DEVELOPMENT OF CONTINUOUS ELECTROSPUN PRECURSORS FOR CARBON FIBER MANUFACTURING

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Abstract
In our research the aim was to develop uniform nanofibrous yarns as a special precursor of nano-sized carbon fiber reinforcement. Different electrospinning setups were created and compared from the view of yarn production. The morphology and tensile properties of the different samples were investigated. Uniform nanofibrous yarns were successfully produced with an average fiber diameter of approximately 350 nm and a length of >20 m in every case. It was found that application of the yarn-way and the correction electrode introduced in this study were both favorable. They increased the tensile strength by 84% and the modulus of nanofibrous yarns by 115% compared to those of the yarns produced with the basic setup.

1 Introduction
Electrospun nanofibers have a wide variety of applications for example in filtration, sensor technology and biomedics [1]. On the other hand these fibers could also possibly be used in composites. Electrospun nanofibers can have a secondary reinforcement or interlaminar toughening role in hybrid composite structures [2-3]. They can even be composites themselves if they are combined with other nanomaterials, such as embedded carbon nanotubes, nanoclay, etc. [4-5]. From the viewpoint of the composites industry, maybe the most interesting is to produce nanofibers which can become the primary reinforcement materials of composite structures [6-7].
One of the reasons which led many scientists to develop special electrospinning devices and electrode configurations which makes possible to produce nanofibrous yarns is the necessity of these yarns as fiber reinforcement materials.
Generally the collector electrode is modified to produce unidirectional, oriented nanofibrous structures. Rotating drum collector is widely-used. Oriented, well-aligned structures can be produced, but only with a finite length which makes this method hardly implemented in industrial scales. Two parallel rings or wires can also be used, but these also results in structures with limited length [8].
Fiber yarns can be processed in a continuous way by for example using liquid surface collectors [9]. Smit et al. [10] developed a method which also uses open liquid (water for instance) surface to collect nanofibers. The wet nanofibers are then pulled out of the liquid bath with a rotating drum with continuous traction speed. Fiber orientation is formed when the nanofibrous mat leaves the bath resulting in a continuous yarn. Starting the process is not

easy because the nanofibers are formed on the surface of the liquid collector as a fiber mat, thus they should be pulled out somehow. At starting the process a classical yarn is attached to the drum and placed on the surface of the water collector. As nanofibers are sticked to the end of this piece of yarn, it can be pulled out together with the forming nanofibrous yarn. Thereafter nanofibrous yarn can continuously be produced without any auxiliary yarn.

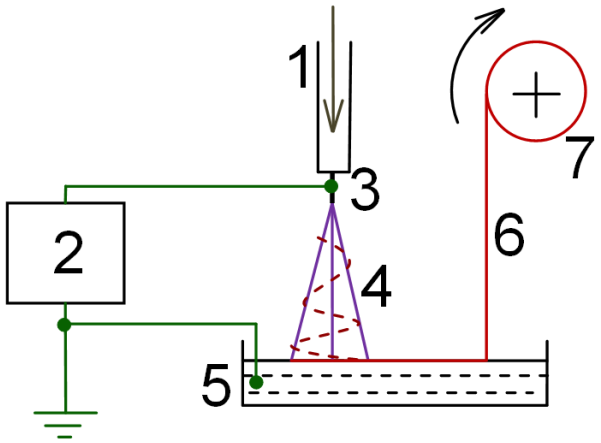

Figure 1. Schematic drawing of nanofibrous yarn processing technique developed by Smit et al. [10]
1: solution feed, 2: power supply, 3: capillary spinneret electrode, 4: fiber formation space, 5: grounded water resevoir with a free surface, 6: nanofibrous yarn, 7: rotating drum

The material used for electrospinning is usually a polymer solution or melt and the resulted fibers are generally thermoplastics. These nanofibers can have an increased tensile strength according to the size-effect though it is still not enough to apply these in thermosetting composites as reinforcement mainly because of the smaller orientation. The research activities are therefore mainly focused on the process of polyacrylonitrile (PAN) nanofibrous yarns. In this case the thermoplastic PAN can be oxidized then carbonized in order to get carbon nanofibers. There are many studies dealing with carbonization of such nanofibrous materials [11-13], but the adequate precursor formation is still a challenge.
Therefore the aim of our study was to further-improve the quality and uniformity of continuously-spun nanofibrous yarns. As the base material was supported by a carbon fiber manufacturer company these continuous nanofibrous yarns could possibly be used as special precursors of carbon nanofibers.

2 Materials and testing methods

Polyacrylonitrie (PAN) co-polymer precursor fibers which had got from a carbon fiber manufacturer was dissolved in dimethyl-formamide (DMF). The optimal concentration for electrospinning was found to be 12 m% based on preliminary experiments. The mixing was carried out with for 6 hours with the aid of magnetic mixer at a temperature of 60°C.
For producing nanofibrous yarns the electrospinning setup of Smit et. al [10] was applied. In this case a self-made electrospinning device was used. In this case fibers are randomly deposed on the surface of the water reservoir, then continuously pulled out by the rotating drum to form oriented yarns. In our research we use the abbreviation S for this yarn processing mode (see Figure 2.). Some modifications of this electrospinning setup was applied in order to further increase the quality of fiber yarns.
In the next case (C), a correction electrode was applied that makes possible to focus the fiber deposition to a smaller area. The correction electrode was charged at the same voltage as the capillary electrode and the plane of the correction electrode was perpendicular to the axis of

the capillary spinneret. The correction electrode was made of a metal plate and had a diameter of 100 mm.
The second modification (Z) of the system includes a further development. After fibers are pulled out from the surface of the water reservoir the yarn is pulled through between small rings and metal rods. Some kind of a rope-way is formed this way for futher drawing and named 'yarn-way'. The copper wire rings in the beginning and the end of the yarn-way had an inner diameter of 10 mm, the two applied steel rods had a diameter of 3 mm. The distance between each ring and rod was 50 mm. The schematic drawings of the three different electrospinning configurations can be seen in Figure 2.

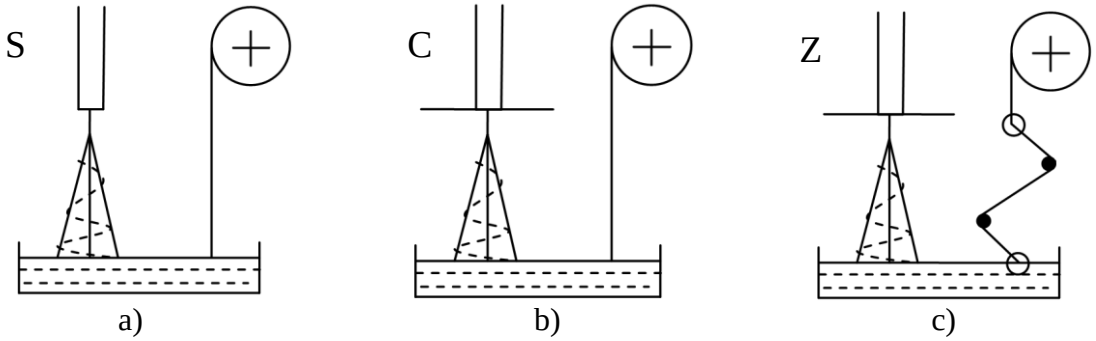

Figure 2. Schematic drawings of different electrospinning configurations for yarn production. a) S-type b) C-type with correction electrode c) Z-type with correction electrode and yarn-way

Samples of nanofibrous yarns were produced with the three different processing modes with the same conditions. The production was continuous, at least 20 m of yarns were produced in every case. The applied voltage was 23 kV supplied by M NP-35/P (Hungary) type power supply, the distance of the capillary electrode and the surface of water was 100 mm, temperature was 25 ± 1°C and the relative humidity of air was 27 ± 2%. The maximum flow rate which could be applied without dripping of the solution was 5 ml/h fed by Aitecs SEP-10S plus (Lithuania) syringe pump. The traction speed of the yarns was set to 500 mm/min in every case which was held precisely and constantly by a stepper motor controlled by a microcontroller (Atmel ATMega8). As the flow rate of the solution and the traction influence the yarn morphology and linear density therefore these data are denoted. For instance, 5-500C type yarn refers to a yarn produced by the C-type process, had a flow rate of 5 ml/h and a traction speed of 500 mm/min.
For tensile tests the linear density of fibrous yarns was determined. 40 ± 0.1 mm long yarn samples were cut and their mass was measured by Perkin Elmer AD-2 type balance with an accuracy of 1 μg. The linear density of every tensile specimen was determined respectively by dividing the mass of the specimen with the length. The cross section was determined by dividing the linear density with the density of the bulk PAN co-polymer.
Tensile tests were carried out by Zwick Z005 (Germany) type universal equipment, the force sensor had a maximum load of 20 N with a resolution of 0,001 N. The speed of displacement was set to 5 mm/min the gauge length was 25 mm.
Scanning electron microscopy (SEM) was carried out by JEOL JSM-6380 (Japan) type device. The yarns were sputtered by a thin layer of AuPd alloy for the experiments. Image processing was performed by UTHSCSA ImageTool 3.0 software. The diameter of 100 fibers were determined in case of every 3 type of yarns.

3 Results and discussion

Tensile diagrams of nanofibrous yarns produced by different ways are depicted in Figure 3.

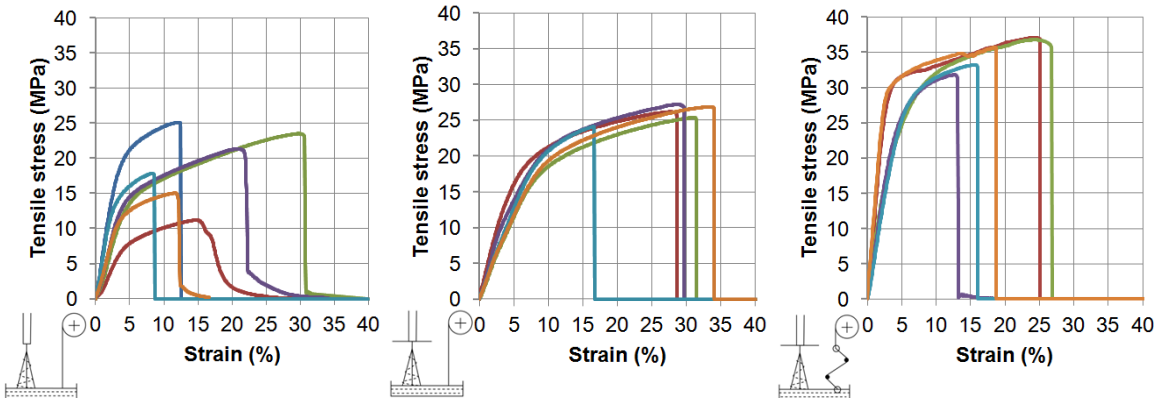

Figure 3. Measured stress - strain curves of the different yarns. a) 5-500S b) 5-500C c) 5-500Z

The diagrams reveal that the elongation at break have a huge deviance in every three case. Both modulus and tensile strength have the highest value in case of the last (5-500Z) sample. The characteristics of the tensile diagrams are quite similar to those of nanofibrous mats which can imply the moderate orientation of fibers and/or the viscoelastic behavior of PAN. The beginning of the curves can be characterized by the tensile modulus. This first straight segment is followed by another straight one which can be characterized by the slope of this plateau. There is a transition zone between the two linear parts. Breaking occurs suddenly. The tensile process of nanofibrous materials had been modeled earlier, in our previous research, for further details see [14].

The tensile strength and breaking elongation of the yarns can be seen in Figure 4. Application of the correction electrode lead to the increase of the tensile strength. The drawing by the rope-way was also found to be effective, because it lead to a further increase. The elongation at break values have a high standard deviation (25-52%) therefore there is no significant change in this behavior. On the other hand it can be seen that the correction electrode somehow improved the yarn structure. In the third case the maximum elongation decreases possibly due to better fiber orientation. Namely, fibers with random orientation turn to the direction of pulling during tensile tests until being transformed into an oriented structure. It leads to a surplus elongation before break, compared to the naturally oriented structure. The tensile modulus and the slope of the second linear part can be seen in Figure 5.

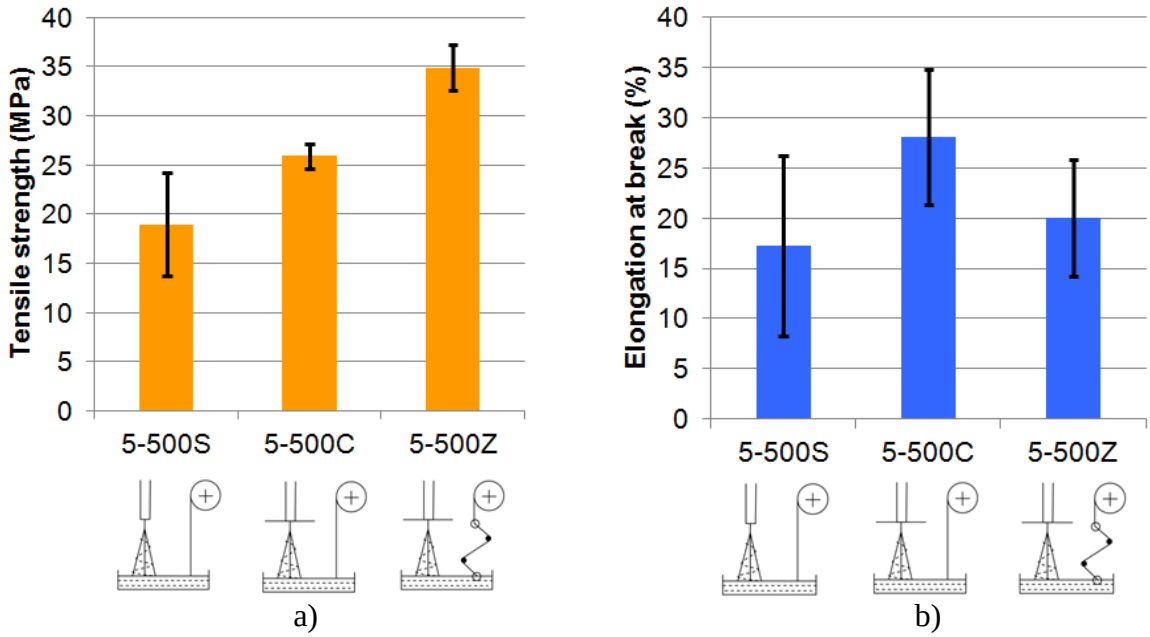

Figure 4. Mechanical properties of nanofibrous precursor yarns. a) Tensile strength, b) Elongation at break

While in the first two cases (S and C) the value of modulus seems to be similar, the third yarn (5-500Z) shows a significantly higher value. Considering the standard deviations the slope of the second linear part of the tensile curves are essentially similar which means the damage process of the yarns is the same.

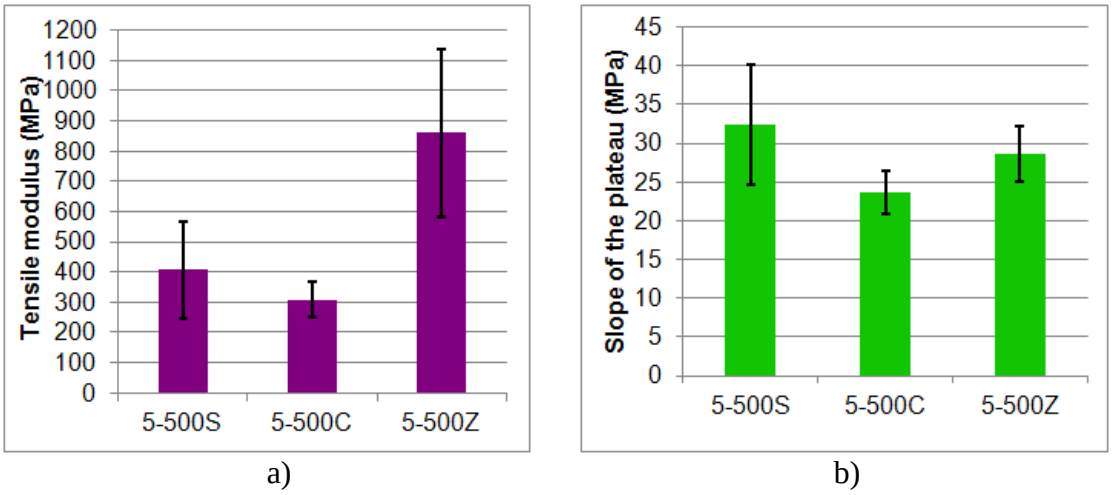

Figure 5. Tensile modulus of nanofibrous yarns. a) Tensile modulus b) Slope of the second linear part of the tensile curve

The mechanical properties are summarized in Table 1.

Type of yarn		**5-500S**	**5-500C**	**5-500Z**
Tensile strength	[MPa]	19.0 ± 5.3	25.9 ± 1.3	34.9 ± 2.3
Elongation at break	[%]	17.3 ± 9.0	28.1 ± 6.7	20.0 ± 5.8
Tensile modulus	[MPa]	407 ± 161	309 ± 58	861 ± 277
Slope of the plateau	[MPa]	32.4 ± 7.7	23.6 ± 2.8	28.6 ± 3.5

Table 1. Main mechanical properties of nanofibrous yarns

Application of the correction electrode has influenced the main mechanical properties of yarns in a favorable way. Although the tensile strength, modulus and elongation at break values are principally the same, compared to the 5-500S yarn the deviation of the values are much lower in case of 5-500C yarn. It can also be seen in the tensile diagrams (Figure 3), because the correction electrode lead to more similar tensile curves. It can be attributed to the better homogeneity of the yarns along its length. Every small sample of the yarn have similar linear density, fiber structure which lead to more balanced tensile behavior.
It is worth to apply the drawing with the yarn-way because compared to the S-type yarns it causes 84% increase in tensile strength, 115% increase in tensile modulus, from which 49% of increase in tensile strength and 35% increase in modulus is caused by the drawing of the yarn.
SEM micrographs of the nanofibrous yarns can be seen in Figure 6. Fiber diameters and fiber orientations were determined based on these pictures. The micrographs show moderate, but significant fiber orientations along the yarn axis.

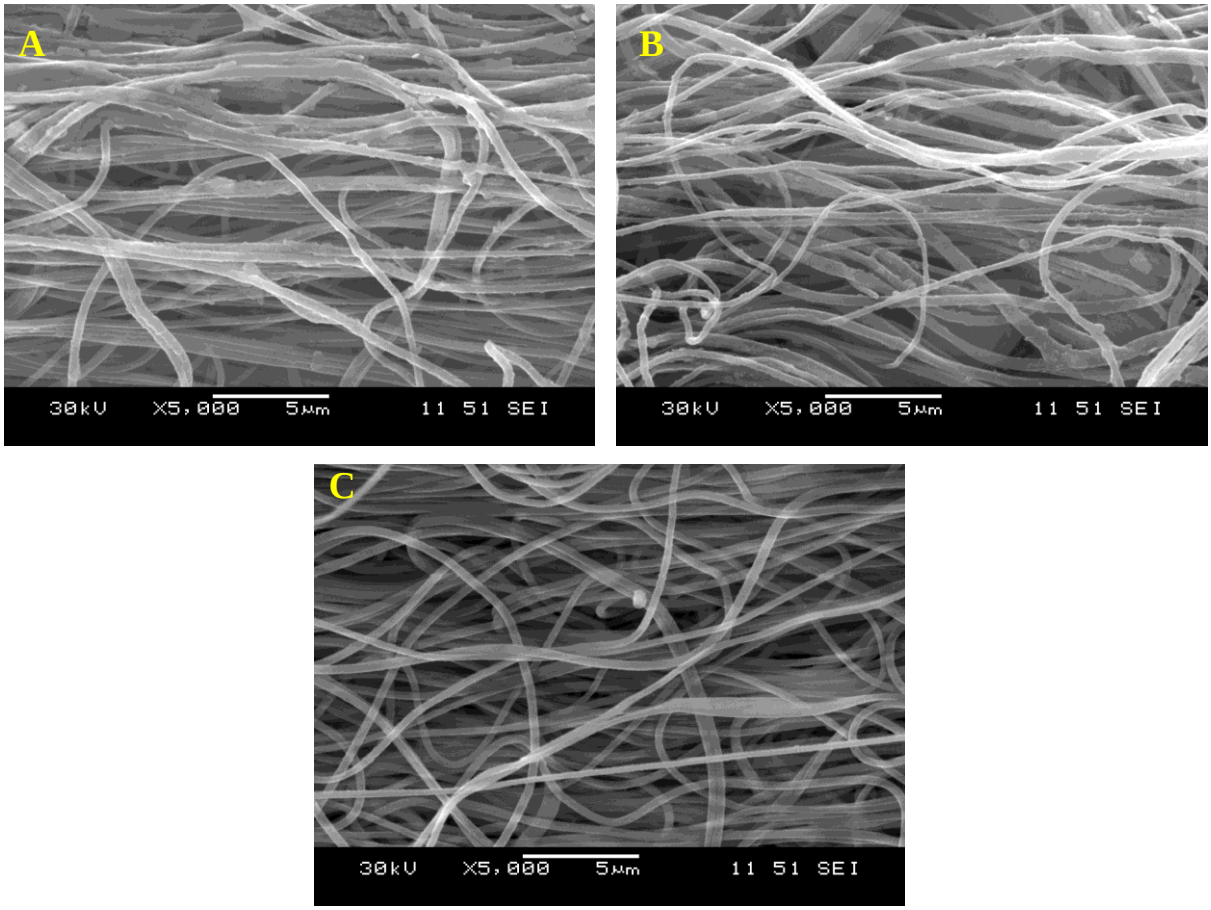

Figure 6. SEM micrographs of different nanofiber yarns. The axis of yarns are horizontal in case of all pictures a) 5-500S b) 5-500C c) 5-500Z

The results of fiber diameters and the Herman's orientation factor, which quantitatively characterizes the fiber orientation, are summarized in Table 2.

	5-500S	**5-500C**	**5-500Z**
Fiber diameter	353 ±55 nm	345±114 nm	342 ± 60 nm
Herman's orientation factor	1,38	1,36	1,44

Table 2. Average fiber diameters and fiber orientations of the different yarn types

The results show that fiber diameters did not change significantly by changing electrode configuration. The correction electrode had only had an effect on fiber deposition on the liquid surface as it focused the fibers to a smaller area. The drawing of the yarn with the Z configuration also did not change the fiber diameters. Although the Herman's orientation factor increased, but it shows only a minor improvement. It must be noted that only the surface of nanofibrous yarns were investigated, thus no information has been obtained from the inner part of the yarn which can possibly more or even less oriented. This implements that the yarn-way drawing can mainly influence the porosity of the structure. It can lead to a more compact structure where fibers have more friction between one another. It can possibly lead to an increased modulus and tensile strength. The fiber utilization of the structure is increased this way.

4 Conclusions

The nanofiber production method of Smith et al. [10] was improved by applying a correction electrode and a fiber yarn-way applied for drawing the yarn. Nanofibrous yarns can continuously be produced with this method. The fiber diameters, orientation and mechanical properties were determined. It was found that application of the yarn-way and the correction electrode were favorable as they increased the tensile strength by 84% and the modulus of nanofibrous yarns by 115%. Drawing of the structure mainly takes place when the fibers are pulled out of the water bath, the further drawing has only a minor effect. On the other hand it can change the porosity and compactness of the structure which can lead to higher friction forces between fibers and therefore to a better fiber utilization. The correction electrode favorably focus the fibers deposition to the surface of the water collector and somehow leads to the formation of a more uniform yarn. These nanofibrous yarns can be applied as precursors of carbon nanofibers in the near future.

Acknowledgements

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