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Research article

Electrospinning water-soluble/insoluble polymer blends

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Abstract: Electrospun nanofiber mats can be used, e.g., as filter materials, in biotechnological and medical applications, as precursors for the preparation of carbon nanofibers, etc. In most cases, the large surface-to-volume ratio and correspondingly large contact area with the environment is utilized. This ratio can even be further increased by introducing nanostructures into the nanofibers. One possibility to modify the morphology of the nanofibers or the whole mats is based on the introduction of water-soluble additions in spinning solutions of insoluble polymers and afterwards washing them out. In this paper, polyacrylonitrile (PAN) nanofiber mats were blended with eight water-soluble polymers to test which blends are spinnable and result in which modifications of the single nanofibers and the nanofiber mats. Optical examination shows a broad range of possible morphologies which can be gained in this way, paving the way to tailoring the desired geometric properties of PAN nanofiber mats.

Keywords: electrospinning; nanofiber mats; polyacrylonitrile; biopolymers

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1. Introduction

Nanofibers with diameters between some ten and several hundred nanometers can be created by electrospinning [1–4]. Electrospinning is most often performed by pressing a polymer solution or melt through a syringe and dragging the resulting fiber in a high electric field to a substrate. Needleless electrospinning methods include rotating drums or wires which are coated with the polymer melt or solution.

Due to their large surface-to-volume ratio, nanofiber mats from different polymers and polymer blends can be used, e.g., as filter materials [5–7], catalyzers [8], in medical [9] or biotechnological applications [10–12]. Several water-soluble polymers have additionally interesting intrinsic properties. Poloxamers (poly(oxyethylene-b-oxypropylene-b-oxyethylene)) were used in blends with other polymers for drug delivery [13], skin tissue engineering [14] or wound healing [15]. Dextran was used for drug delivery [16,17] or electrochemical applications [18] in different blends. Poly(ethylene glycol) (PEG), on the other hand, is often used as a spinning agent for materials which cannot form fibers solely [19,20]. For most applications, however, the necessity arises to crosslink these materials afterwards which may cause severe problems since techniques typically used for membranes or similar shapes do not work anymore for nanofibers [21,22].

Besides these often bio-based polymers, polyacrylonitrile (PAN) is of high interest since it can be electrospun from dimethyl sulfoxide (DMSO), a low-toxic solvent, and is waterproof. Due to these properties, PAN is often used for electrospinning, especially as a precursor to create carbon nanofibers [23–27].

Finally, blends of different materials are often investigated to create multi-material systems with new properties. PAN was, e.g., blended with pitch to enhance crystallinity and conductivity of the afterwards carbonized nanofibers [28]. The absorption properties of activated carbon nanofibers were increased by blending PAN with cellulose acetate [29]. Blending PAN with poly(vinylidene fluoride) and thermoplastic polyurethane was used to create a gel electrolyte [30].

The possibility to tailor nanofiber diameters as well as fiber and mat morphology are on the one hand important for a broad variety of applications, such as using PAN to create carbon nanofibers or for promotion of cell growth. On the other hand, only little research has been performed yet to investigate the influence of adding water-soluble polymers to a PAN electrospinning solution. First tests to modify nanofiber mat morphologies by blending PAN with dextran [22] or poloxamer [31] were not yet satisfactory. This is why in this paper, we report on blending PAN with diverse water-soluble polymers and depict the resulting changes in the fiber and mat morphologies to create a base for future systematic tailoring of these parameters.

2. Materials and method

PAN solutions were prepared with PAN concentrations of 7.5% and 16% in DMSO (min. 99.9%, purchased from S3 Chemicals, Germany) by stirring for two hours at room temperature. PAN-based yarn (needlework yarn “Emma”) was taken as a PAN source. The used water-soluble polymers were dextran (500 for biochemistry, 500,000 kDa, Carl Roth GmbH + Co. KG, Karlsruhe/Germany), gelatin (Abtei, Germany), agarose, PEG (600 kDa, S3 Chemicals, Bad Oeynhausen, Germany), starch, casein (technical grade from bovine milk containing 90% protein, Sigma, St. Louis, USA), poloxamer (“lutrol F 68”, 7680–9510 Da, 2 × 40% hydrophilic parts, BASF, Germany) and agar in different concentrations as shown in Table 1. The few missing combinations were shown in previous tests to show insufficient properties [31] and were thus not repeated.

Electrospinning was performed using a “Nanospider Lab” needleless electrospinning machine (Elmarco, Czech Republic). A polypropylene (PP) fiber mat (purchased from Elmarco) was used as a substrate. The spinning parameters such as high voltage, electrode-substrate distance, carriage speed, etc. were varied to find the optimum conditions for the different mixtures and biopolymers. The parameters are shown in Table 2.

Table 1. Concentrations of water-soluble polymers used for electrospinning without PAN and with two different concentrations of PAN.

Water-soluble polymer	Concentration without PAN (%)	Concentration with 7.5% PAN (%)	Concentration with 16% PAN (%)
Dextran	24.5	-	1.4
Gelatin	22.6	13.04	6.89
Agarose	3	3.38	1.32
PEO	9.2	2.3	3.1
Starch	7.05	-	1.85
Casein	4.8	5.75	2.09
Poloxamer	saturated	6.79	-
Agar	1.32	1	0.4

Table 2. Spinning parameters used in this study.

Parameter	Value
Voltage (kV)	45–80
Current (mA)	0.01–0.13
Nozzle diameter (mm)	0.6–1.5
Carriage speed (mm/s)	100
Substrate speed (mm/min)	0
Ground-substrate distance (mm)	240
Electrode-substrate distance (mm)	50
Temperature in chamber (℃)	21–23
Relative humidity in chamber (%)	32–34

To reduce the relative humidity from approximately 60% to 30–35%, dry (oil- and water-free) compressed air was fed into the spinning chamber for up to 60 minutes before the start of the experiments.

The nanofiber mat morphologies were studied using a VK-9000 (Keyence) confocal laser scanning microscope (CLSM) with a nominal magnification of 2000× before and after wetting the samples in aqua dest. for 1–3 weeks.

3. Results and discussion

Firstly, tests were performed to spin all water-soluble polymers (besides poloxamer which was already shown to perform electrospraying instead of electrospinning earlier [31]) solely from DMSO. The results of all experiments which led to material being added to the substrate are depicted in Figure 1. For dextran, agar, and casein, no fiber or droplet creation nor a coating of the original fibers occurred.

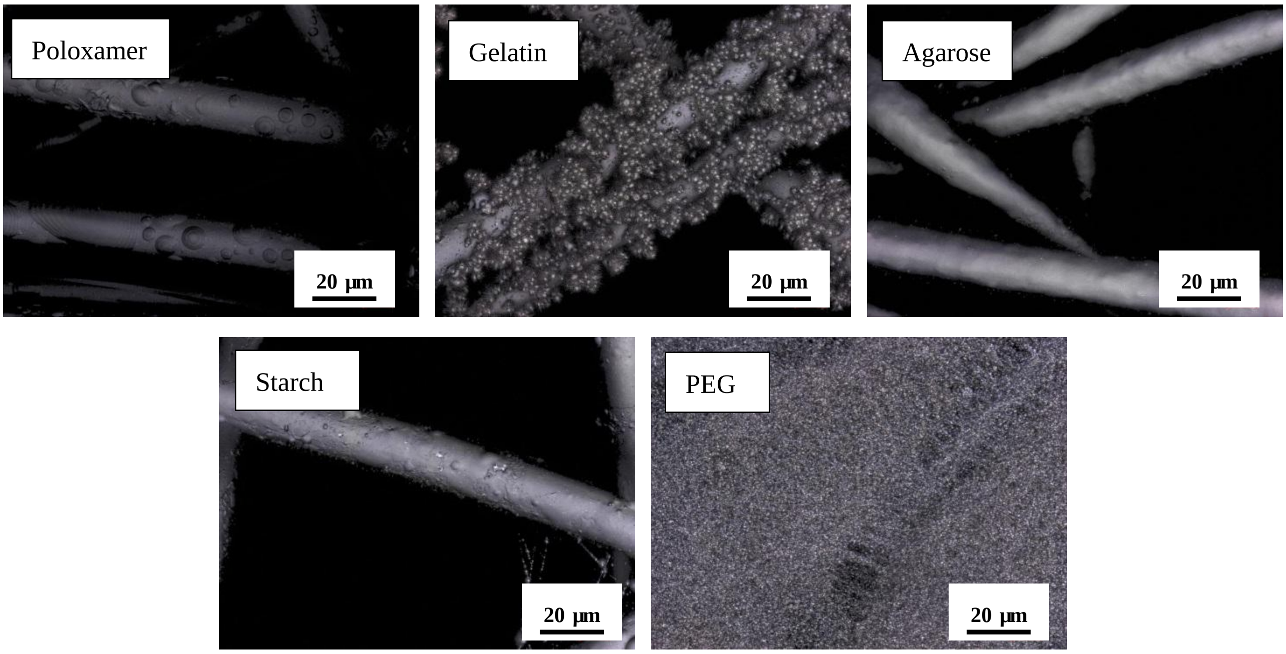

Figure 1. Different water-soluble polymers, electrospun/electrosprayed from DMSO.

Depending on the polymer, completely different effects can be realized. For poloxamer, electrospinning from DMSO gives a similar result as electrospinning from water [31], i.e., small droplets which seem to partly dry on the substrate fibers. For gelatin, shiny little pearl-like structures are formed, while agarose and starch form a coating on the substrate fibers. PEG, finally, builds a mat from fine nanofibers, similar to those created by electrospinning PEG from water [20].

As a next step, the water-soluble polymers were added to a 7.5% solution of PAN which is approximately half the typical solid content for electrospinning PAN. This value was chosen to allow for relatively high quantities of other polymers being added without increasing the solution’s viscosity to values too high for needleless electrospinning. The results are depicted in Figure 2, together with pure PAN with 12% concentration which is the lowest concentration found spinnable in the Nanospider.

PAN blends with agar, casein, and PEG result in relatively dense nanofiber mats with clearly visible, long, straight fibers. This is especially remarkable for agar and casein which could not be spun solely. For agarose and poloxamer, an electrospraying process has occurred instead, resulting in a thick structured coating on the substrate fibers. Gelatin, finally, forms a mixture of coating and relatively thick fibers. While gelatin was found to be electrosprayed from DMSO (Figure 1), it can be electrospun from water, which makes this “intermediate” result understandable. However, it should be mentioned that there is no clear correlation between the results of electrospinning the water-soluble polymers solely from DMSO and blending PAN with them.

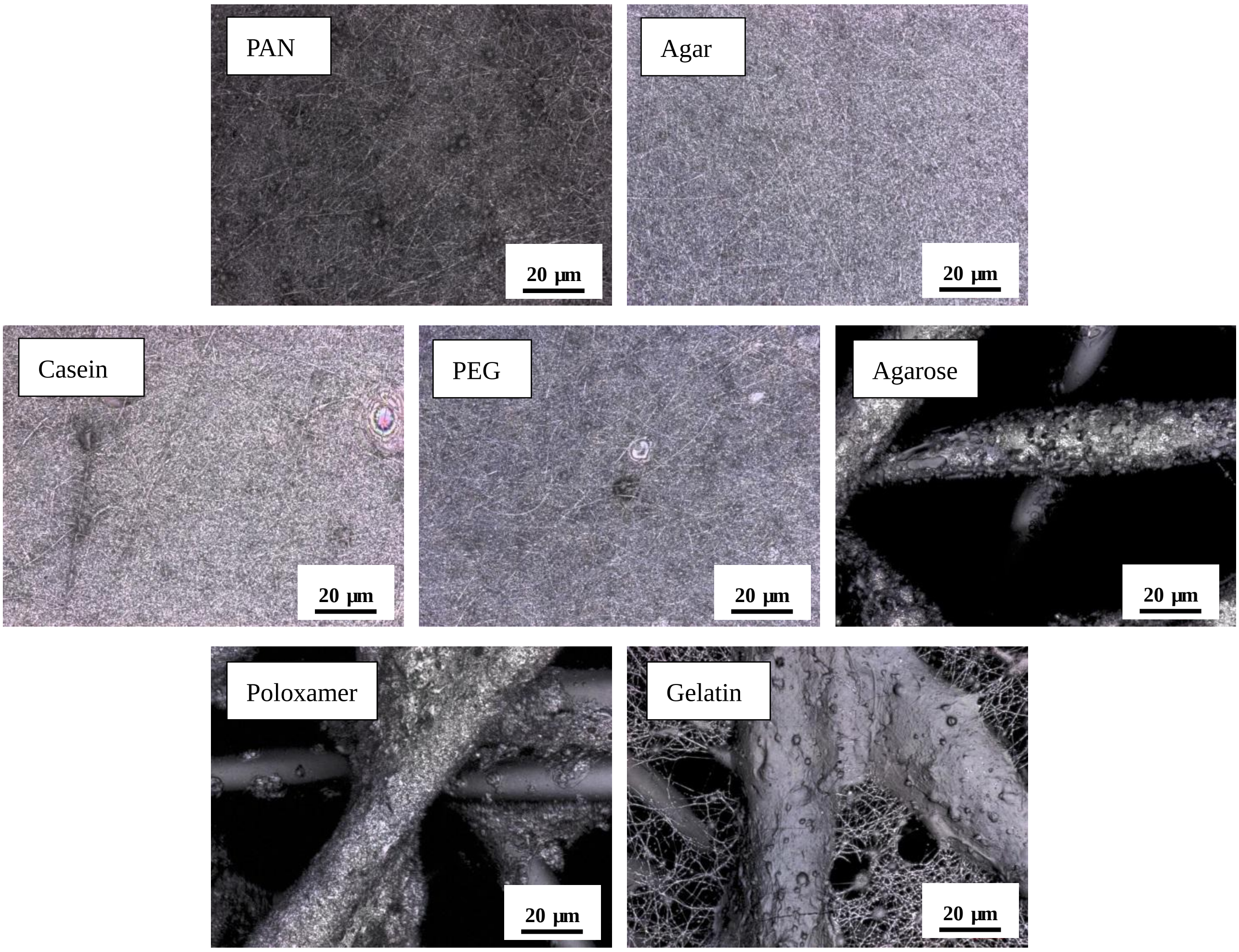

Figure 2. Nanofibers electrospun from pure PAN 12% and PAN 7.5% blended with different polymers.

To test the water-stability of the resulting fiber mats or droplets, respectively, the samples were wetted for one week. The results after drying are shown in Figure 3. While for agar and PEG as spinning partners, parts of the nanofiber mat seem to be kept without large deviations, other parts are clearly washed away. The strongest effect is visible for casein where the mat is completely dissolved, leaving back only residues along the substrate fibers.

For blends with agarose and poloxamer, no strong deviations are visible. For PAN/gelatin, the thicker fibers—probably consisting of more gelatin since typical gelatin fibers have similarly thick diameters—are mostly vanished, leaving back thinner fibers and coated areas.

These first experiments show that strongly reducing the amount of PAN, as the water-stable part of the blend, does not support formation of water-resistant fibers with small pores, but results in decomposition of parts of the mat. In the next test series, the PAN solid content was thus kept at a typical value of 16%, and smaller amounts of water-soluble polymers were added (Figure 4).

In all cases, nanofiber mats are created now, with slightly different fiber diameters. For gelatin as the blending partner, significantly thicker fibers are created which makes this biopolymer especially interesting for thickness modifications of PAN nanofibers. Nevertheless, keeping in mind the possibility that the thickest fibers consist of pure gelatin and are dissolved by wetting, tests of the watered and afterwards dried nanofiber mats were performed again. The results are visible in Figure 5.

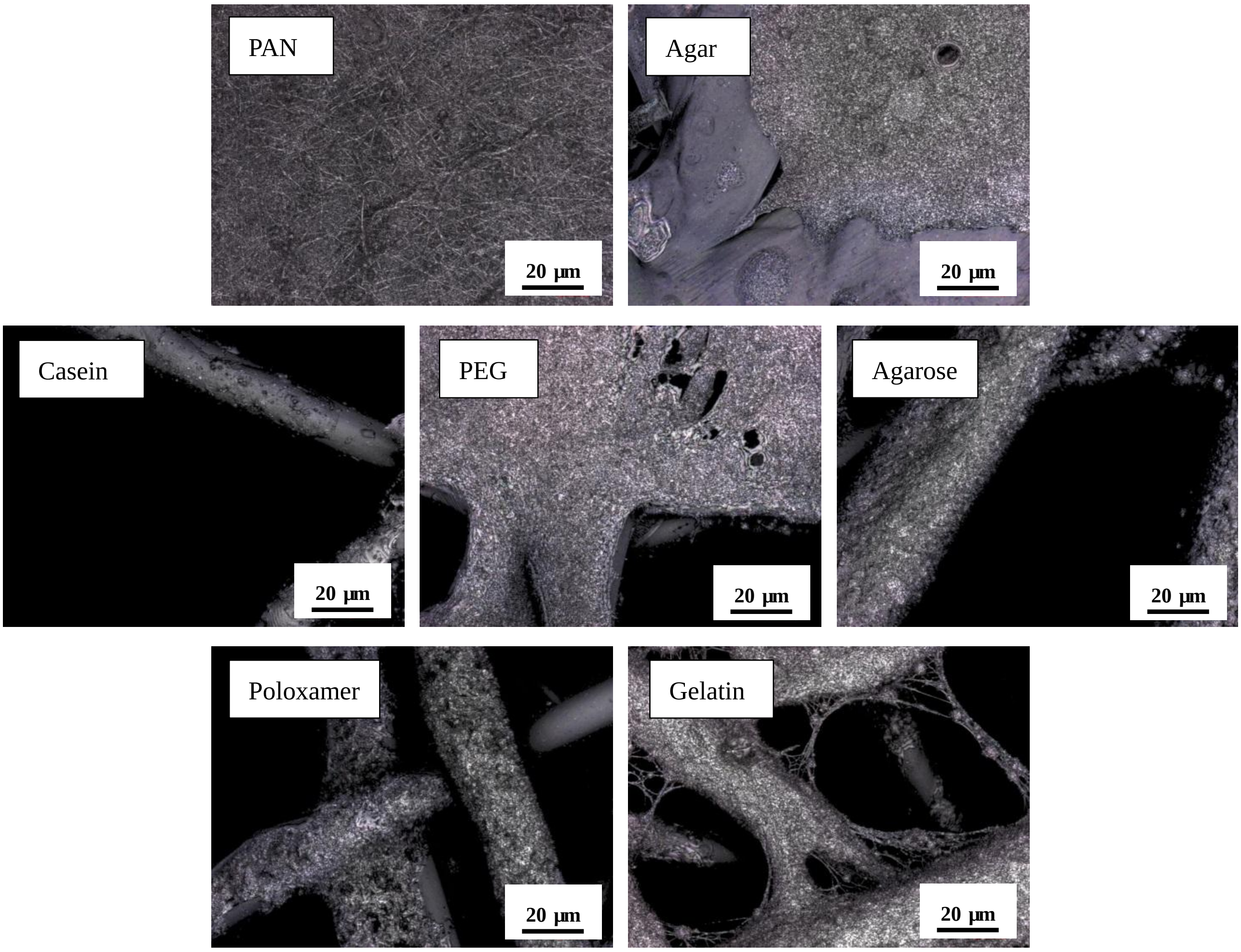

Figure 3. Nanofibers electrospun from pure PAN 12% and PAN 7.5% blended with different polymers after wetting in aqua dest. for 1 week.

In most cases, slight color variations are visible which are correlated with thickness modifications of the mats. This shows that mostly the blending process was not completely successful, but apparently left some inhomogeneity which has to be reduced by either longer stirring processes or additional ultrasonic treatment, etc. to increase the uniformity of the mixture.

Interestingly, the typical thicker gelatin fiber structure is partly kept after washing, showing clearly that the morphology of the residual PAN fibers must have been permanently modified by adding gelatin to the spinning solution. This finding makes gelatin most promising for future tests to modify fiber diameters and mat morphologies, while more detailed examinations are necessary to investigate the possible introduction of finest pores into the nanofibers by blending PAN with the here described or similar water-soluble polymers.

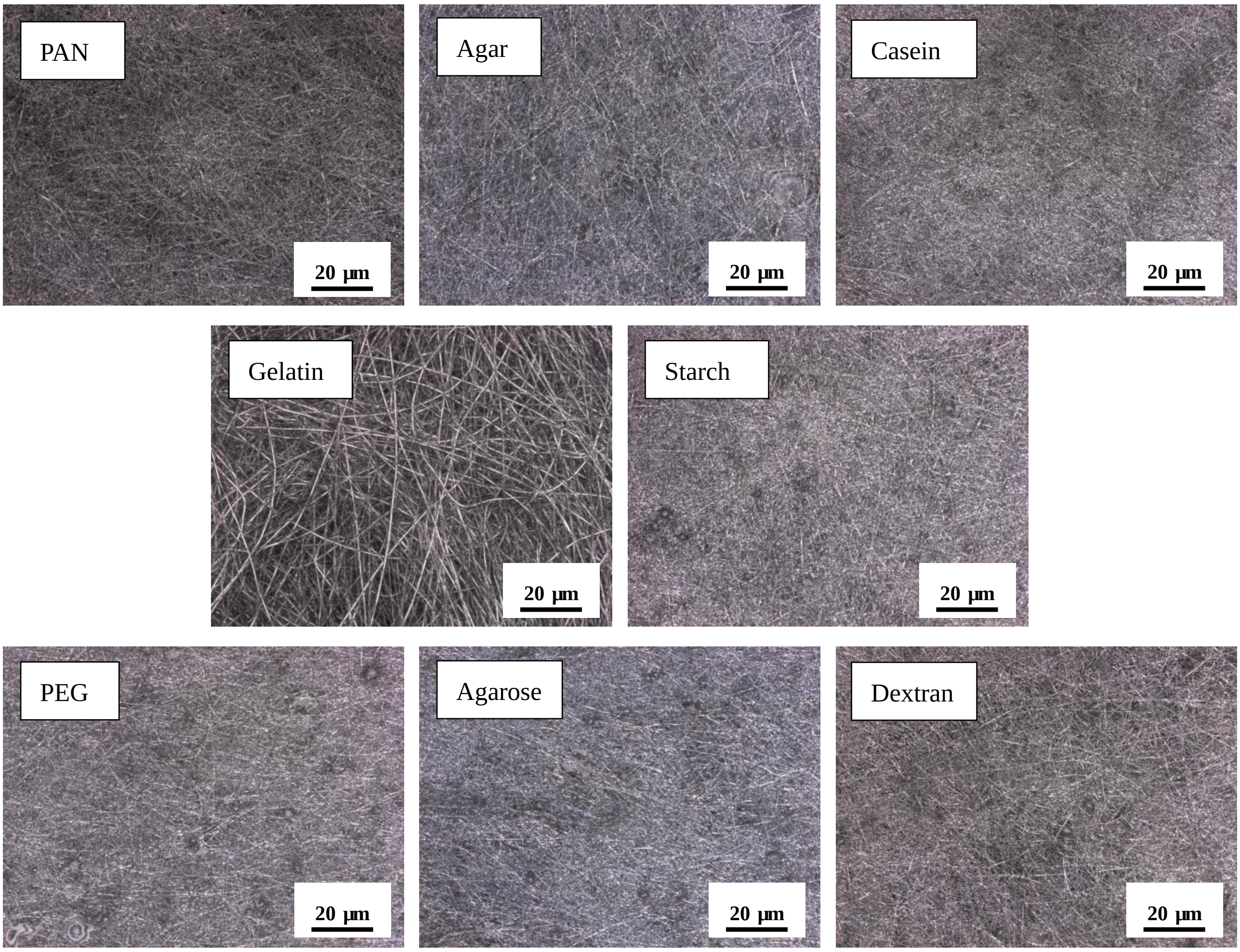

Figure 4. Nanofibers electrospun from PAN 16% pure and blended with different polymers.

The differences in the influence of an added water-soluble polymer on the PAN fiber morphology may be attributed to the ability of the water-soluble polymer to be spun solely in combination with its fiber/droplet morphology. In Figure 1, only PEG showed to be spinnable from DMSO. Former tests with gelatin electrospun from water, however, have revealed relatively thick, even fibers [32,33]. All other water-soluble polymers used in this experiment were found to tend to electrospraying instead of electrospinning or did not even create a coating on the substrate (Figure 1). This suggests that the fiber diameter of the PAN fibers can only be modified by polymers which can also be electrospun solely—i.e., PEG and gelatin—and which additionally result in significantly different fiber diameters in this case—i.e., gelatin only. This idea will be tested using other water-soluble polymers in the near future. Additionally, it is necessary to examine a test series with different amounts of PAN and gelatin to evaluate which ratio of insoluble to water-soluble polymer—or which minimum PAN concentration—is necessary to preserve a fiber structure after soaking the nanofiber mat into water, and in which range the fiber diameters can be modified in this way.

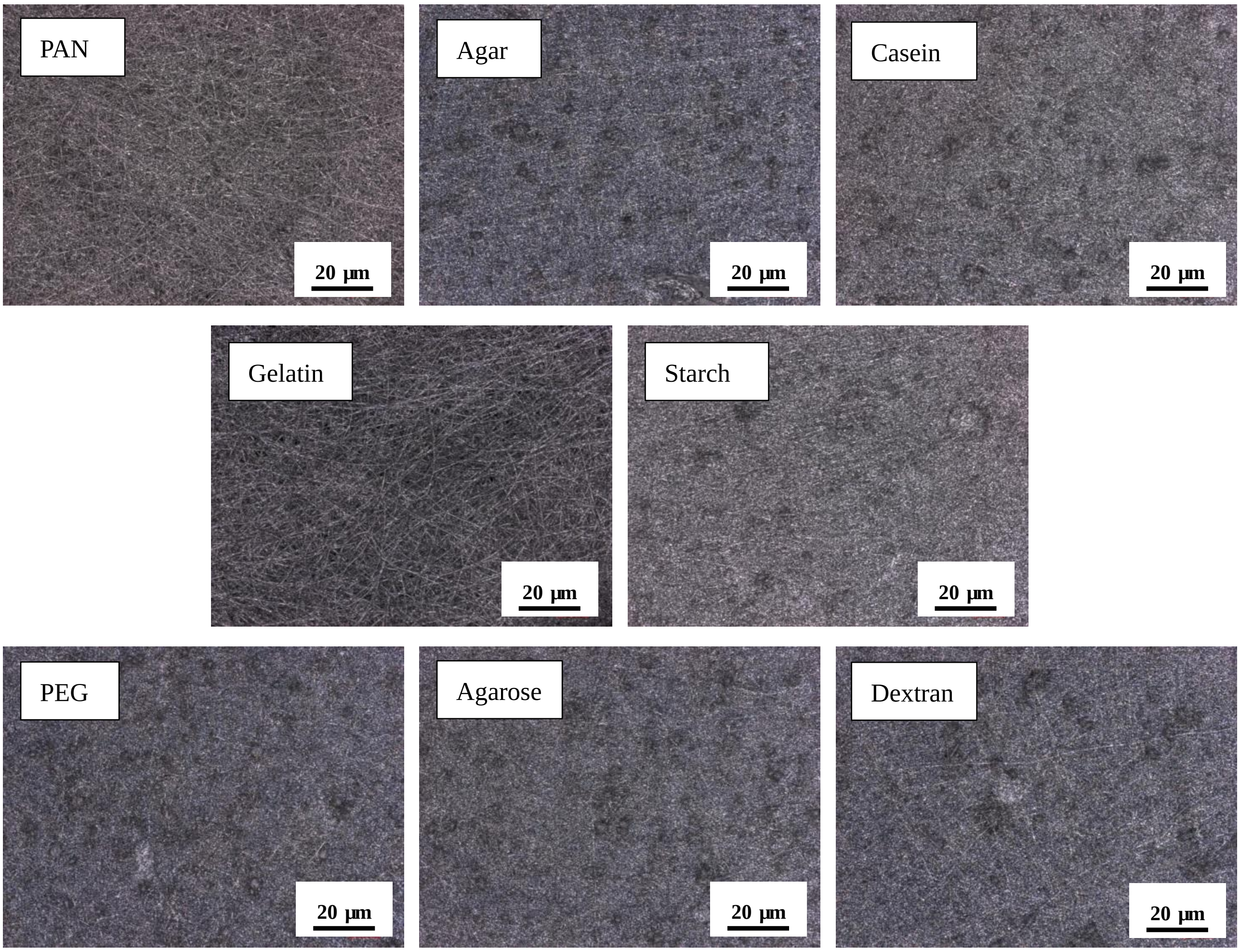

Figure 5. Nanofibers electrospun from PAN 16% pure and blended with different polymers after wetting in aqua dest. for 3 weeks.

4. Conclusions

To conclude, we have examined the possibility to modify the morphology of electrospun nanofibers and fiber mats by blending PAN with different water-soluble polymers. While a reduction of the typical PAN solid content resulted in partly or completely dissolved mats after wetting and often to electrospraying instead of the desired electrospinning process, addition of the water-soluble polymers to a typical spinning solution with 16% PAN allowed for creation of nanofiber mats which kept stable after 1–3 weeks in water. Especially gelatin was found to significantly influence the nanofiber diameter and will thus be examined further with respect to its ability to tailor the fiber diameters without completely breaking up the resulting nanofiber mats during wetting. For the other water-soluble polymers, more detailed examinations will be performed to investigate whether they are able to integrate nano-pores in the nanofibers and, if so, which concentrations can be used to optimize the fiber sub-structure.

Acknowledgements

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Conflict of interest

All authors declare no conflicts of interest in this paper.

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