Positioning and Aligning Electrospun PAN Fibers by Conductive and Dielectric Substrate Patterns

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During electrospinning, the flying nanofibers can be attracted by conductive areas such as copper tape on a nonconductive substrate, especially in case of magnetic nanofibers. The question arises, however, whether the conductivity or any other physical properties of these areas are responsible for this effect. Here, electrospinning polyacrylonitrile (PAN) on nonconductive polypropylene (PP) substrates is reported, modified with conductive copper tape as well as with diverse coatings with varying dielectric constants. The results show that in case of non-magnetic PAN fibers, especially BaTiO$_3$ with its high dielectric constant strongly, attracts the fibers formed during electrospinning, which can be explained by local modification of the electric field due to the introduced dielectric. This process can be used to tailor the nanofiber mat thickness depending on the position.

1. Introduction

Electrospinning is a technology enabling the production of nanofibers or nanofiber mats from diverse polymers or polymer blends.[1–3] Such nanofiber mats can, for example, be used for filtration,[4] tissue engineering,[5] in nanocomposites,[6] batteries,[7] etc. For many of these applications, the fiber orientation is of interest. More precisely, aligned fibers are often advantageous in comparison with the usually isotropic fiber orientation. One of the possibilities to reach fiber alignment is using a fast rotating collector[8,9] or a collector prepared by a pair of blades.[10] For the special case of magnetic nanofibers, magnetic field assisted electrospinning can be used to gain fiber alignment.[11,12] An easier approach, not necessitating rebuilding the electrospinning equipment, was suggested in a former study of our group, based on making defined areas of a common polypropylene (PP) substrate conductive by adding conductive copper tape or the like.[13] While this approach works for magnetic nanofibers, it was found less suitable for non-magnetic ones.[13]

Another possibility to modify the electric field during electrospinning may be given by using dielectric coatings on parts of the substrate. Unexpectedly, only very few papers mention this possibility. Nguyen et al. report on using a cylindrical collector, rotating at high speed and shielded by two curved dielectric films, which not only redirect the air flow due to the cylinder rotation, but also intensify the electrostatic field in a thin slit between them. This enabled fiber alignment and position control.[14] A combination of substrate topography and dielectric substrate properties was suggested by Zhao et al. to define fiber positioning.[15] Most recently, Nagle et al. mention dielectric properties of fibers in near-field electrospinning as a limitation for the maximum layer height, which can be spun on a defined position.[16]

Here, we investigate the influence of conductive or dielectric areas on a common PP substrate on fiber orientation and localization for the case of polyacrylonitrile (PAN), a polymer often applied as carbon precursor and thus of technological relevance,[17,18] due to the resulting modifications of the high electric field in the electrospinning chamber.

2. Results and Discussion

Figure 1a gives an overview of one of the samples used for investigating the influence of a partly conductive substrates. Some of the conductive areas are grounded, that is, on the same electric level as the ground electrode (marked with “g”). The conductive strips are glued on the front (“f”) or on the back (“b”) of the nonconductive PP substrate.

Firstly, it is clearly visible that more fibers are coating the grounded strips than the not grounded ones, showing that also non-magnetic fibers can be influenced by partly conductive substrates. As Figure 1b depicts, this is especially valid along the edges of the conductive paths. Next, Figure 1c indicates a clear fiber orientation perpendicular to the neighboring conductive strips. This orientation is also visible in the FFT plot (inset in Figure 1d), showing a clearly anisotropic pattern. It should be mentioned that the nanofibers found here have a relatively narrow diameter distribution and a smaller average diameter (Figure 1d) than the PAN nanofibers electrospun under very similar conditions, reported in,[13] suggesting future research
on the possible influence of partly conductive substrates on the diameter distribution.

In the second part of our study, the influence of highly dielectric substrate areas is tested. Figure 2 gives an overview of the effect of diverse dielectric materials on the substrate.

Indeed, the influence of different dielectrics on the spinning results is obvious for most materials (cf. Figure 2). For water, the wetted areas on the substrate are clearly visible, especially for spinning only 5 min. The number written with Edding 30 is also clearly visible although the dye was partly dried during spinning; however, apparently enough solvents were still included. The strongest effect, as expected, is reached with BaTiO$_3$, which has the highest dielectric constant. For the 3D printed "T" from PLA, the thick object apparently shaped the electric field differently, indicated by more fibers approaching the substrate along the borders of this object. The materials not depicted here had a weaker impact on the spinning results, in case of the pens most probably due to fewer dye on the substrate and faster drying of the Edding 363, while in case of the glass rod, the round shape seems to be responsible for the difference in comparison with the T-shaped PLA object.

Both ways to shape the electric field in order to collect fibers on defined places are especially important for composite applications and sensors[14] as well as for stem cell differentiation, biomimetically engineering of functional tissues, and other biomedical applications.[15]

3. Conclusion and Outlook

Making an electrospinning substrate partially conductive can be used to tailor fiber positioning and orientation, while highly dielectric parts strongly influence fiber positioning. The latter will be investigated further in the future, using aligned structures to test whether fiber orientation can also be defined by highly dielectric coatings on distinct substrate areas or 3D items behind the substrate. In addition, nanofiber layers growing on partly conductive structures which sometimes grounded, sometimes not may result in an interesting mixture of aligned and chaotic layers with again different mechanical properties. Finally, a theoretical analysis of the structural parameters is necessary in comparison with experimental results.

4. Experimental Section

Electrospinning was performed using the wire-based electrospinning machine “Nanospider Lab” (Elmarco, Liberec, Czech Republic) with the following spinning parameters: 80 kV / 65 kV voltage for spinning on conductive / dielectric surfaces, nozzle diameter 0.9 mm, carriage speed 100 mm s$^{-1}$, substrate speed 0 mm min$^{-1}$, distance between bottom electrode and substrate 240 mm, distance between substrate and ground electrode 50 mm, relative humidity and temperature in the spinning chamber 32% and 23°C, respectively.

The polymer solution for electrospinning was prepared by dissolving 16% PAN (X-PAN, Dralon, Dormagen, Germany) in dimethyl sulfoxide...
Figure 2. Nanofiber mats, electrospun on PP substrate modified by different materials.

(DMSO, min 99.9%, S3 chemicals, Bad Oeynhausen, Germany) and stirring for 2 h at room temperature on a magnetic stirrer.

The PP substrate (Elmarco) was modified with copper tape (5 mm width; dooppa, Hubei, China), glued on the PP substrate (dielectric constant \( \varepsilon_r \approx 2 \)), as well as the following materials with different dielectric constants, applied to the backside of the PP: deionized (DI) water (dielectric constant \( \varepsilon_r \approx 78 \)), BaTiO\(_3\) (dielectric paste no. 8153, DuPont, Bristol, UK) (\( \varepsilon_r \approx 100–1000 \)), a glass rod on top of the substrate (\( \varepsilon_r \approx 5-10 \)), a 3D printed polylactic acid (PLA) T-shaped object on top of the substrate (\( \varepsilon_r \approx 7 \)), [19] and numbers written with the following pens: Edding 363, whiteboard marker, solvent ethane-1,2-diol (\( \varepsilon_r \approx 40 \)).

Investigations were performed using a Canon EOS 1300D with Tamron SP AF 17–50 mm F/2.8 XR Di II LD Aspherical lens, a digital microscope VHX 600 (Keyence, Neu-Isenburg, Germany) and a scanning electron microscope (SEM) Helios NanoLab DualBeam 600 (FEI Company, Hillsboro, Oregon, United States) were used.

ImageJ 1.51j8 (National Institutes of Health, Bethesda, MD, USA) was used for investigations of fiber diameters and fast Fourier transform (FFT) evaluations, showing single lines for oriented fibers.[20]

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

dielectric, electrospinning, fiber orientation, polyacrylonitrile (PAN)

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