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Water-born 3D nanofiber mats using cost-effective centrifugal spinning: comparison with electrospinning process: A complex study

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Abstract

A comparison of the electrostatic and centrifugal spinning of poly(vinyl alcohol) and poly(vinyl pyrrolidone) is shown in terms of the resulting fiber morphology and the process conditions. Specific parameters of centrifugal spinning, such rotational speed of spinneret and the relative humidity, were extensively investigated in details. Morphologies and diameters of resulting fiber mats were investigated by a scanning electron microscopy and compared between the two spinning techniques. The results revealed that formation of fibers is mainly affected by the initial polymer concentrations (and resulting viscosities) of polymeric solutions, which is in line with previous reports. However, the key novel finding of this work is that increasing relative humidity during centrifugal spinning process leads to greatly reduced fiber diameters to the levels typical for electrospinning. The obtained comparison is discussed and clearly shows technological advantages of the centrifugal spinning over electrospinning, enabling quantitative production of fibers with same or similar diameters.

KEYWORDS

centrifugal spinning, electrospinning, fibers, microscopy, synthesis and processing techniques

1 | INTRODUCTION

Fibrous materials represent very interesting structures with unique characteristics among other materials. They

[Correction added on 24 September 2020, after first online publication: the article title has been updated.]

possess a high porosity, a large specific surface area and a good breathability. Polymeric fibers are the most exploited until now, but also inorganic as well as hybrid fibers were already extensively studied.[1–5] Depending on the composition, fibers possess different chemical, mechanical and temperature stabilities, biocompatibility, but also electrical conductivity and catalytic activities,

and so on. Owing to these properties, fibers have been exploited mainly for filtration media, tissue scaffolds and catalysts, among others.

There are many techniques for production of fibers such as electrostatic spinning (electrospinning), melt blowing, flash spinning, bi-component spinning and also the centrifugal spinning. Until now, the electrospinning has been the most common method in the lab to prepare fibers of various diameters (ranging from tens to hundreds to nanometers).[6–8] The principle of this method is based on an application of the electrostatic field and subsequent accumulation of the electrostatic charge induced on the surface of the spinning solution or the melt. When the electrostatic field is sufficiently high, it causes destabilization of the surface energy and the formation of jets of nanofibers resembling a conical shape, known as the Taylor's cone. The fiber jets are driven to the negatively charged collecting electrode and while reaching the collecting electrode, they undergo evaporation. Finally, nanofibers deposit in a very random manner on the substrate covering the electrode—typically nonwoven textile.[9–10] By using various collectors and spinneret with different designs, it is also possible to prepare coaxial or core-shell nanofibers and also networks of oriented nanofibers with a certain degree of alignment. What is more, the production of nanofibers can be enhanced by utilization of nozzle-less electrospinning head in the shape of regular metallic cylinder, known from the commercially available Nanospider™ tool (produced by Elmarco Ltd., Liberec, Czech Republic). This tool (or its derivatives) has been widely used for the research and development of various nanofibers (and their applications) in many labs worldwide.[11–12] However, from the industrial point of view, electrospinning (regardless the particular design) has numerous disadvantages that include the necessity of application of a very high electric field within a highly flammable solvent (with implications on fire hazards), an overall low production rate and significant sensitivity on atmospheric conditions. What is more, the yield and efficiency of this process depends on wide range parameters, such as solution properties (concentration, viscosity, conductivity, and surface tension) and process parameters (flow rate, electric potential and distance between electrodes) that have to be tediously optimized. Last but not least, temperature and humidity play a pivotal role in the reproducibility of the process, and their effect is frequently overlooked in the literature.[13] Choktaweesap et al.[9] reported that formation of nanofibers is mainly affected by Coulombic forces, viscoelastic forces and the surface tension. In general, for this process to yield a reasonable quality and quantity of nanofibers, it is necessary to optimize the concentration of the polymer, conductivity of the solution, applied voltage and collector distance. In general, too low concentration of the polymer in the spinning solution (typically less than 4 wt.%) causes formation of fibers with very small diameter and an overall poor process yield. On the other hand, too high polymeric concentration (typically more than 20 wt.%) increases viscoelastic strength with a negative impact on the process[9,12] and frequently leads to a huge variation in the fiber diameter.

The centrifugal spinning is a very modern and industrially robust technique that eliminates the shortcomings of electrospinning described above. Centrifugal spun fibers are formed due to a high centrifugal force applied on the solution in the rotating spinneret, which has numerous nozzles with a certain diameter (typically a few hundreds of μm). When the equilibrium between the surface tension and the centrifugal force (which is significantly high for spinneret rotations of generally several thousands of rpm) is disrupted, the solution is expelled out from the nozzles of the spinneret in the form of many jets of fibers. Due to evaporation and strong air flow in the spinning chamber and the subsequent evaporation of the solvent, the newly born fibers reach the fiber collector and stay there.[14] Theoretically, the fiber yield should be mainly affected by the speed of a spinneret, the distance of the collector and diameter of the spinneret nozzle. On the other hand, the fiber morphology and dimensions should depend primarily on the viscosity of solution, the rotational speed of the spinneret and the evaporation rate. Depending on the process parameters and spinning solution, fiber with the diameter in the range of few hundreds of nm to few μm can be made. Centrifugal spinning has been already employed to make fibers from a variety polymers, such as poly(methyl methacrylate),[15] poly (D,L-lactide-co-glycolide),[16] poly(vinylidene fluoride),[17] poly(butylene terephthalate),[18] poly(ε-caprolactone),[4] blend of poly(ε-caprolactone), poly(vinyl pyrrolidone),[19] blend of poly(vinyl pyrrolidone) and poly (L-lactic acid),[20] poly(methyl methacrylate),[21] blend of poly(vinyl alcohol) and chitosan with addition of citric and tannic acid,[22] poly(carbonate), poly(lactic acid), poly(acrylonitrile),[23] blend poly(ε-caprolactone) and gelatin,[24] Nylon 6,[25] cellulose acetate,[26] poly(vinyl alcohol),[27] blend of ethylcellulose and poly(vinyl pyrrolidone),[28] blend of chitosan and poly(amide),[29] blend of kraft lignin and thermoplastic poly(urethane),[30] blend of poly(vinyl pyrrolidone) and poly(ethylene glycol),[31] poly (diacetylene),[32] poly(vinylen fluoride).[33]

Even though these reports are interesting, they did not provide a direct comparison of the results with the same polymers / fibers obtained by electrospinning. There are only three reports that directly compare the spinability, morphology and process conditions of some polymers for both attractive spinning techniques—electrospinning and centrifugal spinning—and that discuss the relation of these parameters in terms of the process.[34–36]

Namely, Krifa et al.[34] and Rogalski et al.[35] examined these spinning methods for the synthesis of

polyamide 6 (PA6) fibers, using formic acid as a solvent. Vocetkova et al.[36] synthesized fibers from polycaprolactone-based materials dissolved in chloroform and ethanol mixtures. The common feature of all these three reports is that they used the same laboratory scale centrifugal spinning tool (Cyclon L-1000, FibeRio), with a spinneret consisting of two symmetric needles (with a diameter of 160 μm). Even though, this tool is handy for the lab scale synthesis of fibers, it is not suitable to study centrifugal spinning processes (and relevant phenomena) on the semi-industrial or industrial scale. Only in report by Vocetkova et al.[36] a rather fair comparison was made, because the used electrospining tool was commercial (Nanospider NS 500, Elmarco, Czech Republic), allowing somewhat more balanced comparison between the scale of the tools used.[36] Remaining two reports employed a home-made electrospinning tools, rendering the technology transfer rather difficult.[34–35] In addition, in all reports toxic solvents were used and none of them specified or even varied relative humidity or temperature during the process. Last, but no least, Krifa et al.[34] used only two PA6 concentrations, and Krifa et al.[34] and Vocetkova et al.[36] used only one fixed rotational speed. Thus, it is clear, that these reports, beside they are very pioneering in terms of the comparison of both spinning techniques, do not answer all questions that the researchers might have. A complex study, comparing spinning process conditions of some basic, ideally water soluble, polymers, is still missing.

To address this gap, we conducted in this work a direct comparison between both spinning techniques in such a complex matrix of conditions that has not been carried out yet. We used three different tools: one laboratory electrospinning tool (4SPIN®), one pilot-scale electrospinning tool (Nanospider™ NS LAB 500S) and one pilot-scale centrifugal spinning tool with a high solution throughput (Cyclone Pilot G1). We carried out an extensive comparison of following process parameters: concentrations of polymeric solution, applied electrical potential, rotational speed and relative humidity. Based on the literature survey and discussion with industry representatives, we picked up two standard, environmentally friendly and water soluble—polymers poly(vinyl alcohol) (PVA) and poly(vinyl pyrrolidone) (PVP)—that bear a large application potential especially in biomedical fields. These polymers have reasonably good properties (compared to their low price) such as chemical resistance, thermal stability, physical properties and biocompatibility.[37–38] Except low cost and many application opportunities, these polymers also possess very good spinability from aqueous solutions. The resulting nano- and microfibers were characterized by scanning electron microscopy (SEM) and statistically evaluated and compared.

2 | EXPERIMENTAL

2.1 | Material

Poly(vinyl alcohol) with commercial name Poval 13–88 (PVA, average molecular weight Mw ≈ 123,000 g·mol^{-1} and 88% hydrolyzed) and poly(vinyl pyrrolidone) with commercial name K-90 (PVP, average molecular weight Mw ≈ 600,000 g·mol^{-1}) were purchased from Prochema (Austria). These exact types of polymers with the given molecular weights were chosen based on our previously obtained experience from proof-of-concept experiments, where same types of polymers, but with lower or higher Mw were used with limited or no spinability. Distilled water was used as a solvent for all spinning solutions used in this work.

2.2 | Solutions analyses

Aqueous solutions of PVA and PVP were prepared in various concentrations (within the range from 10 to 24 wt. %). These polymer solutions were characterized by the dynamic viscosity using ARES-G2 rheometer with cone-and-plate geometry (40 mm, 1° angle) in the shear rate range from 0.01 to 0.1 s^{-1}. All measurements were carried out at temperature 25 °C.

2.3 | Electrospinning

Electrospinning was carried out using commercially available lab tool 4SPIN® (Contipro, Czech Republic) and pilot tool Nanospider™ NS LAB 500S (Elmarco, Czech Republic). After each process, the electrospun fibers were collected from the collector and stored in a dry place in the lab prior further analyses.

Figure 1(a) shows the schematic drawing of the technology used in the 4SPIN® tool. At first, the spinning solution is dosed into a syringe of a volume 10 ml. The feeding rate, controlled by a dosage piston was applied in the range of 40–50 μl/min. The quantity of produced fibers is rather low (lowest from all three tools) and it is due to the limited amount of Taylor cones formed on the needle tip. The spinning process was realized at an electrical potential of 20 kV at temperature 20 ± 5°C and a relative humidity 30 ± 15%. The speed of rotary collector was 300 rpm. Fibers were collected on the collecting electrode coated with an Aluminum foil. The distance between needle tip and collector was kept on 150 mm.

Figure 1(b) shows the schematic drawing of the technology used in the Nanospider™ tool (NSLAB 500, Elmarco, Czech Republic). Unlike the electrospinning within the
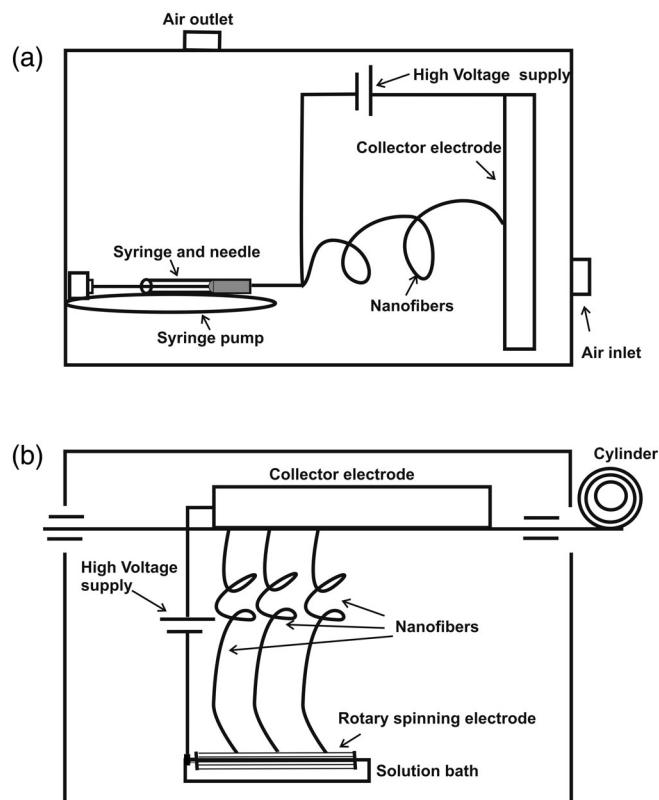
FIGURE 1 Schematic representation of electrospinning tools used in this work: (a) 4SPIN® tool, (b) Nanospider™ tool

FIGURE 2 Schematic representation of centrifugal spinning setup

4SPIN® tool, the Nanospider™ tool produces fibers from the free (continuously recovered) surface of a spinning solution allowing formation of a greater number of Taylor cones and thus significantly higher yield of fibers per unit of time. To ensure continuous fiber production, one rotating cylinder (with a length of 50 cm and regular cylindrical shape) is placed in the spinning solution and it rotates with a constant speed during the process. The rotational speed of the electrode was set for PVA solutions on 1.4 rpm. A higher speed (2.9–5 rpm) was needed for a sufficient PVP fiber yield. Fibers were collected on the non-woven polypropylene textile substrate. Due to a different design of the electrodes, a higher voltage (in the range from 52 to 68 kV) had to be applied in comparison to 4SPIN®, beside the same working distance (15 cm). The process was carried out at ambient laboratory conditions (20 ± 2°C and 30 ± 6% RH).

2.4 | Centrifugal spinning

Fibers obtained from centrifugal spinning were prepared using pilot tool Cyclon Pilot G1 (Pardam Ltd., Czech Republic). Figure 2 presents scheme of the centrifugal spinning tool. Polymer solution was dosed in a spinneret (diameter 15 cm) tightly fixed on the rotor shaft. The
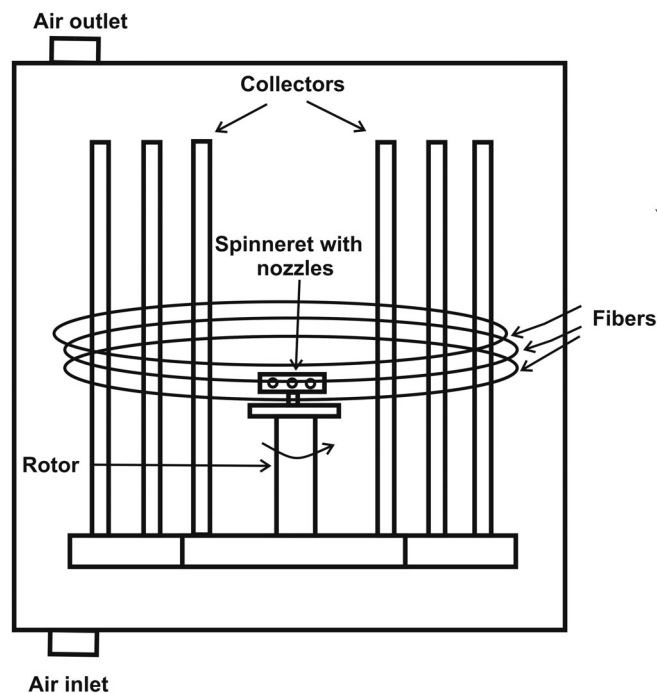
spinneret consists of a large steel block with 16 nozzles win an average internal diameter of 150 μm. The spinneretax is identical to the rotational ax. The distance between the center of the spinneret to collector bars is 35 cm. The rotational speed of spinneret was varied in the range from 5000 to 13,000 rpm. Due to the built-in air conditioning, the temperature and the relative humidity were set for all experiments at 40°C and 15% RH, respectively, if not denoted otherwise. After each process, fibers were removed from the collectors and subsequently characterized. This tool is more robust than frequently used Cyclone L-1000 (from FibeRio), because it has numerous nozzles (16 compared to 2) and therefore a higher throughput of the solution and a significantly higher fiber yield. In terms of the control of process humidity and temperature, it is significantly advanced compared to Cyclone L-1000 and typically used electrospinning tools, as it is directly connected in a closed loop to a very efficient and precise air-conditioning unit. This unit allows to set (monitor and control) the relative humidity and temperature inside the spinning chamber, so the environment during the spinning is completely independent on the atmospheric conditions (and the season) outside the tool. This means that spinning on this tool give reproducible results in terms of fiber morphology and quality, regardless the season. Therefore, this tool possesses clear technological advantages for the fiber synthesis compared to the conventional electrospinning tools.

2.5 | Analyses of resulting fibers

Morphological analyses of the produced fibers were carried out by a scanning electron microscope (Verios 460 L, FEI). Before SEM analyses, fibers were coated by gold layer (20 nm) using laboratory sputter coater to facilitate a sufficient conductivity for morphological observations. Mean diameters of resulting fibers were statistically evaluated from at least 30 values per sample, obtained from typically two or three SEM images. To check on the residual water content in fibers (from water as a solvent), we carried our vacuum drying of some fibers and compared their weight loss with untreated fiber samples. No significant weigh loss for revealed among both groups of fibers. The electrostatic charge in fibers was measured according to IEC norm (nr. 61,340–1) using handheld electrostatic fieldmeter (FMX-004, Simco-Ion).

FIGURE 3 Viscosities for PVA and PVP spinning solutions with various polymer concentration

2.6 | Statistical analyses

Analysis of obtained dimensional data was performed using statistical program Origin. The bivariate Pearson Correlation Test with significance level of $\alpha = .05$ was used to analyses the correlation between the viscosity of the used solutions and resulting fiber diameters.

3 | RESULTS AND DISCUSSION

3.1 | Viscosities of the polymeric solutions used for spinning processes

Viscosities of PVA and PVP solutions with different concentrations, entering the spinning processes, were analyzed in order to obtain some background information valuable for the evaluation of the results achieved in this work. An overview of the measured viscosities is shown in Figure 3. As one can see, with an increasing concentration of both polymeric solutions, their viscosity exponentially increases. Slightly higher dynamic viscosities were determined for the PVA solution. This is caused by higher intrinsic viscosity of PVA solutions compared to PVP solutions as given by the Mark-Houwink equation and as shown in literature.[39,40]

3.2 | Electrospun fibes: Effect of polymeric concentration and the used tool

Two sets of electrospun fibers were prepared by 4SPIN® and Nanospider[TM] tools from PVA and PVP solutions.
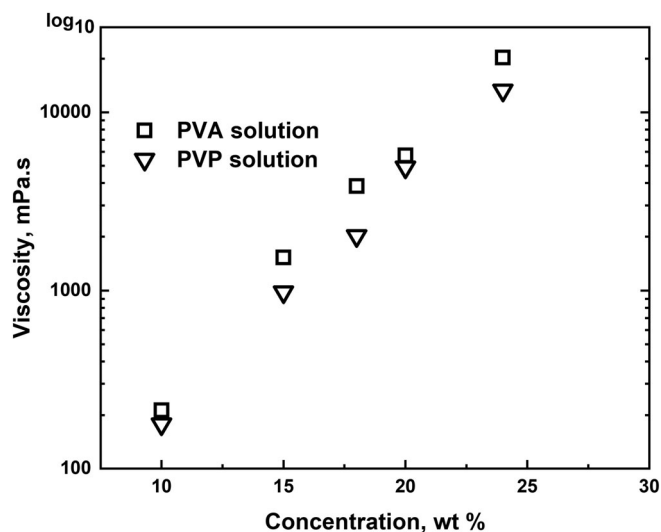
Bots tools yielded macroscopically (by a naked eye) planar layers of fibers on the used substrates without obvious defects or cracks. Comparison of the dimensionality of the resulting fibers can be obtained from Figure 4, which shows macroscopic photographs of the fibers produced using all three tools (including the centrifugal spinning one), along with representative cross-sectional SEM images.

In terms of the quantity, the 4SPIN® yielded smaller amount of fibers per unit of time than Nanospider[TM], which is simply due to the fact that Nanospider[TM] allows spinning from a large free surface, whereas 4SPIN® uses only one nozzle.

Inspection of the fibers under higher magnification was carried out. Figure 5 presents scanning electron microscopy (SEM) images of PVA and PVP electrospun fibers obtained from the 4SPIN® tool from solutions with different polymeric concentrations. As it can be seen, fibers formed in all cases up to the 20 wt.%. Upon detailed investigation, SEM images also revealed a smooth fiber surface without visible defects, such as beads, droplets, cracks or other imperfections. However, for the lowest concentration of PVP (10 wt. %), fibers contained beads. Their presence can be caused by the lowest viscosity from all the solutions (Figure 3) or due to some cross-linking events prior to spinning process, caused by the aromatic structure of PVP.

Figure 6 shows SEM images of electrospun PVA and PVP fibers prepared by the Nanospider[TM] tool. This comparison shows that fibers with beads appear again from PVP solution with the lowest concentration (10 wt.%) and viscosity. Apparently, the higher voltage using during the electrospinning with the Nanospider[TM] tool (50 kV and more) had no visible effect on the
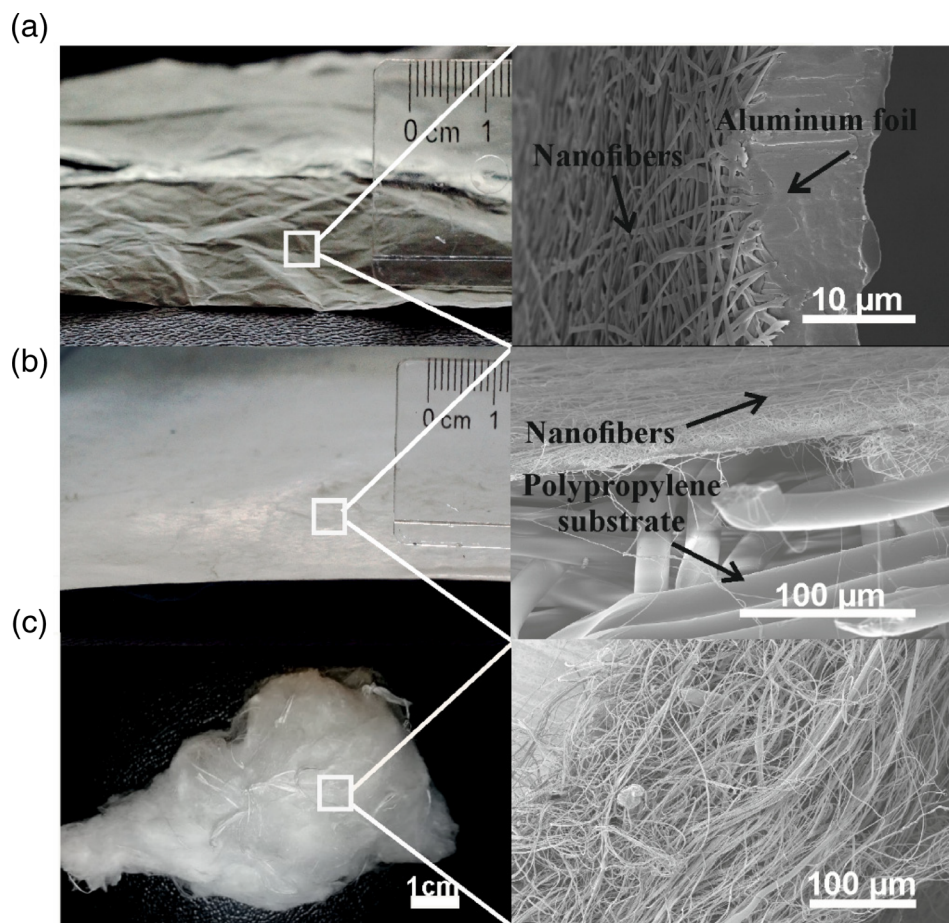
(a)

(b)

(c)

morphology of fibers and presence of beads. Thus, based on these results, it becomes evident that viscosity is the main determining factor for preparation of electrospun fibers, regardless the tool used.

As it can be further seen in the SEM images in Figures 5 and 6, the average fiber diameter noticeably increases with the increasing polymeric concentration. This is also confirmed mathematically, based on a statistically rich enough set of measurements (n = 30 or more fibers for each sample measured), as shown in Figure 7. These results and observations are in line also with the study of Supaphol and Chuanghote[37] and Ding et al.[41]

However, it is not only solely the polymeric concentration that is responsible for this trend. One has to take also in account the influence of increasing viscosity of spinning solutions (as shown in Figure 3) that stems from the increasing polymer content in the solutions. This influence was also confirmed by positive Persons correlation coefficients, determined between viscosities and fiber diameters. Strong correlation was achieved for PVA fibers prepared by 4SPIN® tool, as evidenced by the Pearson coefficient of $\approx$0.9693. Also for PVP fibers (prepared on the same tool) the substantially high value of $\approx$0.8529 was revealed. Comparably lower correlation coefficients

were achieved for polymeric fibers using the Nano-spider™ tool: 0.7817 and 0.7037 for PVA and PVP, respectively. This is due to the fact that electrospinning from free surface of a rotating cylinder has more degrees of freedom. For example, compared to 4SPIN®; fibers from Nanospider™ can elongate more broadly, they also have somewhat longer distance to travel to the collector, as fibers are generated from the free surface of the cylinder (= rotating spinning electrode in Figure 1(b) that is just about to get soaked in the spinning solution, or just left the solutions, while the cylinder rotates.

3.3 | Centrifugal spun fibers: Effect of polymeric concentration and process parameters

Centrifugal spinning yielded bulky 3D structures, similar to a cotton wool, as shown in Figure 4(c). In terms of the quantity, it also yielded the largest amount of fibers per unit of time. As in the case of electrospun fibers, no visible macroscopic defects were visible on the fibers. So as the next step, SEM investigation was carried out. The morphologies of PVA and PVP centrifugal spun fibers

FIGURE 5 SEM images of electrospun fibers prepared using the 4SPIN® tool (all scale bars correspond to 3 μm)
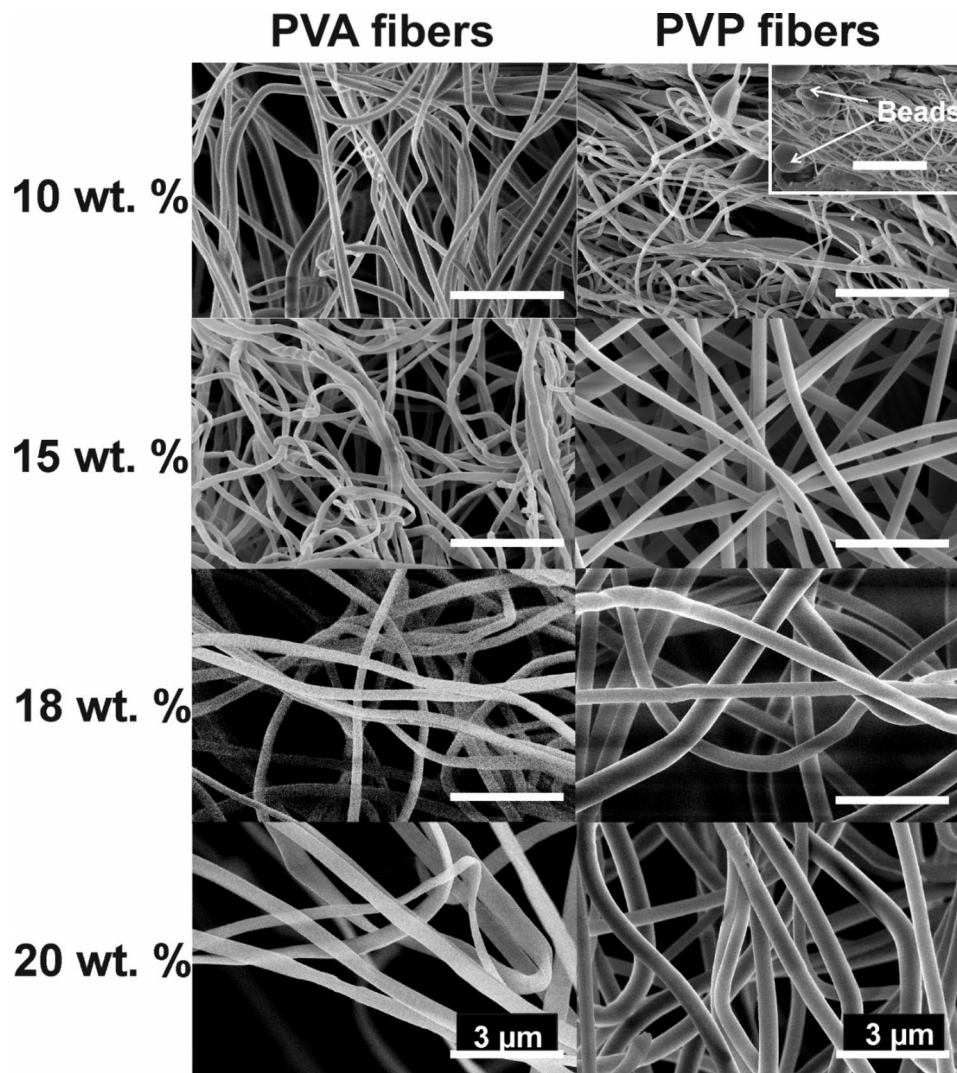
prepared from solutions with the concentration in the range of 10 to 24 wt.% are shown in Figure 8. From these SEM images it is clear that relatively uniform and homogenous fibers were prepared in all cases. This concentration range is in generally wider than the range plausible for the electrospinning experiments as previously described. But there are some differences and exceptions in trends. While electrospinning was able to produce fibers from 10 wt.% solutions of both polymers, centrifugal spinning did not work for the 10 wt.% PVP solution. Nevertheless, for the 10 wt.% PVA solution, fibers could be produced by centrifugal spinning, however, they contained beads. This fact can be caused by a very low viscosity of the 10 wt.% PVP solution, as shown in Figure 3, which is somewhat slightly below the threshold of centrifugal spinability. Looking at the other polymer concentration extremes, centrifugal spinning was able to produce fibers from solutions of up to 24 wt.% of the polymer content, while the maximum for

electrospinning was 20 wt.%. Most likely also solutions with even higher concentrations could be centrifugally spun, however, the solutions were already at 24 wt.% highly viscous and difficult to prepare, even using advanced stirring tools. In fact, for the PVA 24 wt.% solution (the most viscous one from all used) it was absolutely necessary to increase the rotational speed from 7000 rpm (otherwise used in all cases) to 11,000 rpm to push the solution through the nozzles by additionally increased centrifugal forces.

Figure 9 summarizes the statistical evaluation of diameters of those fibers that are shown in Figure 8. It is clear that the fiber diameter increases with the increasing solution concentration for both polymers. This again features the same trend as for the electrospun fibers obtained in this work. Also, this fact can be confirmed with positive Pearson correlation coefficients between viscosities and diameters which were obtained for these fibers from PVA and PVP and were equal to ≈ 0.8862
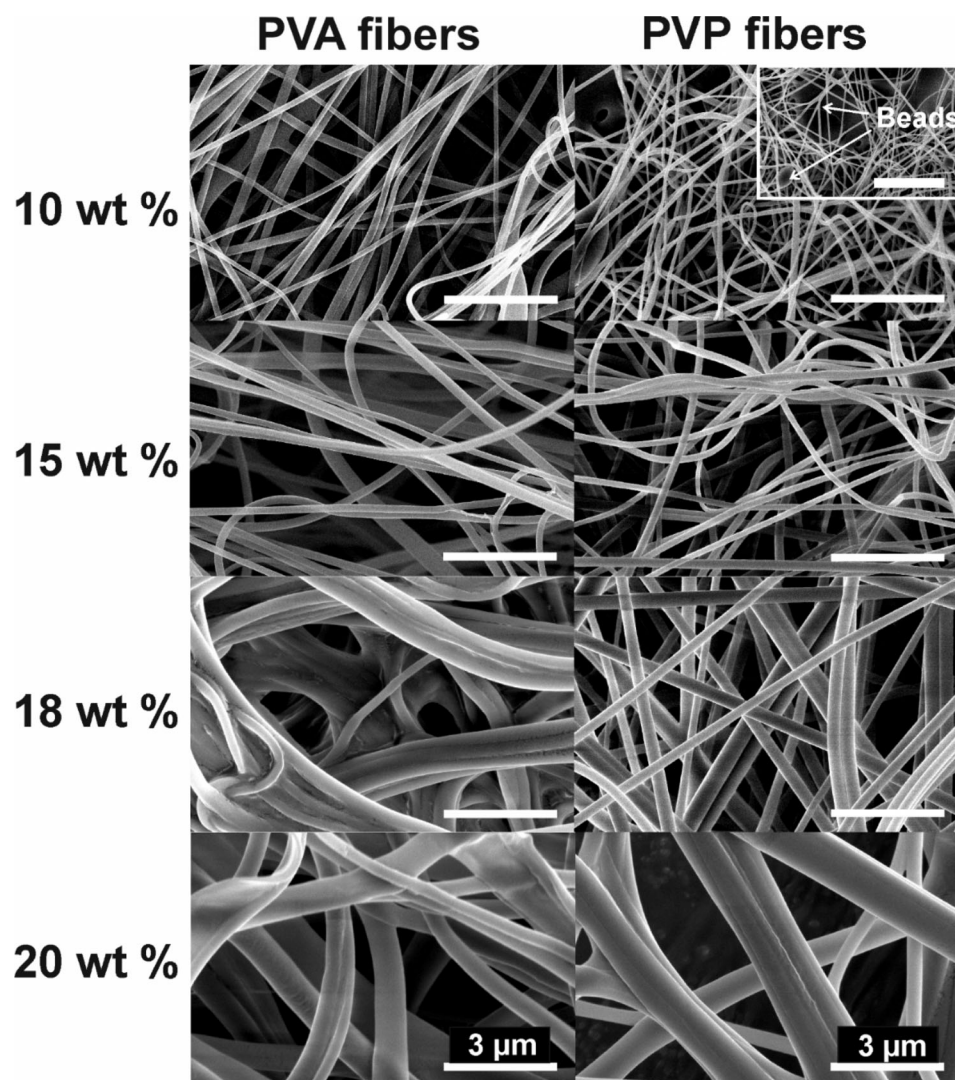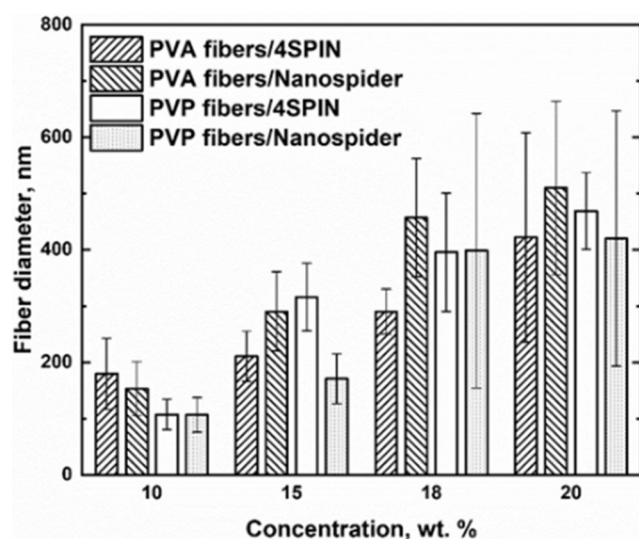
PVA fibers   PVP fibers

FIGURE 7 Diameters of electrospun PVA and PVP fibers obtained from solutions with different concentration using 4SPIN® and Nanospider™ tools

and ≈ 0.9900, respectively. Moreover, by comparison of diameters obtained by electrospinning (Figure 7) and centrifugal spinning (Figure 9) it is clear that centrifugal spun fibers had larger diameters compared to electrospun fibers. These findings are in line with trends described in reports on the centrifugal spinning of PA6.[34–35] Another interesting aspect is that the PVA fibers in average had larger diameter than PVP fibers, while for electrospinning this trend was opposite. One can emphasize that due to the difference among both techniques, this trend must be somehow dependent also on the rotational speed and the relative humidity present in the spinning chamber. Thus, we conducted more experiments in this regard to reveal more details that are further described in this article.

The effect of rotational speed was investigated for both PVA and PVP solutions in the whole concentration range (10–24 wt.%). All processes in this set were produced at temperature 40°C and relative humidity of 15%

FIGURE 8 SEM images of the centrifugal spun fibers. These fibers were prepared using rotational speed of 7000 rpm (except for PVA 24 wt.% where 11,000 rpm was used), x indicates no formation of PVP fibers 10 wt.% (all scale bars correspond to 10 μm)
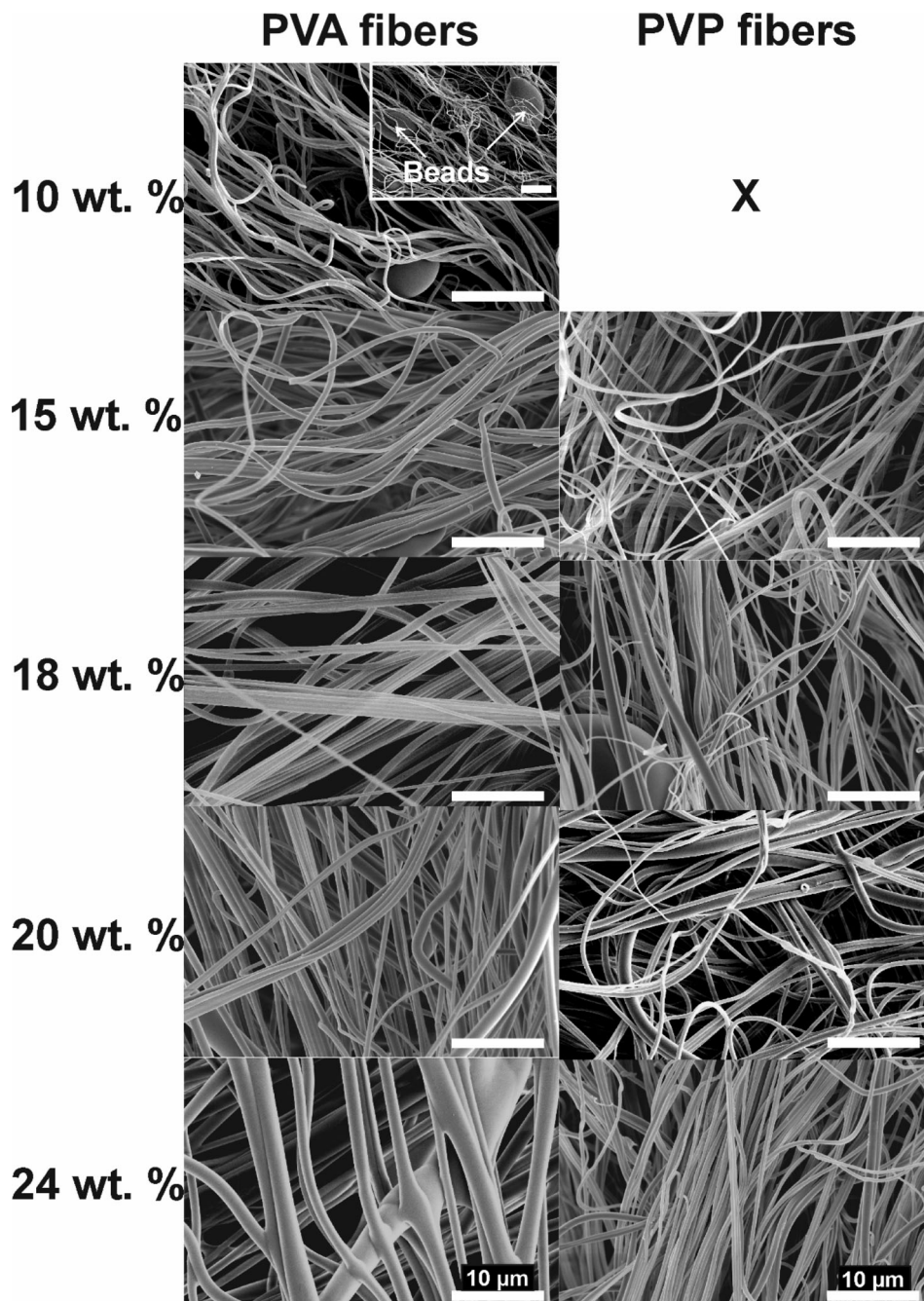
and the only variable for a given solution was the rotational speed. The resulting spinability of solutions of different concentrations at different rotational speeds is summarized in Table 1 for both polymers used in this work. Different production regimes are indicated in the table. By a detailed inspection of this table, one can see that the spinning capability depends on the rotational speeds, but also on the types of polymers and their concentrations (i.e., also viscosities). PVA fibers could be prepared in a wider range of concentrations than PVP fibers. However, to prepare PVA fibers with a higher concentration (more than 20 wt.% by weight), only the three

highest rotational rates were sufficient. On the other hand, PVP solutions (10 wt.%) with the lowest concentration (Figure 3) did not form fibers at any rotational speed and for 15 wt.% only spraying of droplets of PVP solutions from the nozzles was achieved. For 18, 20, and 22 wt.%, very uniform PVP fibers could be formed. Special case was for PVP fibers (24 wt.%) obtained at the two highest rotational speeds. In this process, a fiber ring (located between the spinneret and the collector) was observed, causing insufficient fiber elongation. The resulting fiber diameter was strongly influenced by the fact that these fibers did not fly the same or similar
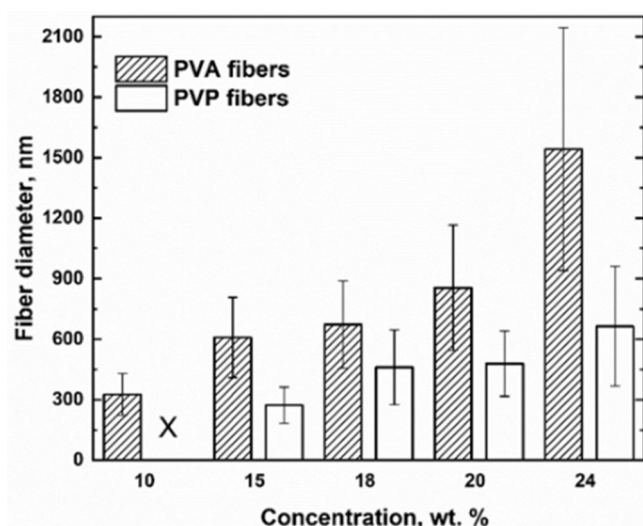
FIGURE 9   The diameter of centrifugal spun fibers as a function of the polymeric concentration in spinning solutions, x indicates no formation of PVP fibers 10 wt.%

TABLE 1   Regimes of the centrifugal spinning achieved for PVA and PVP solutions with different concentration and at various rotational speeds

	Rotational speed, rpm				
	5000	**7000**	**9000**	**11,000**	**13,000**
PVA					
10	f	s	s	s	s
15	f	f	f	f	f
18	f	f	f	f	f
20	x	f	f	f	f
22	x	x	f	f	f
24	x	x	f	f	f
PVP					
10	x	x	x	x	x
15	s	s	s	s	s
18	f	f	f	f	f
20	f	f	f	f	f
22	f	f	f	f	f
24	f	f	f	r	r

Note: f indicates formation of fibers, *x* indicates no formation of fibers, *s* indicates spraying of droplets, *r* indicates formation of ring of fibers.

distance as in previous case. Therefore, these fibers were not taken into statistical consideration.

Representative SEM images of fibers prepared from 15 wt.% PVA and 18 wt.% PVP are shown in Figure 10. These concentrations were selected, because they were the lowest ones for each polymer, where fibers were

formed in the whole range of rotational speeds, summarized in Table 1. This means that the resulting fibers did not contain any visible droplets or beads. In general, for other solutions, similar results were obtained as well, but for the PVA 10 wt.%, the fibers contained beads as in the case of 7000 rpm sample, shown in Figure 8. Lower rotational speeds than 5000 rpm were not effective, as there were no fibers withdrawn from the nozzles. On the other hand, higher rotational speeds than 13,000 rpm led to the spraying of droplets due to high inertial and aerodynamic forces formed at so high rotational speed. Similar results were discussed in the related literature.[42]

Figure 11 summarizes diameters of fibers produced at 15 RH% under various rotational speeds for the four distinct types of solutions, provided that two of them are identical as in Figure 10 for the sake of consistency. Apparently, the increase of rotational speed from 5000 up to 13,000 rpm did not significantly affect the diameter of PVA and PVP fibers prepared in concentrations 15 and 18 wt.%, respectively. Also, the next higher concentration of PVA (18 wt.%) did not result into a clear trend. However, for the 22 wt.% PVP solution, an increase of diameters was observed with increased rotational speeds.

O'Haire et al.[43] reported a reduction of fiber diameters with increasing rotational speed, but in their case PVP polymer was used. However, the authors did not submit standard deviations for single-diameter fibers, and in this case the standard deviations are the decisive factor of individual measurements.

According to Chen et al.,[42] an increase of the rotational speed increases the centrifugal forces and air frictional forces this leads to reduction of fiber diameters. But when the rotational speed reaches a critical value,[42] the total flight time of polymer jet is reduced and the average diameter of the fibers increases with further increased speed.[42]

Last, but not least, centrifugal spinning experiments at various relative humidities were carried out, namely at 15, 30, and 40% of RH. The motivation for this set was straight forward. In none of the relevant comparisons,[34–36] an influence of the relative humidity during centrifugal spinning process was investigated. In general, in all spinning reports this parameter is overlooked, because it is difficult to regulate it, in particular for the home-made spinning tools. But the evaporation of solvents during spinning processes is strongly dependent on the relative humidity, that changes over the course of the year, even between two following days. So it is highly relevant to look upon the influence of relative humidity on the spinning processes. Having the advantage of a precise control of relative humidity on our centrifugal spinning tool (see the relevant description in the Experimental part), a set of experiment using different relative humidities were carried out.

FIGURE 10 SEM images of centrifugal spun fibers (PVA 15 wt.% and PVP 18 wt.%) prepared using various rotational speeds (all scale bars correspond to 10 μm)
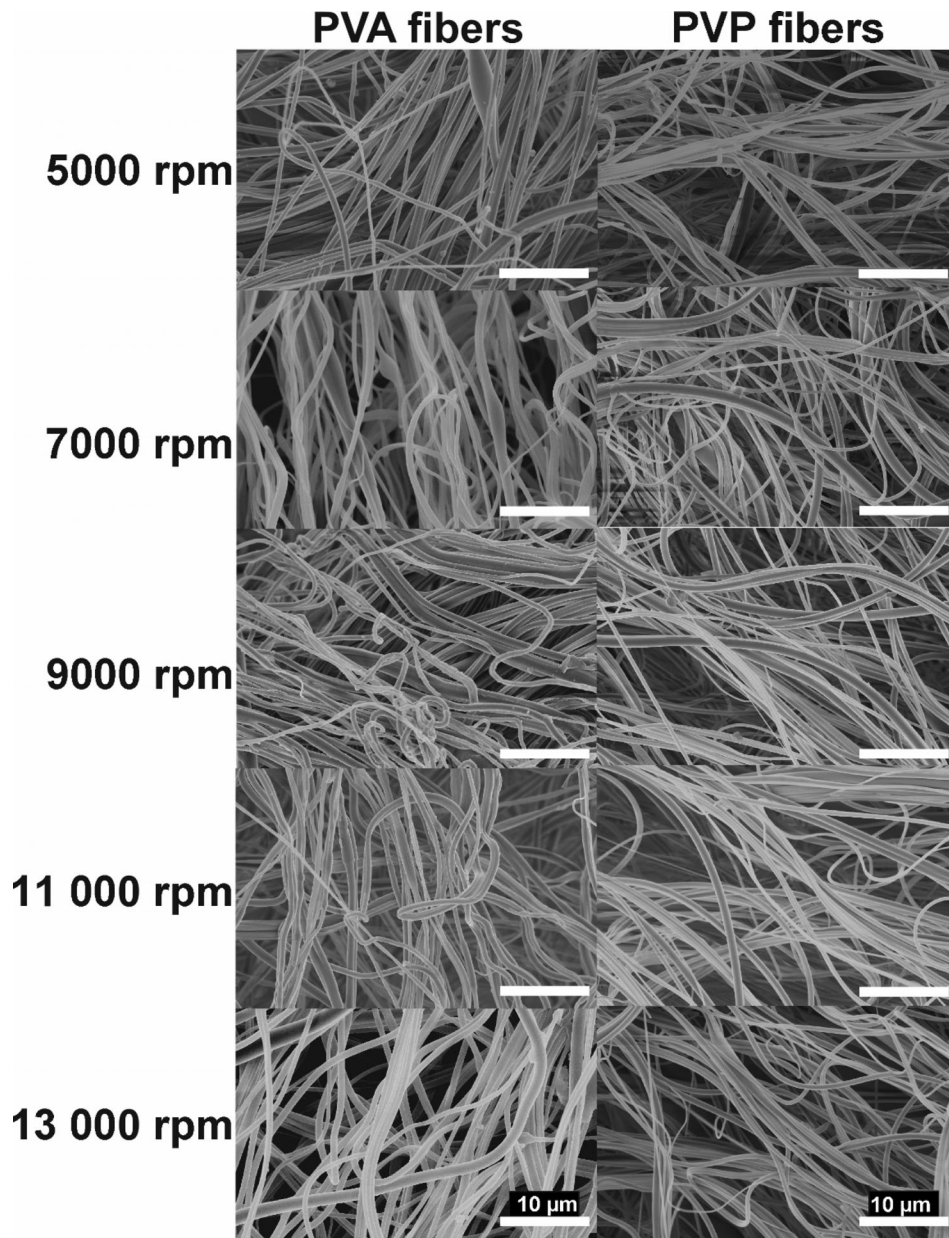
In order to exclude the influence of other parameters, these experiments were conducted in such manner, that the only variable was indeed the relative humidity of the incoming air, delivered by the air-condition unit of the centrifugal spinning. The temperature and rotational speed were fixed on 40°C and 7000 rpm, respectively, based on the success of these conditions within previous experiments. As in the previous case, experiments were conducted with 15 wt.% PVA and 18 wt.% PVP solutions.

Resulting fibers prepared from 15 wt.% PVA and 18 wt.% PVP under various relative humidities had no visible droplets and defects, except one case of 18% PVP and 40% RH, where spraying was achieved, instead of spinning of fibers. Nevertheless, upon further exploitation, it was found that for the 22 wt.% and 24 wt.% PVP

solutions, fibers could be prepared even at 40% RH. The results are summarized in Figure 12 that presents SEM images for PVA (15 wt.%) and PVP (22 wt.%) fibers produced at all three relative humidities. These results can be considered as very good and important, because they show that for an optimized solution and fixed temperature, the centrifugal spinning can produce high quality fibers across a quite wide range of humidities.

Figure 13 shows an evaluation of diameters of fibers produced at three different relative humidities in the spinning chamber—15%, 30%, and 40% RH, based on samples discussed and shown in Figure 12. It can be seen that the fiber diameter gradually reduced with an increased relative humidity for both types of polymeric fibers. This is again a very interesting observation,

because it is clear that the increased relative humidity has a major effect on the reduced fiber diameter, in case that other process parameters are hold constant. Therefore, for optimized solutions and other process

conditions, fibers from centrifugal spinning can be made to approximately the same diameter level (i.e., below 500 nm), as the electrospun fibers (see Figure 7, in particular concentrations 18 and 20 wt.%) obtained in this work, with all the advantages of the centrifugal spinning.

Our results are in direct contrast to the results of Almetwally et al.,[44] who reported that higher relative humidity during electrospinning process yields larger diameter fibers, due to higher electrostatic charge density on the fiber surface. However, as there is no direct applied electrostatic field during centrifugal spinning, different features apply. In particular, at higher relative humidities, one can expect a reduced speed of solvent evaporation (in our case water). This finding obtained in this work is very important, because apart the fact that it has not been previously shown in any centrifugal spinning report, it clearly shows that it is possible to obtain fibers with as low diameters as it is usual for the electrospinning processes.

Last, but not least, we carried out measurements of the electrostatic charge in all types of fibers produced by all techniques right after the particular process and also after fibers relaxed in the spinning chamber for 15 minutes. We found approximately the same
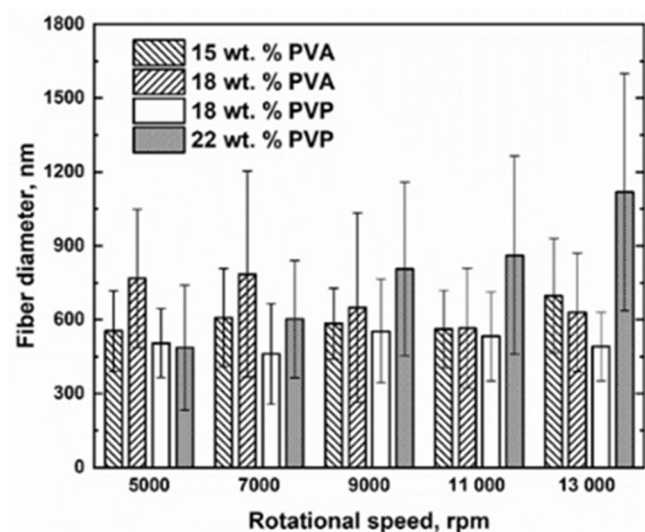

FIGURE 11 The diameter of centrifugal spun fibers (at 15 RH %) as a function of the used rotational speed
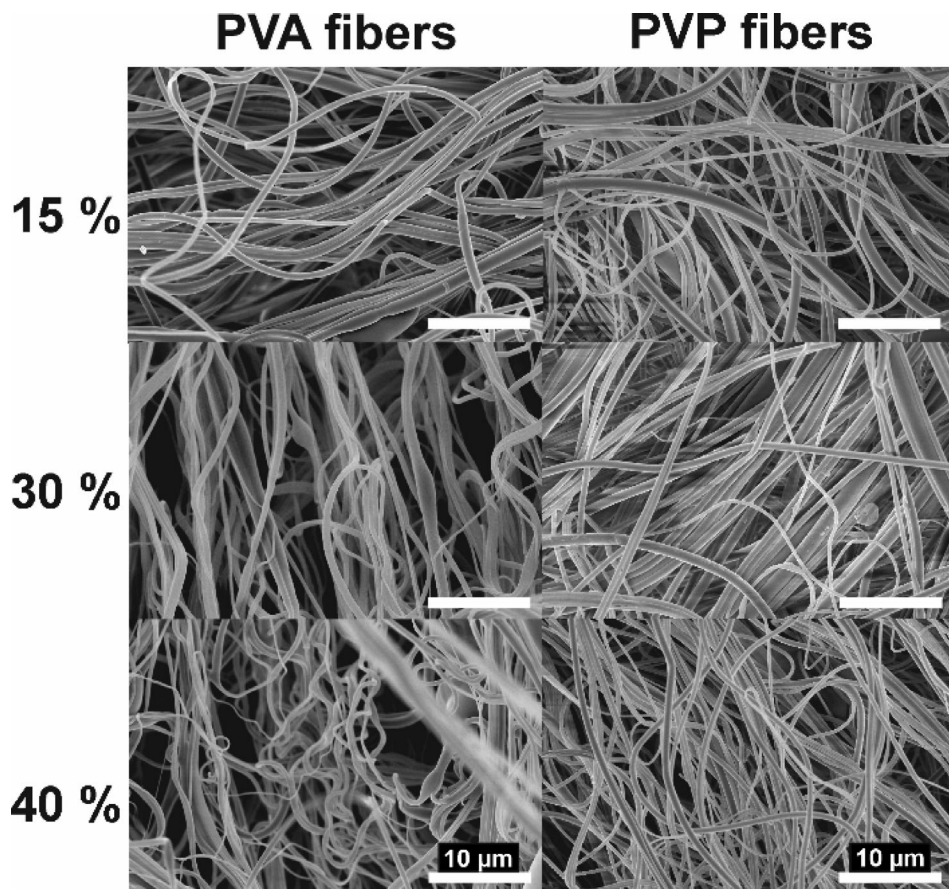

FIGURE 12 SEM images of centrifugal spun fibers (PVA 15 wt.% and PVP 22 wt.%, 7000 rpm) prepared under various relative humidities (15, 30 and 40% RH). All scale bars correspond to 10 μm
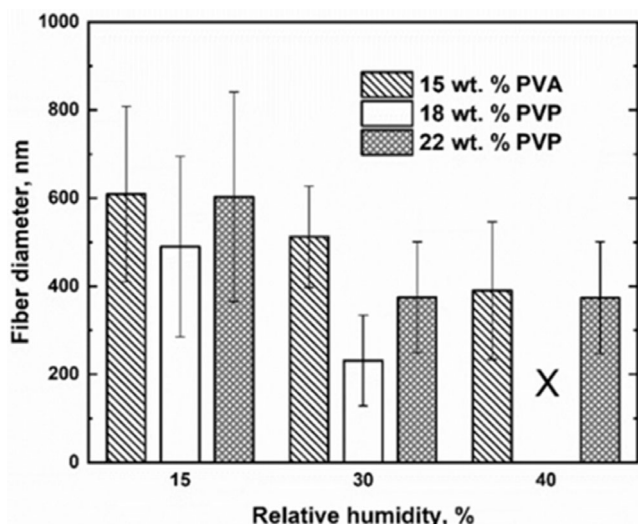
FIGURE 13 The diameter of centrifugal spun (7000 rpm) fibers as a function of the relative humidity, (x indicates no formation PVP fibers 18 wt.%)

electrostatic charge in all fibers right after the spinning processes were finished. While the presence of such charge is not surprising in the electrospun fibers, it has not been yet, to the best of our knowledge, anywhere shown that centrifugal spun fibers also possess some residual electrostatic charge. We believe that this is due to the mechanical friction of fibers, caused by an intimate contact among one another, while flying to collectors and being deposited there. In any case, the charge has a clear tendency to disappear in time from all fibers, likely due to a contact with discharging materials (collectors, collecting electrodes, etc.)

4 | CONCLUSIONS

In this work, polymeric fibers from PVA and PVP solutions of different concentrations were prepared by electrostatic and centrifugal spinning techniques using three different tools. Results of the processes were compared among the two techniques for the first time, providing a clear clue of particular advantages and disadvantages of each of the processes. While electrospinning yielded planar 2D layers of fibers, centrifugal spinning yielded bulky 3D structures, similar to the cotton wool. For all three tools used in this work, optimized conditions were identified to obtain good quality fibers, without droplets or beads. A common feature for all processes was that the average fiber diameter increased with increasing polymeric concentration in the solution (which is directly linked to increasing solutions' viscosities) and that fibers from centrifugal spinning had larger average diameter. However, the correlations between

fiber diameters and solution viscosities were found significantly stronger for centrifugal spun fibers, compared to electrospun fibers. Nevertheless, electrospinning was able to yield fibers with from relatively diluted solutions (10 wt. % of polymers), while centrifugal spinning was able to yield fibers from very viscous solutions, where electrospinning did not produce any fibers.

In addition, the effect of two variables of centrifugal spinning, namely rotational speed of the spinneret and relative humidity, were investigated in detail. Regimes of spinability of solutions with different concentrations under these variables were identified, along with other, undesired regimes, such as spraying of droplets. While there was no clear overall trend between the fiber diameter and the rotational speed of the spinneret, it clearly turned out that the increasing relative humidity reduced the average fiber diameter.

This work contributes to the knowledge of the preparation of polymeric fibers by electrospinning and centrifugal spinning. The obtained comparison clearly shows technological advantages of the centrifugal spinning over electrospinning, such as complete utilization of the spinning solutions (in contrast to bath of the Nanospider™, where always some 20%–30% of the total volume remain as waste).

CONFLICT OF INTEREST
The authors declare no conflict of interest.

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