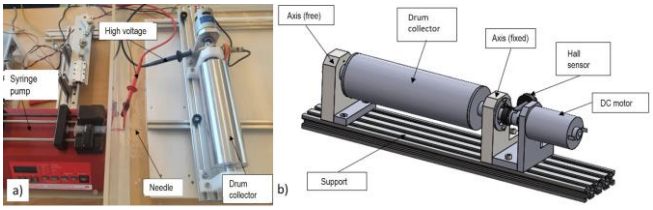

Fig. 1. Electrospinning system with drum collector: a) photo of the system with a syringe pump and needle (left) and drum collector (right); b) CAD system design 3D view (designed using SolidWorks).

The system allows for adjustment of the cylinder rotation speed, up to 4000 rpm, monitored by a Hall sensor. Repetitive lateral needle displacement during electrospinning covers a displacement range of 14 cm, by using a motorized crankshaft for adjustable operation at frequencies of a few Hertz. System validation tests were performed using PEO at various drum collector speeds. Then, pullulan was used for large area fiber mat production.

This work has been financially supported by HES-SO, project PROINDAV, IA-EXT18-23-90668.

IV. Results and Discussion

A. *Chitosan-gelatin and pullulan nanofibers*

The viscosity of the chitosan-gelatin solution was 136 ±23 mPa·s. Fig. 2 shows representative SEM images of electrospun chitosan-gelatin nanofibers.

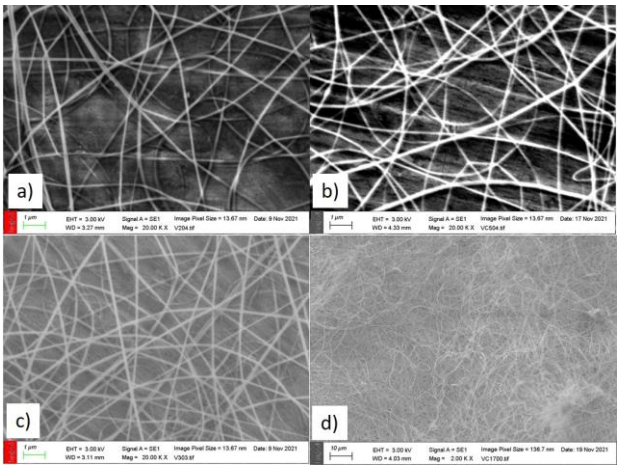

Fig. 2. SEM images of chitosan-gelatin fibers. Examples: a) base parameter set used for electrospinning: needle-collector distance 20 cm; high voltage 19 kV; deposition rate 0.1 ml/h, time 30 s; b) increased voltage (21 kV); c) increased deposition rate (0.2 ml/h); d) increased deposition time (2 min); scale bars: a)-c) 1 μm, d) 10 μm.

For samples corresponding to Fig. 2., fiber diameters are: a) (179±42) nm, b) (173±38) nm, c) (154±30 nm), d) (167±46) nm, demonstrating stable electrospinning results over a large range of parameters (specified in section II). Fig. 2d) furthermore shows that dense fiber mats are obtained upon electrospinning.

The viscosity of the pullulan solution was 2020±160 mPa·s. Fig. 3 shows SEM images of electrospun pullulan fibers.

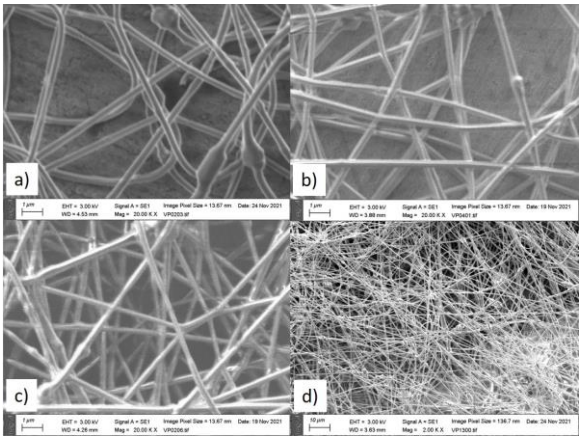

Fig. 3. SEM images of pullulan fibers. Examples: a) base parameter set used for electrospinning: needle-collector distance 17 cm; high voltage 15 kV; deposition rate 0.1 ml/h, time 30 s; b) decreased voltage (12.5 kV); c) increased deposition rate (0.2 ml/h); d) increased deposition time (1 min); scale bars: a)-c) 1 μm, d) 10 μm.

For samples corresponding to Fig. 3., fiber diameters are: a) (367±49) nm, b) (320±58) nm, c) (360±83) nm, d) (488±86) nm, demonstrating essentially stable electrospinning results over a large range of parameters (specified in section II). The observed increase of fiber diameters for longer deposition time (Fig 3d) is possibly related to solvent evaporation over time, and thus an increase in polymer concentration. Fig. 3d) furthermore shows that dense pullulan fiber mats are obtained upon electrospinning.

B. System validation and large area fabrication of nanofiber mats

Fig. 4 shows results from system validation tests performed by electrospinning of PEO. The PEO microfibers were collected on an aluminum foil placed around the drum collector. The fibers have a diameter of about 1.6 µm and are oriented essentially along the cylinder circumference. The observed inclination of the fiber orientation with respect to the circumference (aligned parallel to the vertical of Fig. 4) can consistently be attributed to the lateral needle displacements performed during electrospinning. The system has thus been validated for angular speeds up to 4035 rpm.

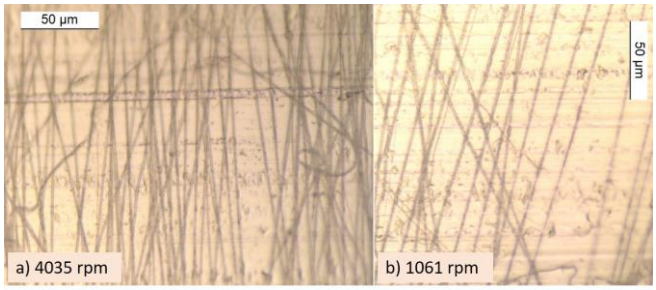

Fig. 4. Optical micrographs of electrospun PEO fibers at drum collector speeds of a) 4035 rpm and b) 1061 rpm. The lateral needle displacement speed was adjusted with a linear stepper motor to 98.97 mm/s.

Fig. 5. shows a large area of pullulan nanofiber mat (Fig 5.a) upon electrospinning using the drum collector system, as well as an optical micrograph of the pullulan fibers (Fig. 5b).

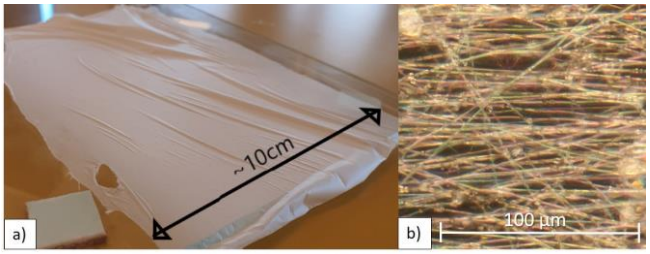

Fig. 5. a) Photo of a large area electrospun pullulan nanofiber mat; b) optical micrograph of the pullulan fibers.

The obtained large area pullulan nanofiber mats are thus promising for the development of active food packaging using bio-sourced polymer nanofiber or microfiber mats.

V. SUMMARY

Nanofibers of chitosan-gelatin and pullulan were produced by electrospinning. For both material formulations, a wide range of electrospinning parameters leads to the stable formation of nanofibers. Our designed electrospinning system using a drum collector electrode for large area fiber mat fabrication has been tested and validated for angular speeds up to 4035 rpm. Large area pullulan mats were successfully fabricated. The results are promising for the adaption of the system design towards a roll-to-roll production and large area fiber mat pilot studies on bio-sourced polymer nano- and microfiber membranes and coatings for active and edible packaging applications.

ACKNOWLEDGMENT

We kindly acknowledge contributions to early-stage prototyping by Fanny Carrard, Adrien Aymon, and Julien Gerber for the mechanical design of the electrospinning pilot system, as well as Pierre Burdet for initial assistance in SEM data acquisition.

REFERENCES

[1] Shayan Ebrahimi, Milad Fathi, Mahdi Kadivar, “Production and characterization of chitosan-gelatin nanofibers by nozzle-less electrospinning and their application to enhance edible film’s properties,” Food Packaging and Shelf Life, 2019, vol. 22, 100387.

[2] Carlos Alberto Fuenmayor, Erika Mascheroni, Cosio, Luciano Piergiovanni, Simona Benedetti, Alberto Schiraldi, and Saverio Mannino, “Encapsulation of R-(+)-limonene in Edible Electrospun Nanofibers,” Chemical Engineering Transactions, 2013, vol. 32, pp. 1771-1776.

[3] Leidy Ricaurte, Edisson Tello-Camacho, and Maria Ximena Quintanilla-Carvajal, “Hydrolysed Gelatin-Derived, Solvent-Free, Electrospun Nanofibres for Edible Applications: Physical, Chemical, and Thermal Behaviour,” Food Biophysics, 2020, vol. 15, pp. 133–142.

[4] T. Senthil Muthu Kumar, K. Senthil Kumar, N. Rajini, Suchart Siengchin, Nadir Ayrilmis, A. Varada Rajulu, “A comprehensive review of electrospun nanofibers: Food and packaging perspective,” Composites Part B, 2019, vol. 175, 107074.

[5] Tyliszczak, B., Drabczyk, A., Kudłacik-Kramarczyk, S., Sobczak-Kupiec, A. (2020). Sustainable Production of Chitosan. In: Królczyk, G., Wzorek, M., Król, A., Kochan, O., Su, J., Kacprzyk, J. (eds) Sustainable Production: Novel Trends in Energy, Environment and Material Systems. Studies in Systems, Decision and Control, vol 198. Springer, Cham.

[6] María Gudjónsdóttir, Manuel D. Gacutan Jr., Ana C. Mendes, Ioannis S. Chronakis, Lene Jespersen, Anders H. Karlsson, “Effects of electrospun chitosan wrapping for dry-ageing of beef, as studied by microbiological, physicochemical and low-field nuclear magnetic resonance analysis,” Food Chemistry, 2015, vol. 184, pp. 167-175.

[7] Stefano Farris, Ilke Uysal Unalan, Laura Introzzi, José Maria Fuentes-Alventosa, Carlo A.Cozzolino, “Pullulan-Based Films and Coatings for Food Packaging: Present Applications, Emerging Opportunities, and Future Challenges,” J. Appl. Polym. Sci., 2014, vol. 131, p. 40539.