# HOLLOW FIBERS BY ELECTROSPINNING IN SUPERCRITICAL $CO_2$

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## INTRODUCTION

Electrospinning is the only way to get fibers with a diameter below one micron.
A polymer solvent solution is delivered in a capillary. In a certain distance a collector for the product is mounted. High voltage (10 kV – 30 kV) is applied to capillary and collector. The electrical field deforms the drop at the tip of the capillary to the so called taylor cone [1]. If the voltage reaches a certain level the polymer can override the surface tension of the taylor cone. A jet is drawn to the collector. While the jet crosses the gap, the solvent is removed. The resulting fibers are gathered on the collector [2]. The principle of electrospinning is shown in Figure 1.
Up to now there are three possibilities to produce hollow fibers by electrospinning:
The first to mention is the tubes by fiber templates (TUFT) process. A fiber spun via electrospinning is coated in a second step with another material. The core fiber has to be pyrolysed – the hollow fiber remains [3]. The problems at this technique are the limitation of applicable materials due to the high temperatures and the extensive three steps to get hollow fibers [4].

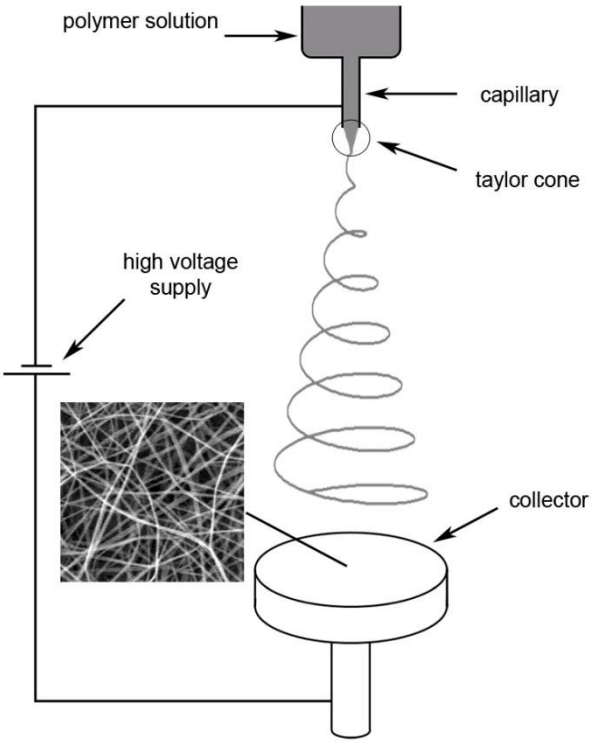



**Figure 1: Principle of electrospinning**

Another possibility to obtain hollow fibers is electrospinning with a coaxial capillary [5, 6, 7]. Here two different solutions which are not fully miscible have to be spun simultaneously. The outer shell dries and the inner, still in liquid state, has to be removed in a second step.
Both techniques require a more or less complex post processing of the product to get the desired hollow fibers.
By contrast electrospinning into an atmosphere of supercritical carbondioxid needs only one step for producing hollow fibers [8, 9]. McHugh et al. developed a hypothesis of the mechanism therefore. It is depicted in Figure 2:

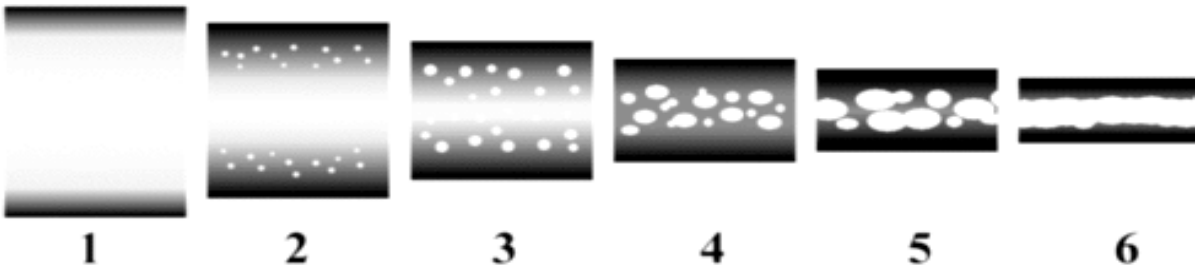



**Figure 2: Hollow fiber formation in $scCO_2$ - hypothesis**

**1: Skin formation, 2: Nucleation of polymer-lean phases**
**3: Growth of polymer-lean phases; 4: Coalescence of CO2-rich voids**
**5: Further coalescence of CO2-rich voids; 6: Hollow fiber formation**

In nearly every sector of industry the use of those nano scale hollow fibers could be very high. Apart from advancing existing technologies to smaller sizes complete new products, like new kinds of filters for nanofiltration or new textiles, could be possible.

## MATERIALS AND METHODS

At the University of Erlangen a new high pressure autoclave was developed for electrospinning into pressurized gases. In contrast to common autoclaves, the flanges have to be electrical isolated from each other. In addition, the wall has to resist temperature, pressure and organic solvents. Polyether ether ketone (PEEK), which is able to cope with all the named requirements, was chosen as material for the wall of the autoclave. The wall withstands pressures up to 120 bar and temperatures up to 80°C. The autoclave is shown in Figure 3.
A flowsheet of the complete installation is depicted in Figure 4. The autoclave is temperate with a

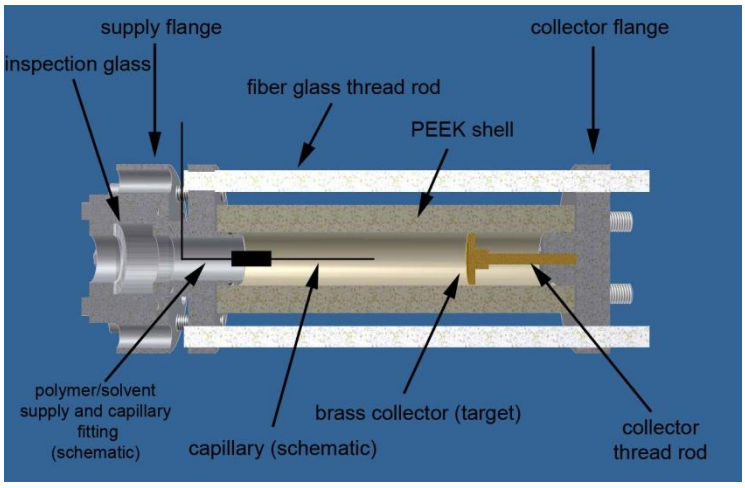



**Figure 3: Autoclave**

fan heater. Two feed pipes lead inside the autoclave, one for carbon dioxide, the other one for polymer solution.

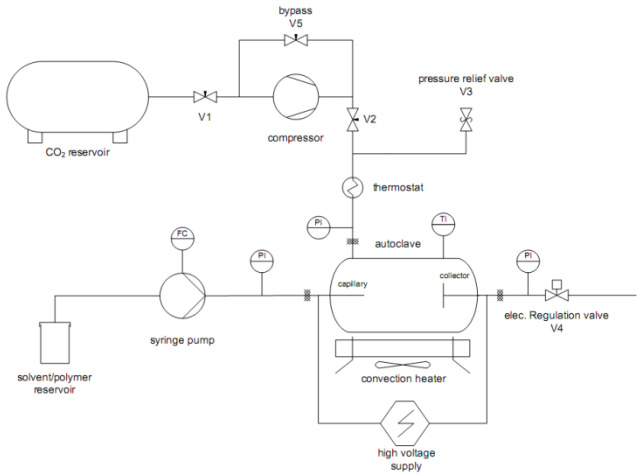
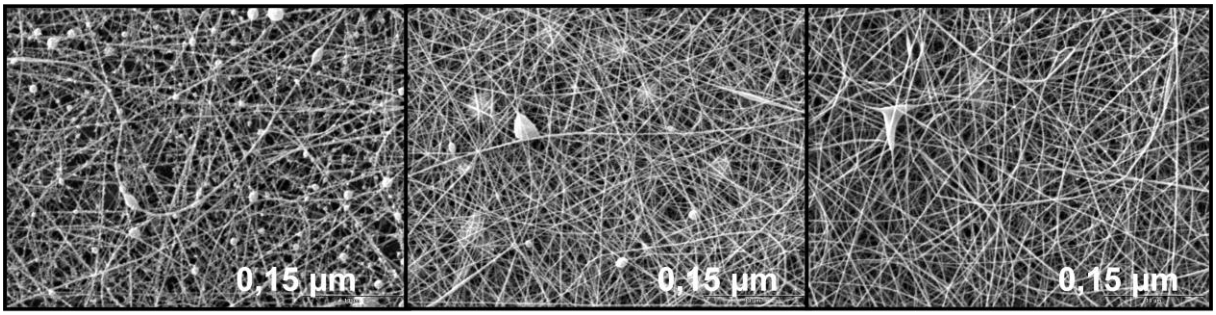



**Figure 4: Process flowsheet**

The $CO_2$ is compressed to the desired pressure and afterwards preheated in a thermostat. The polymer solution is delivered with a syringe pump. These pumps are pulsation free and can work against high pressures, properties which are eminent for the conducted experiments.
The used polymer is polyvinyl-pyrrolidone (PVP). It is soluble in water, has a density of 1,2 $\frac{g}{cm^3}$ and a molar mass of 1.300.000 $\frac{g}{mol}$. With this polymer we were able to obtain hollow fibers with an outer diameter of less than five microns.
To understand the mechanism of fiber formation experiments are carried out with three different solvents: Dichloromethane (DCM, boiling point: 40°C), ethanol (boiling point: 78°C) and N,N-dimethylformamide (DMF, boiling point: 153°C) are applied.

## RESULTS

All following pictures were taken with a SEM. The samples were spun through a 70 mm capillary with an inner diameter of 500 µm. The distance between capillary and collector was always 70 mm.
In all orange edged pictures hollow fibers are depicted.
The first series of experiments were done with a 5 wt% PVP/Ethanol system:




P = 1 bar, T = 25°C  P = 1 bar, T = 50°C  P = 1 bar, T = 70°C

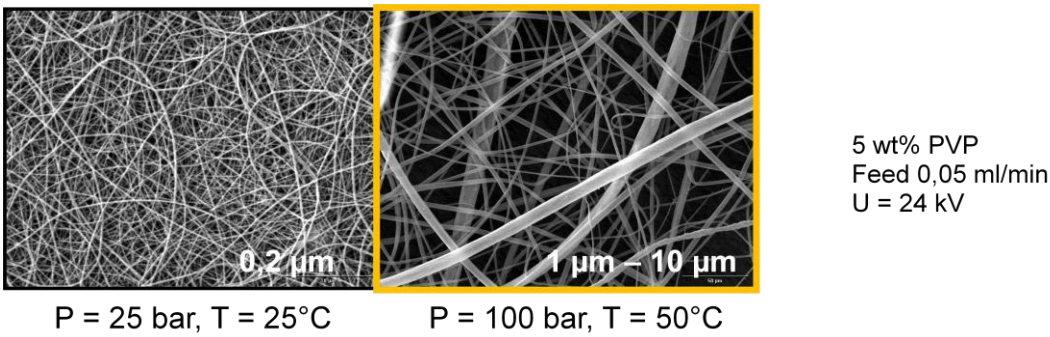



**Figure 5: PVP/Ethanol**

In the first picture you can see a sample which was produced at 1 bar and 25°C. There are many small droplets in the fibers – the so called beads. These beads are formed when the solvent is not removed completely. At 1 bar and 50°C there are barely any and at 1 bar and 70°C the beads are removed. The fiber diameter at these conditions is always 0,15 µm. If you compare the two pictures on the left side, you can see that a higher pressure (25 bar) has the same influence like a higher temperature but the fiber diameter is slightly increased. For experiments in the supercritical regime, the fibers are blown up and the outer diameter rises dramatically up to 10 µm.
The next experiments were performed with PVP/DMF:

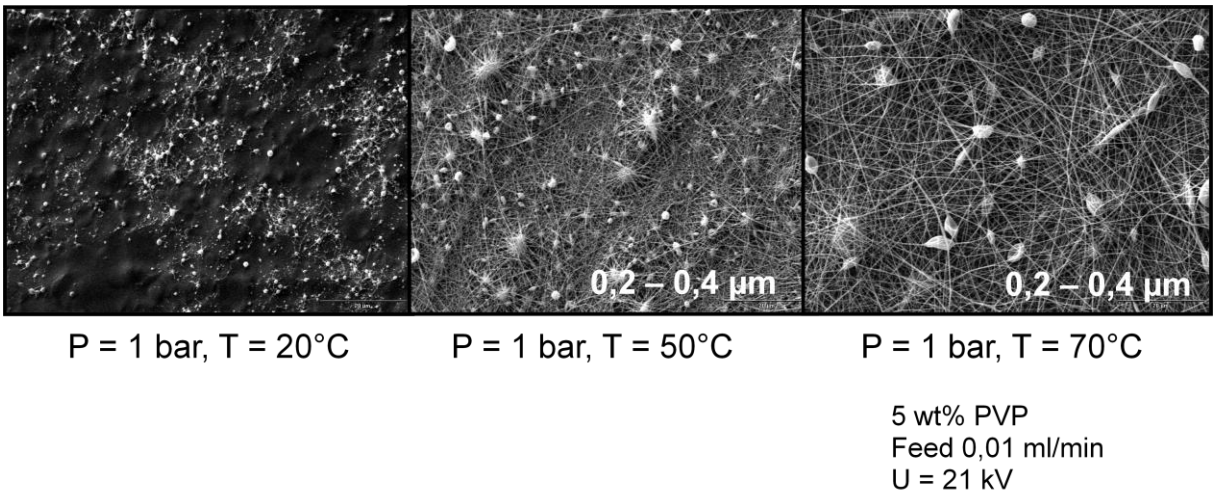



**Figure 6: PVP/DMF**

With this polymer solvent system it was hardly impossible to achive reasonable samples at the used conditions. Just at a pressure of one bar and raised temperatures some fibers could be obtained. Higher temperatures mean a better phase change of the solvent. At 1 bar and 20°C a polymorph surface with a few small spheres could be observed. Even at 70°C and 1°bar there were still many beads. A calculation with the Peng Robinson equation of state showed that DMF dissolves very bad in carbon dioxid (Figure 7).

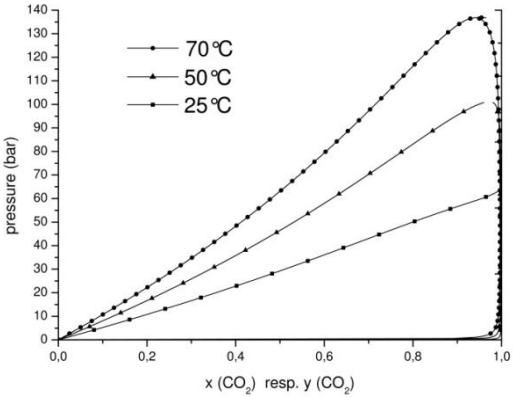



**Figure 7: P-x, y- phase diagram DMF/$CO_2$**

The last tested system was PVP/DCM:

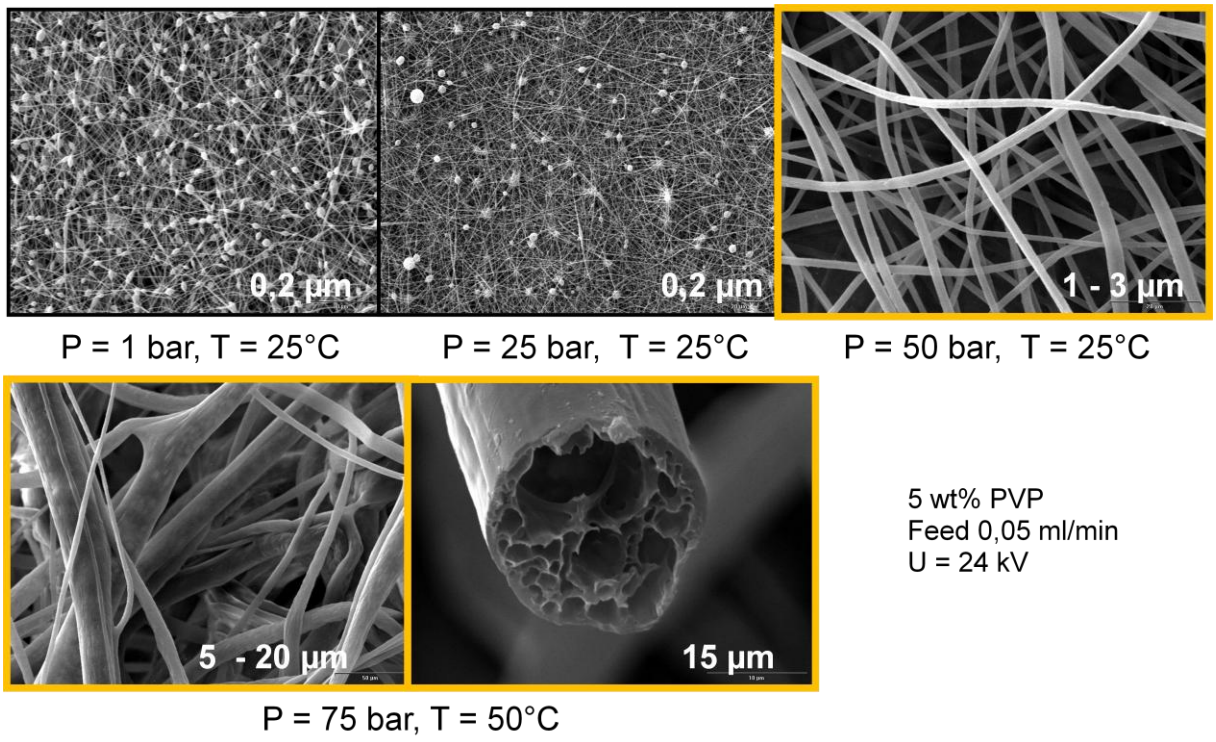



**Figure 8: PVP/DCM**

For these three solvents best results were obtained with Dichloromethane. In the upper row of pictures the influence of the pressure is shown at a temperature of 25°C. With rising pressure the quality of the fibers is getting better. At a certain pressure the fibers are blown up again and the outer diameters get much bigger. In the supercritical area (Figure 8 bottom row) the growth and the allocation of the fiber diameters is even higher. The fiber diameter can increase up to 20 microns. A porous structure could be found inside the fibers.

## CONCLUSION

In all of these initial experiments the formation of hollow fibers depends on temperature, carbon dioxide pressure and the vapor pressure of the used solvent. Under atmospheric conditions it was not possible to spin hollow fibers.
Higher temperatures are better for evaporating the solvent - the quality rises. At a certain pressure of $CO_2$ the diameter of the fibers enlarges and they get hollow. The vapor pressure of the solvent is also important for the removing speed.
More experiments have to be done to check the hollow fiber formation hypothesis and to bring the process parameters in consistence with the morphology of the produced samples.

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