Final Report

Development of electrospun thermoplastic nanofibers and related composites (OTKA PD 116122)

1. Introduction

The main topic of the research project was electrospinning, a technique, which makes possible to produce nanofibers from various polymer solutions with controllable morphological parameters. The process uses electrostatic forces acting in an electrostatic field to draw fibers (unlike classical fiber forming processes, where mechanical forces are applied). There are several current problems exist, which hinders the industrialization of the method.

At first, electrospinning has low productivity compared to classical synthetic fiber drawing mechanisms. The classical electrospinning technique, widespread in research, generates the nanofibers from a single metal capillary. The forming jet typically has low travel speed and the amount of the solvent within the jet is approximately 80-95 weight%. This results in a productivity rate of only 0.01-0.5 g/h for a single capillary. Other disadvantage is that at classical electrospinning expensive and harmful solvents are applied, their regeneration is also an issue. Application of polymer melt can be feasible, but the high viscosity and the low electrical conductivity of the polymer melt only makes possible to produce microfibers in general. At solution electrospinning viscosity can easily be set by the dilution of the solution and by admixing salts or conductive nanoparticles to the solution. Decreasing the viscosity leads to using more solvent and resulting in smaller fiber productivity of the capillary. Moreover, after reaching a minimum viscosity limit, no fibers can be obtained. We choose either the solution or the melt electrospinning, strong compromise must be taken.

2. The goals we expected prior to the project application

When applying for the project, our main goal was to elaborate the basics of an industrially feasible melt electrospinning process and to further develop our formerly invented solution-based technology, both in laboratory scales. We expected to create nanofibers with appropriate morphology and mechanical properties by cost-effective ways. The results would make possible to be able to design thermoplastic nanofiber structures and their composites for different mechanical and thermo-mechanical loads. The project was destined to answer several environmental concerns such as the productivity optimization, minimization of organic solvents, generation of easy-to-recycle self-reinforced composites both leading to lower environmental impact. Hereby, we introduce how we reached our goal during the given 3-year period.

3. Solution electrospinning results

The needleless electrospinning method was invented, which works with one or more thin and preferably adjustable orifices between high voltage moving electrodes. Shear stresses are generated by the relative motion of the electrodes surrounding the orifice(s). This makes possible to alter the apparent viscosity of the non-Newtonian liquid during electrospinning, leading to higher throughput and adjustable fiber diameters. In the case of pseudoplastic (shear-thinning) or thixotropic liquids the viscosity is reduced. Lower viscosity means smaller intrinsic resistance against deformation that helps to initiate more fiber jets and also to generate thinner fibers. Lower viscosity also makes possible to work with higher polymer concentrations (*id est* better production rates and less solvent evaporation). With the method invented, the processing of thixotropic polymeric solutions, higher molecule mass polymers and sol-gels becomes possible. Moreover, by adjusting the speed of the motion the shear stress can be adjusted, leading to the ability to control fiber diameter during the process without modifying the solution concentration, surface tension or other process parameters. The new invention allows easy maintenance & cleaning and high processing flexibility. The scheme of the device is depicted in Figure 1.

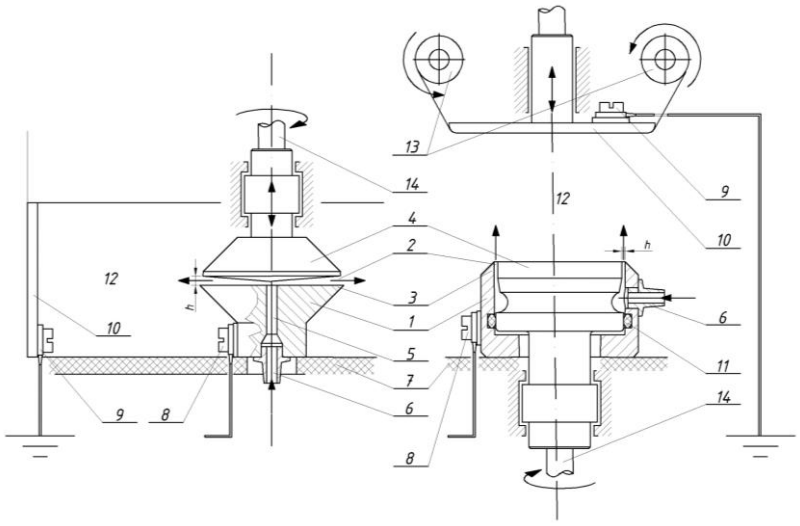

Figure 1. Schematic representation of the electrospinning setup according to the current invention using a) radial arrangement (cone-plate, plate-plate, or cone-cone arrangement) b) axial arrangement,

1: Electrospinning spinneret housing, 2: Orifice (or gap), where h denotes its characteristic size, 3: Bounding part A.: high voltage electrode (stator), 4:Bounding part B.: moving part (rotor), 5:Runners, 6: Material inlet, 7:Base, 8: High voltage connector, 9: Collector electrode electric connector, 10: Collector electrode, 11: Sealing, 12: Electrospinning (fiber forming) space, 13: Winding rollers, 14: Drive shaft

One exemplary embodiment of the device is shown in Figure 2. With the 50 mm diameter spinneret, nanofibers with a flow rate of 25 ml/h was produced from shear-thinning polyethylene oxide solutions. Figure 2 d shows the Taylor-cones forming from the meniscus of the solution.

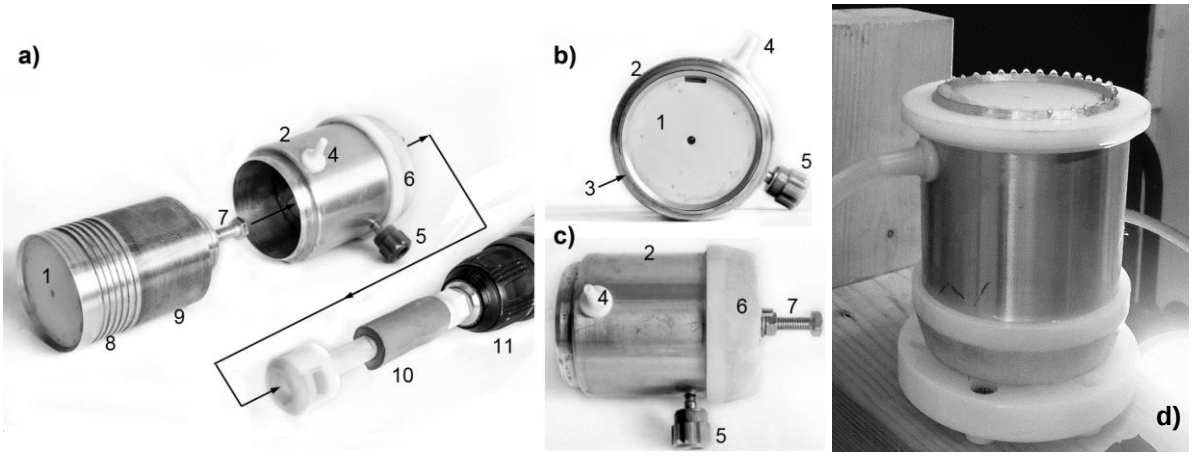

Figure 2. The spinneret in a) exploded, b) top, c) side views and d) in operation. 1: rotor, 2: stator, 3: orifice, 4: solution inlet, 5: high voltage connector, 6: base, 7: hexagonal drive connection, 8: solution take-up thread, 9: sliding bearing, 10: flexible plastic/rubber shaft, 11: chuck

With another exemplary embodiment of the device, we found a relationship between the nanofiber diameters and the rotation speed and also for the diameter *vs*. viscosity (see Figure 3.).

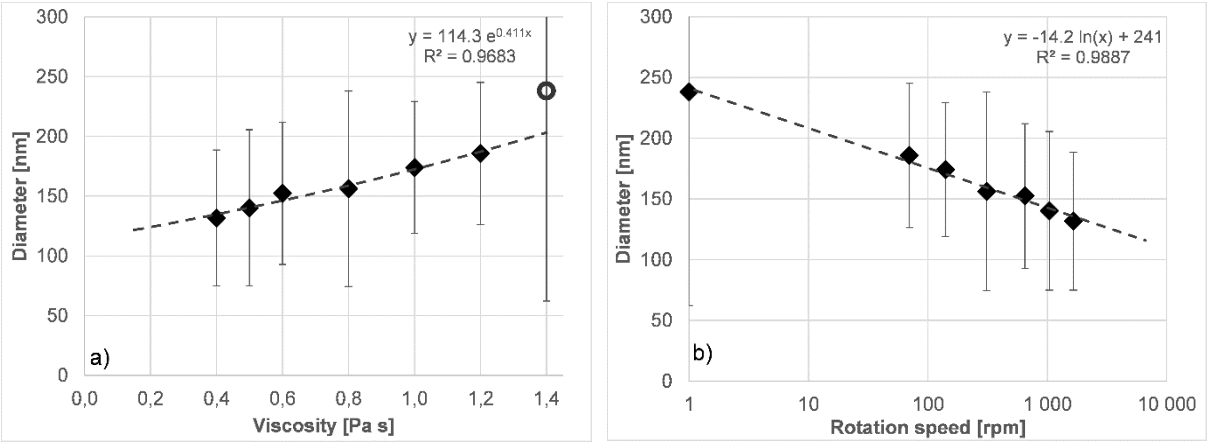

Figure 3. Fiber diameters as a function of dynamic viscosity (a) and rotation speed (b) (here the stationary spinneret was depicted as 1 rpm for better representation in logarithmic scale)

We demonstrated that the fiber diameters can be set in a wide range by simply adjusting the rotation speed of the motor, a phenomenon which originates from the variable and controllable shear conditions. During classical electrospinning, the parameters to control are usually the solution concentration, surface tension, molecular weight, etc. but here the diameter can be set by adjusting the angular velocity of a motor, even during operation.

Related publications [1, 2, 5, 6, 8, 17, 18, 19, 21, 22, 23]

4. Melt electrospinning and melt blowing

The other aspect of the project was to study the generation of nanofibers from polymer melts that is summarized shortly in this chapter. For the experiments a special isotactic PP (Borealis Borflow hl512fb type) material having extremely low melt viscosity (MFI: 1200 g/10 min; 230°C and 2.16 kg) and small polydispersity index was selected.

4.1. Melt electrospinning from single capillary

We designed and built a prototype that basically works like a capillary plastometer, but it can be charged at high voltage. The prototype includes state-of the art temperature control loop and an interchangeable metal capillary, however it cannot maintain a continuous operation for more than a few minutes. First the material granules are dispensed into a 12 mm diameter barrel of a piston. The heating is implemented from outside of this barrel. The piston can be pressed and the desired flow rate (after setting the desired temperature) can be achieved by applying force on the piston, hence a given melt flow goes through the capillary. To describe the relation between the flow rate and the necessary force (pressure) the Hagen-Poisseuille equation was used. With the aid of the calculations the necessary capillary diameter and the force was calculated.

Scanning electron microscopy (SEM) revealed (Figure 4.) the average fiber diameter was only 500 nm in average [8]. For melt electrospinning very high voltage (50 kV) was necessary that made issues in further electro melt-blowing experiments. *Related publications: [5, 6, 9, 20, 21]*.

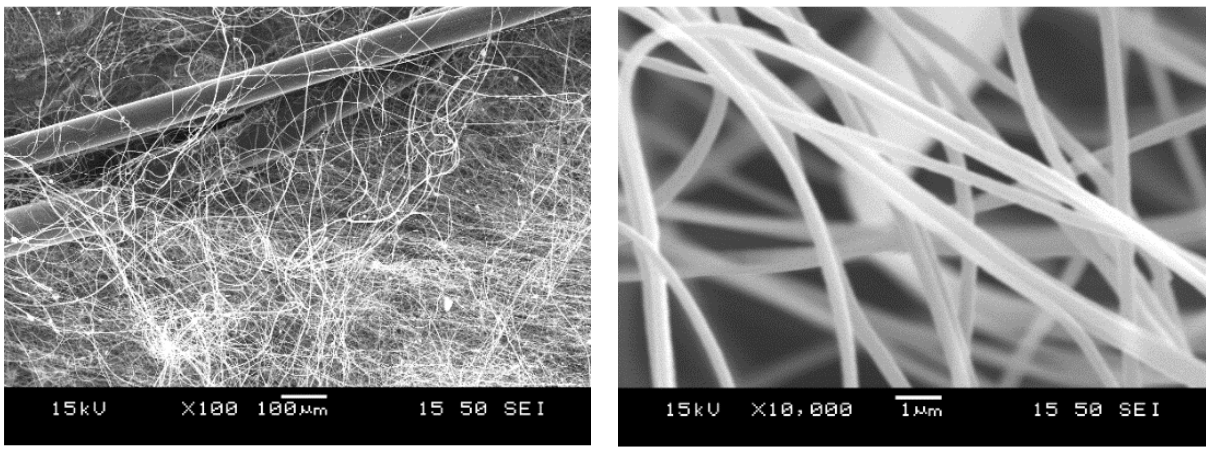

Figure 4. SEM images of electrospun fibers obtained from 240 °C PP melt.

4.2. Melt blowing

Continuous nanofiber process was tried to be implemented form polymer melts by melt-blowing. A small laboratory extruder with a conical screw diameter of 18/8 mm was obtained and a dedicated melt blowing die was designed and manufactured (Figure 5.). As problems

arose with the electric isolation of the die from the extruder electrostatic assistance (i.e. electro melt-blowing) was not applied at the end. The design of an equipment for collecting the fibers and the development and control of an appropriate air support system was also done (Figure 6.).

Figure 5. Image of the disassembled melt-blowing die (without sensors and heaters)

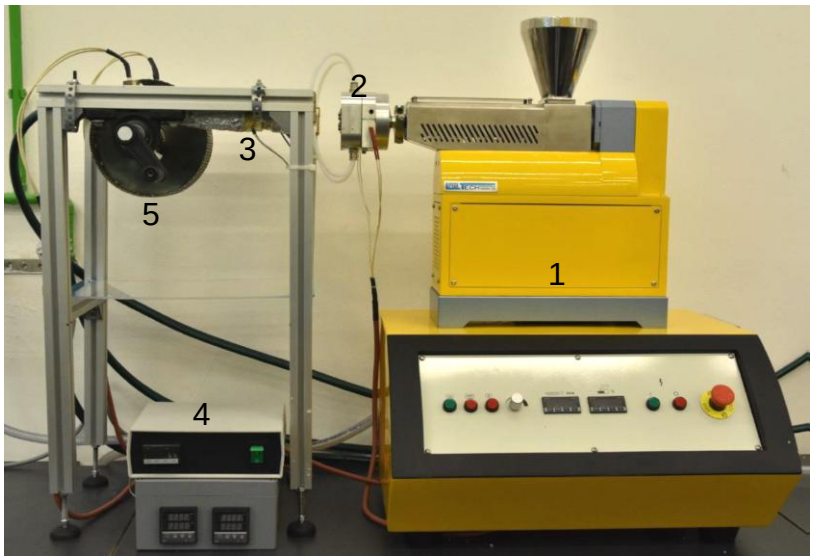

Figure 6. The custom melt-blowing equipment including the extruder (1), heated blowing die (2), air heaters (3), control units for air and die (4) and rotating drum for fiber collection (5)

Investigation of the morphology was carried out by scanning electron microscopy. The average fiber diameter was below 1 μm and the smallest fiber diameter measured was 110 nm. The results were surprisingly good, because the average fiber diameters of webs that are commercially available, are in the range of 1-2 μm (Figure 7). *Related publications: [5, 6, 9, 20, 21]*

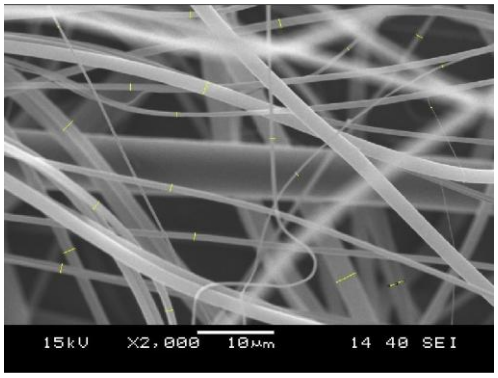

Figure 7. SEM image of melt-blown PP fibers

5. Nanofiber characterization and nanofiber composites

At the characterization of nanofibers and composites mainly tensile tests and dynamic-mechanical analyses were carried out. The tensile test results revealed that nanofibers are having one order of magnitude less tensile strength and modulus than traditional fibers of the same material that is still an issue for making the related composites. The results can be originated from the residual solvent in the fibers, the different degree of crystallinity and molecular orientation in general. We concluded that nanofibers can be used as an auxiliary reinforcement of composites, mainly for toughening purposes.

With the KU Leuven (Belgium) group we tested the compressibility of nanofiber interleaved carbon fabrics. We concluded that the nanofiber interleaves in the woven fabric laminates decreased the compressibility of the laminate, increasing the laminate thickness for a given pressure and correspondingly decreasing fiber volume fraction in the consolidated laminate. The fiber volume fraction decreases almost linearly with the increase of the nanofibers areal density. However, up to areal density of the interleaves of 10 g/m^2 the decrease of the fiber volume fraction was below 3% and is practically acceptable. There was a strong interference between the interleaves and the fabric reinforcement, which can lead to effective toughness improvement of composites.

With a group of Research Centre for Natural Sciences of HAS (MTA) we were using electrospun nanofibers in reinforcing ceramics. We concluded that the fracture toughness and strength of dense Si_3N_4 ceramics could be achieved. The ceramic composites were reinforced with partially stabilized ZrO_2 electrospun nanofibers that are also undergone spark plasma sintering (SPS) at a relatively low sintering temperature (1600 °C). The results of fracture toughness and flexural strength measurements showed a significant improvement: 15 wt% of ZrO_2 nanofiber exhibits 10.05±0.7 MPa•m1/2 fracture toughness and 543±19 MPa flexural strength, which means 105 % and 115 % improvements compared to the reinforcement-free samples. We concluded that ZrO_2 nanofibers can increase the mechanical properties of the composites in a complex way, including phase transformation toughening and fiber-toughening mechanisms. *Related publications: [3, 10, 11, 12, 13, 14, 16, 19, 21]*

6. Project-related research in joint cooperations

The current project contributed to several new researches and new cooperations with other departments and institutes. Electrospinning and the characterization of the fibers were made for various materials and even with the developed technology in many cases. Besides the KU Leuven (Belgium) and HAS cooperations introduced in the previous sections, we made further ones.

For instance with the research team of ESITH (Casablanca, Morocco) we developed a system making possible to encapsulate phase change material within nanofibers in order to make thermoregulating textiles, regulating body temperature. These can be used as protective clothing and for competitive sports. The regular yarns are covered by nanofibers (with the invented high productivity method) and then the textile can be knitted.

With the Department of Physical Chemistry and Materials Science, BME, we created fast dissolving polyaspartamide matrices for sublingual drug delivery. The vitamin B12 encapsulated was liberated technically within 1 minute at the pH of the oral cavity (pH = 6.8) as a result of the nanofiber structure.

With the Department of Organic Chemistry and Technology, BME we were also working on the drug delivery of electrospun nanofibers and the scaling up of the technology. The steps of a potential continuous production line (fiber collection, grinding, feeding and tableting) proved to be feasible with the electrospun amorphous solid dispersions without any sign of crystallization, leading to enhanced drug dissolution and better bioavailability.

With the Biomerg Group of the University of Akron (Ohio, USA) we are also developing drug delivery system. In this year AIBA, a special elastomer was used and it turned out that the new method also makes possible to generate fibers with various diameters from elastomers.

With the Xi'an (China) research group we developed a new electrospinning method that uses a using a moving conventional yarn as the spinneret. Both issues of needle clogging in needle electrospinning and intense solvent evaporation due to the open solution surface in most needleless electrospinning techniques can be avoided. *Related publications: [4, 7, 13, 15, 16, 19, 21, 22, 24, 25]*.

Budapest, 09.21. 2018.

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Kolos Molnár

principal investigator