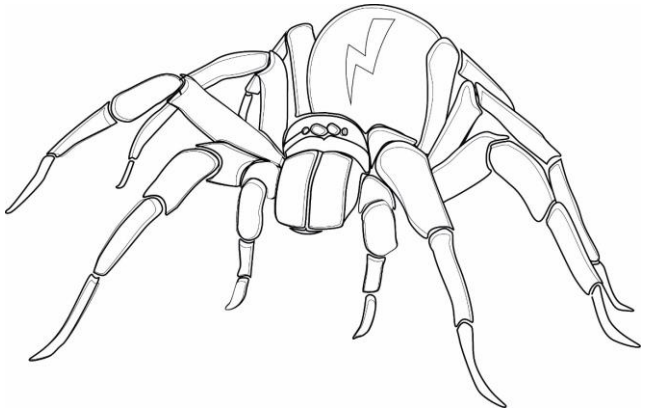
Melt electrospinning towards industrial scale nanofiber production

Chapter 7

Summary and outlook



Summary

In this thesis, a new developed scaled-up melt-electrospinning prototype featuring 600 nozzles, bridging the gap between laboratory-scale and industrial-scale nanofiber manufacturing, is presented (**Chapter 1**). Herewith tackling the industry-relevant key challenge of increasing the production of nanofibers for various applications such as filtration and medicine in a sustainable and efficient way. The prototype device vastly exceeds the capabilities of any state-of-the-art technology and is successfully used to produce nanofibers with comparable quality and properties to nanofibers produced with the more conventional solution electrospinning process.

Chapter 2 focuses on the forces acting on the polymer melt, process parameters and electrospinning setups influencing the fiber formation. Based on the technical principles, the following assumptions are made for this work: The collector of the pilot-scale melt-electrospinning device is positively charged and the spinneret is grounded, the distance between the collector and the spinneret (11 cm), as well as the applied voltage (60 kV) are kept constant for all trials. Hence, the influence of the parameters polymer flow rate and temperature on the fiber diameter as well as material modifications resulting in an increased electrical polymer conductivity and/or decreased polymer viscosity can be investigated and validated uninfluenced by these parameters.

In **Chapter 3**, the feasibility of fabricating polypropylene nanofibers is investigated using the conductive additives sodium stearate, sodium oleate and Irgastat during melt electrospinning with a single-nozzle lab-scale and the 600-nozzle pilot-scale device. A comparison is made between the two devices with regard to the effects on the fiber diameter and the material behavior. The experiments have shown that a transfer of the results from the laboratory- to the pilot-scale melt-electrospinning device is not possible without further ado. The major issues are the dwell time in the spinneret compared to the syringe and the different shear rates. The high melt flow PP HL712FB cannot be processed with the pilot-scale device due to its low viscosity, resulting in an insufficient pressure built up within the spinneret, which leads to droplet formation instead of a continuous fiber formation. The additives – in particular sodium oleate – lead to a strong degradation of the polymer, which requires extensive cleaning of the devices from degradation products and impairs the formation of fibers. The integration of a climate chamber leads to the finest fibers on a laboratory-scale with a fiber diameter of less than 500 nm using the material combination PP HL712FB + 4% (w/w) NaSt and 2% (w/w) Irgastat. At the pilot scale, the smallest fiber diameter of 6.64 µm is achieved with PP HL508FB + 2% (w/w) NaSt, which yields a fiber diameter of 2.07 µm on a laboratory scale.

In **Chapter 4**, the manufacturing of biobased polylactic acid sub-microfibers by melt electrospinning using a single-nozzle laboratory-scale and the novel 600-nozzle pilot-scale device combined with the conductive and viscosity-reducing additives: sodium stearate, sodium chloride and a polyester-based plasticizer is investigated. Additionally,

a two-way variance analysis (ANOVA) is performed to determine the influence of the independent parameters spin pump speed, temperature and additive concentration on the fiber diameter. The first PLA-based fibers in the low micrometer range are sucessfully produced. The addition of 6% (w/w) NaSt is required to produce the smallest average fiber diameter (3.77 µm) using a spinneret temperature of 195 °C and a spin pump speed of 0.5 rpm (0.16 cm^3). The smallest single fiber diameter (1.23 µm) is achieved at the same conditions but using a spin pump speed of 2 rpm (0.64 cm^3). A higher quantity of additive promotes material degradation due to the processing and dwell time, which inhibited fiber formation. Fibers with diameters in the low micrometer range are achieved, comparable with previous reports, without the integration of a heated spinning chamber or additional air flow, which are already widely used at the laboratory scale to achieve further stretching of the fibers. The carried out ANOVA reveals statistical significance for all examined, independent factors (spin pump speed, additive concentration and temperature). Evaluated by the effect strength η, the additive concentration has the greatest influence on the fiber diameter. At the laboratory scale, the effect of viscosity-reducing additives (NaSt and plasticizer) as well as NaCl, which increases the conductivity of the polymer melt, are determined. The smallest average fiber diameter (16.44 µm) is achieved by adding 2% (w/w) NaCl but the spinning process cannot be stabilized. The formation of a Taylor cone followed by fiber deposition is achieved with compounds containing NaSt or plasticizer, but the latter does not reduce the viscosity of the melt at the concentrations tested and its influence on fiber diameter therefore cannot be determined. Concluded is that the additive NaSt has the greatest potential to optimize the material properties of PLA for melt electrospinning.

Since the added salts can potentially increase the hydrolysis and degradation of the moisture-sensitive PLA, the use of the biobased dyes alizarin, hematoxylin and quercetin as conductivity-enhancing additives and a biobased plasticizer in laboratory-scale melt electrospinning is also investigated in **Chapter 4.** All dyes and dye/plasticizer combinations contribute to the desirable reduction of fiber diameter compared to pure melt-electrospun PLA fibers, which facilitates the development of an economical and environmentally friendly process for the production of microfibers and nanofibers that could ultimately replace solution electrospinning. The formation of a Taylor cone followed by continuous fiber deposition is observed for all dyes and dye/plasticizer combinations. The finest fibers (16.04 µm in diameter) are produced by adding 2% (w/w) hematoxylin, reducing the average fiber diameter by 77% compared to pure PLA. However, hematoxylin induces polymer degradation at a spinning temperature of 275 °C, which reduces the M_w and, therefore, favors the production of finer fibers. The addition of alizarin produces finer fibers than pure PLA despite the increase in melt viscosity, indicating that alizarin has a profound effect on the electrical conductivity of the melt. A combination of alizarin (to increase conductivity) and a plasticizer (to reduce viscosity) reduced the fiber diameter to 23.80 µm, which is 63% narrower than the pure PLA fibers. The addition of quercetin reduced the melt viscosity but had a limited effect on electrical conductivity compared to alizarin, and the finest fibers containing this additive (achieved

by adding 2% (w/w) liquid quercetin) were 36.72 µm in diameter. The comparison of fibers produced by melt spinning, melt spinning with post-drawing, and melt electrospinning reveals that the melt-electrospun fibers had a similar degree of crystallinity to partially-oriented filaments and are not comparable to drawn filaments.

In previous experiments, using the pilot-scale melt-electrospinning device without appropriate climate control, fibers exceeding 1 µm in diameter are produced, because the drawing of fibers is inhibited by the rapid cooling of the polymer melt. In **Chapter 5** the effects resulting of an integration of a climate control system in form of a glass chamber are investigated. The glass chamber creates a temperature gradient exceeding the glass transition temperature of the polymer, allowing the further drawing of fibers below the spinneret. An average fiber diameter of 810 nm is achieved using PLA Ingeo Biopolymer 6252 (Figure 7.1), and the finest individual fiber (420 nm in diameter) was produced at a spin pump speed of 5 rpm and a spinneret set temperature of 230 °C. The fiber diameters achieved are the smallest fiber diameters yet achieved with an upscaled multi-nozzle melt-electrospinning device of this size.

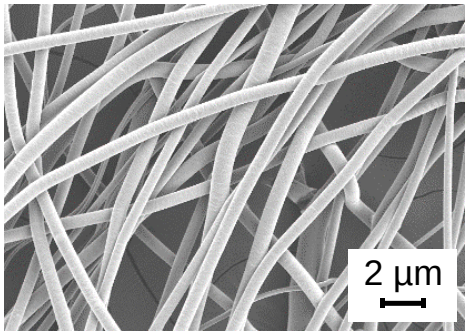


Fig. 7.1: PLA Ingeo Biopolymer 6252 fibers with an average fiber diameter of 810 nm.

The presented upscaled melt-electrospinning process for the manufacture of microscale and nanoscale fibers prevents the use and disposal of toxic solvents, as well as a possible carry-over of the solvent into the final product, making a decisive contribution to a truly sustainable process chain. With the valorization (**Chapter 6**) it is shown that the device technology developed can be used advantageously compared to previous processes for the manufacturing of actual industrially relevant product examples such as filtration nonwovens and medical tissues.

Outlook

There are still opportunities for further improvement of the performance of the device and material. In future attempts a combination of the two salts, NaCl and NaSt, might also be tested in order to combine the respective positive effects of increasing conductivity and lowering viscosity. Thus, lowering the fiber diameter even further. The experiments with PLA and alizarin should be transferred to pilot scale, as they have shown promising

results on laboratory scale. Other polymers such as the biobased, biodegradable polybutylene succinate seem promising to be tested in the melt-electrospinning process. Preliminary tests have shown that the fiber diameter can be halved compared to pure PLA using the same process conditions in laboratory scale. Regarding the thermal degradation problem, the spinneret has to be optimized to reduce dwell times. Furthermore, individually controlled collector tips in a multi-nozzle structure with the writing ability of melt electrospinning could lead to the development of truly innovative microfiber and nanofiber products.