Elise Diestelhorst[1], Fjoralba Mance[2], Al Mamun[1], Andrea Ehrmann[1]

[1] Bielefeld University of Applied Sciences, Faculty of Engineering and Mathematics, Interaktion 1, 33619 Bielefeld, Germany

[2] Polytechnic University of Tirana, Faculty of Mechanical Engineering, Textile and Fashion Department, Tirana, Albania

Chemical and Morphological Modification of PAN Nanofibrous Mats with Addition of Casein after Electrospinning, Stabilisation and Carbonisation

Kemijska in morfološka modifikacija PAN nanovlaknatih kopren z dodanim kazeinom po elektropredenju, stabilizaciji in karbonizaciji

Abstract

Electrospun polyacrylonitrile (PAN) nanofibrous mats belong to typical precursor materials of carbon nanofibres. They have, however, the problem that they need to be fixed or even stretched during stabilisation and ideally also during carbonisation in order to avoid undesired conglutinations and deformations of the original nanofibre morphology, resulting in brittle behaviour of the macroscopic nanofibrous mat, which impedes several applications. In an earlier investigation, blending PAN with ZnO was shown to increase fibre diameters and lead to unproblematic stabilisation and carbonisation of nanofibrous mats. ZnO, on the other hand, may have a negative impact on biotechnological applications such as tissue engineering. Here, we thus report on the morphological and chemical modifications due to blending PAN electrospinning solutions with different amounts of casein. By optimising the PAN : casein ratio, relatively thick, straight nanofibres are obtained, which can be stabilised and carbonised unambiguously, without the well-known negative impact on cell adhesion due to the addition of ZnO.

Keywords: electrospinning, polyacrylonitrile (PAN), casein, nanofibrous mat, stabilisation, carbonisation, tissue engineering

Izvleček

Elektropredene nanovlaknate koprene iz poliakrilonitrila (PAN) predstavljajo tipične prekurzorje za izdelavo ogljikovih nanovlaken. Med stabilizacijo in po možnosti tudi med karbonizacijo morajo biti pritrjene, da bi lahko preprečili neželeno zlepljenje in deformacijo prvotne nanovlaknate oblike, ki vodi v krhkost makroskopske nanovlaknate koprene in zmanjša možnosti njene uporabe. V predhodni raziskavi je bilo ugotovljeno, da mešanje PAN z ZnO vpliva na povečanje premera vlaken in omogoči stabilizacijo ter karbonizacijo nanovlaknatih kopren. ZnO pa lahko po drugi strani negativno vpliva na biotehnološke aplikacije, kot je tkivni inženiring. V članku so zato predstavljene morfološke in kemijske modifikacije, ki so bile dosežene z uporabo predilnih raztopin za elektropredenje PAN z dodatkom različnih količin kazeina. Z optimizacijo razmerja PAN : kazein dobimo relativno debela, ravna nanovlakna, ki jih je moč stabilizirati in karbonizirati, brez da bi zaradi dodatka ZnO prišlo do dobro znanega negativnega vpliva na celično adhezijo.

Ključne besede: elektropredenje, poliakrilonitril (PAN), kazein, nanovlaknata koprena, stabilizacija, karbonizacija, tkivni inženiring

Corresponding author/*Korespondenčna avtorica:*
Prof. Dr. Dr. Andrea Ehrmann
E-mail: andrea.ehrmann@fh-bielefeld

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1 Introduction

Electrospinning can be used to prepare nanofibrous mats with fibre diameters between some ten and several hundred nanometres up to few micrometres [1, 2]. Different technologies exist, from needle-based processes using a syringe to press a polymer through the needle into an electric field to coated high-voltage electrodes in the shape of wires or rotating cylinders to free surface electrospinning [3–5]. Diverse polymers can be electrospun, e.g. biopolymers such as poly(ethylene oxide) [4], gelatine [6] or chitosan [7], but also other polymers such as polycaprolactone [8], poly(vinyl alcohol) [9] or polyacrylonitrile (PAN) [10], as well as blends with different polymers and non-polymeric nanoparticles [11].

PAN is of high interest for electrospinning not only as it can be electrospun from the low-toxic solvent dimethyl sulfoxide (DMSO), but also as it is a typical precursor for carbon nanofibres [12–14]. Such carbon nanofibres can be used as fillers in composites, but due to their conductive properties also as parts of batteries, supercapacitors or dye sensitized solar cells [13, 15–17].

To prepare carbon nanofibres from electrospun PAN nanofibres, it is necessary to firstly stabilise the nanofibrous mat in air, resulting in cyclisation, oxidation, crosslinking and dehydrogenation [18–20]. While diverse heating rates and stabilisation temperatures are discussed in the literature, this process always presents the problem of dimensional changes of nanofibrous mats and fibres themselves. Conglutinations between neighbouring fibres can occur depending on the stabilisation process parameters [21–23]. In addition, the shape of fibres can be strongly deformed from thin, straight nanofibres to thicker, shorter and meandering fibres [24, 25].

Typically, this problem is solved with mechanical solutions [13, 25–27]. In previous research, PAN/ZnO nanofibrous mats resulted in significantly thicker fibres which were nearly unmodified by stabilisation and carbonisation without any mechanical fixing [28], while a similar amount of TiO_2 in the PAN spinning solution did not significantly modify the nanofibres after electrospinning and thermal post-treatments [24]. PAN/gelatine nanofibres, on the other hand, were again much thicker after electrospinning and allowed for stabilisation without mechanical fixing [25].

Here, we report on another blend of PAN and a biopolymer, i.e. casein, for electrospinning. Casein was chosen since it can simply be gained from waste milk and is thus abundantly available [29]. In addition, casein is known to be electrospinnable with different materials as spinning agents [30–32]. Nevertheless, only few reports on PAN/casein electrospun nanofibres can be found in the scientific literature [11]. It is thus of technological interest whether casein can be used to modify PAN nanofibrous mats. We showed that carefully optimising the PAN : casein ratio results in straight, relatively thick nanofibres which can be unambiguously stabilised and carbonised, offering another route to prepare carbon nanofibres, or desired dimensions and morphology. While this effect could also be reached with PAN/ZnO and PAN/gelatine blends [25, 28], the second aim of our study was to find new blends without the cytotoxicity of ZnO to prepare new substrates for tissue engineering or generally cell growth besides PAN/gelatine, which is partly molten during sterilisation by autoclaving at 121 °C [33]. Casein is relatively stable in this temperature range [34] and may thus be an interesting blend for PAN, possibly supporting cell growth similar to gelatine [33] without losing the nanofibrous structure. Combined with the aforementioned material-related approach, another aim was using sufficiently mechanically stable carbon nanofibrous mats as conductive substrates for tissue engineering, which has often been reported in the literature as advantageous for diverse cell types [35].

2 Materials and methods

The wire-based electrospinning machine "Nanospider Lab" (Elmarco Ltd., Liberec, Czech Republic) was used to prepare nanofibrous mats with the following spinning parameters: voltage 80 kV, nozzle diameter 0.8 mm, carriage speed 100 mm/s, bottom electrode/substrate distance 240 mm, ground electrode/substrate distance 50 mm, temperature in the chamber 22–23 °C, and 32–33% of relative humidity in the chamber. A polypropylene (PP) nonwoven was used as the substrate to catch the nanofibres approaching the grounded upper wire.

The spinning solutions of 10 mg overall mass contained PAN (X-PAN, Dralon GmbH, Lingen, Germany), partly casein (according to Hammarsten, purchased from VWR Chemicals, Radnor, Pennsylvania,

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USA) and DMSO as solvent (DMSO, min. 99.9%, purchased from S3 Chemicals, Bad Oeynhausen, Germany). Two different amounts of PAN (i.e. 1.6 g and 1.38 g) were combined with four different amounts of casein (i.e. 0 g, 0.1 g, 0.2 g, 0.4 g), overall resulting in eight spinning solutions, of which the combination of 1.6 g PAN and 0.4 g casein could not be electrospun due to its high viscosity. The amounts of PAN were chosen in the range that is typical of the pure material, i.e. between approximately 14% and 16%, while lower concentrations of pure PAN usually result in beads along the fibres [36].

Parts of all samples were afterwards stabilised in a muffle oven B150 (Nabertherm, Lilienthal, Germany), approaching the typical stabilisation temperature of 280 °C with the heating rate of 1 K/min [14, 24, 25]. Parts of the stabilised samples were afterwards carbonised at 500 °C or 800°, respectively, approached with the heating rate of 10 K/min in a furnace (Carbolite Gero, Neuhausen, Germany) under the nitrogen flow of 150 mL/min (STP). Both isothermal treatments were performed for 1 h each. Carbonisation is of high interest for cell growth experiments on a conductive surface, allowing the application of small voltage to support cell orientation. All samples were afterwards investigated by confocal laser scanning microscopy (CLSM), using a VK-8710 (Keyence, Neu-Isenburg, Germany), and by Fourier transform infrared (FTIR) spectroscopy with an Excalibur 3100 (Varian Inc., Palo Alto, CA, USA).

3 Results and discussion

Figure 1 shows CLSM images of nanofibrous mat surfaces after electrospinning. Generally, no large differences were visible between nanofibrous mats electrospun with 1.38 g PAN or 1.6 g PAN, respectively. As expected, without casein and with only 0.1 g casein, the latter showed a more homogenous nanofibrous mat with less beads and membrane-like areas [36].

The addition of 0.1 g casein to both amounts of PAN did not lead to significant modifications of the nanofibrous mat morphology. This finding abruptly changed with the addition of 0.2 g casein or even 0.4 g casein. In both cases, the nanofibrous mats showed much thicker fibres, sometimes above 1 μm, i.e. were no longer nanofibres. At the same time, standard deviations increased strongly (cf. insets in

Figure 1), i.e. fibre diameters showed a broader distribution. This effect is already known from PAN/gelatine nanofibres [25] and other PAN blends [24], and has been reported several times, while a physical explanation could not be found in the literature. In addition, 0.2 g or more casein led to large membrane-like areas, indicating an incomplete mixture of PAN and casein, with the casein apparently not being solely spinnable, as shown before [11]. It should be mentioned that in the previous study of diverse biopolymers and biopolymer blends, other PAN and casein were used, making the test results not completely comparable.

After stabilisation, the nanofibrous mat colours and morphologies partly changed (cf. Figure 2). Starting with the samples without casein, the typical brown colour of stabilised PAN was visible, which was also the case for PAN 1.6 g + casein 0.1 g. However, for a smaller amount of PAN, the addition of 0.1 g casein was already sufficient to result in silvery areas, indicating molten casein, which did not contribute to the carbonisation process similar to the biopolymer component in stabilized PAN/gelatine nanofibrous mats [25]. These silvery areas became more prominent at larger amounts of casein. It should be mentioned, however, that due to the small area visible in CLSM images, these can always depict only exemplary results which may differ for other areas under examination.

Most interestingly, the combination of PAN 1.6 g + casein 0.2 g led to relatively regular, long, straight fibres, again with the diameters of a few microns, as already visible after electrospinning (cf. Figure 1), which may be promising for the carbonisation process.

Comparing the fibre diameters with those after electrospinning, the diameter distributions stayed relatively similar for the samples prepared with 1.6 g PAN and 0.1 g casein as well as for both samples with 0.2 g casein. This finding suggests that the fibre morphologies were not significantly influenced by the stabilisation process, opposite to pure PAN samples.

The results of carbonisation at 500 °C and 800 °C are shown in Figures 3 and 4, respectively. Firstly, it should be mentioned that nanofibrous mats with smaller amounts of casein in combination with a larger amount of PAN still showed a brownish colour after the carbonisation at 500 °C, indicating that the treatment temperature or duration were not sufficient.

Besides this finding, smaller amounts of casein (0.0 g or 0.1 g, respectively) resulted in relatively fine fibres
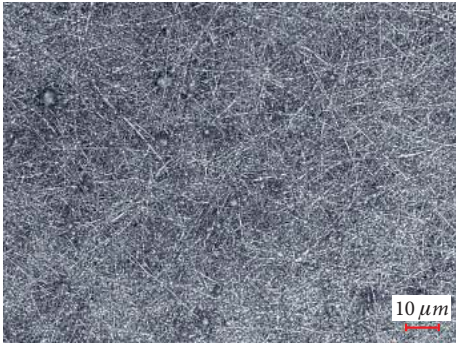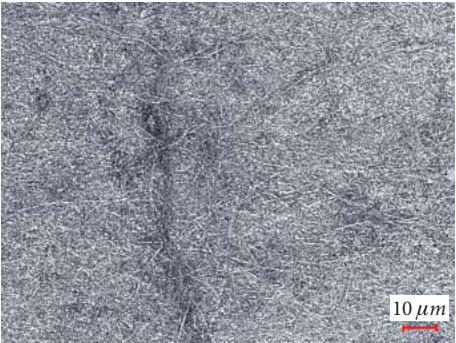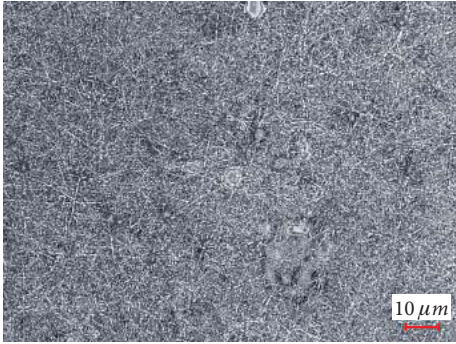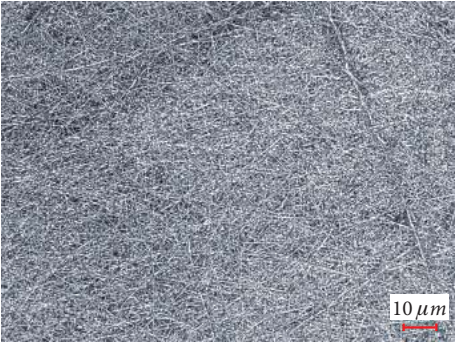
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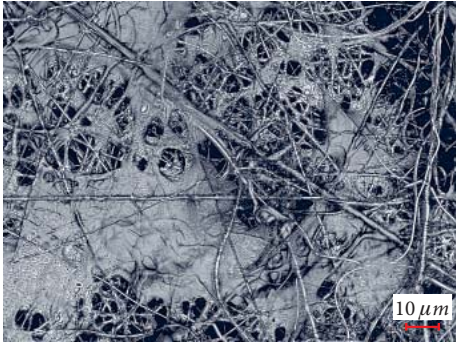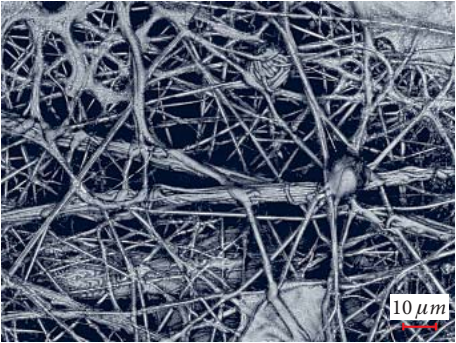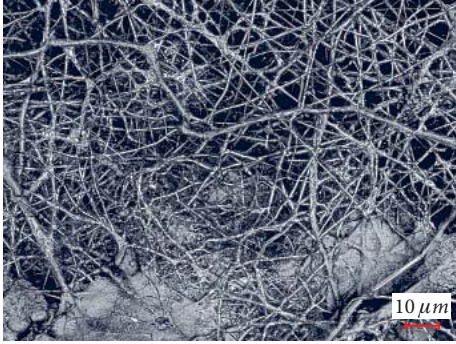|	PAN 1.38 g	PAN 1.6 g
Casein 0.0 g	(230 ± 70) nm	(280 ± 70) nm
Casein 0.1 g	(270 ± 80) nm	(330 ± 100) nm
Casein 0.2 g	(470 ± 250) nm	(550 ± 280) nm
Casein 0.4 g	(460 ± 180) nm	

Figure 1: Nanofibrous mats with different amounts of PAN and casein after electrospinning (scale bars indicate 10 μm, fibre diameters are given as insets)

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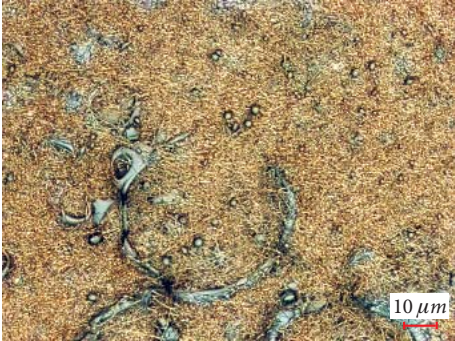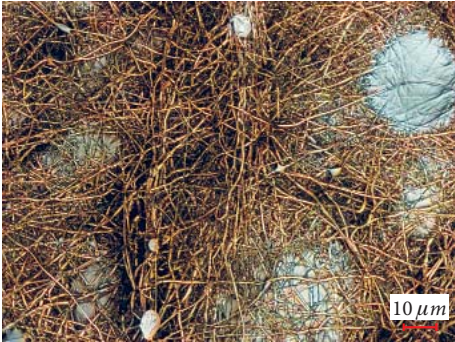
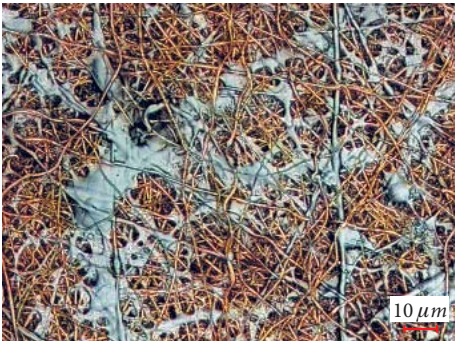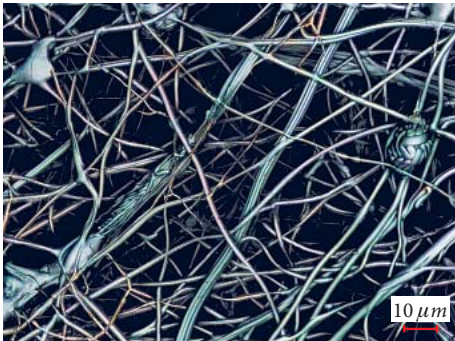|	PAN 1.38 g	PAN 1.6 g
Casein 0.0 g	(310 ± 100) nm	(320 ± 80) nm
Casein 0.1 g	(410 ± 120) nm	(360 ± 110) nm
Casein 0.2 g	(450 ± 140) nm	(630 ± 240) nm
Casein 0.4 g	(680 ± 370) nm	

Figure 2: Nanofibrous mats with different amounts of PAN and casein after stabilisation (scale bars indicate 10 μm, fibre diameters are given as insets)
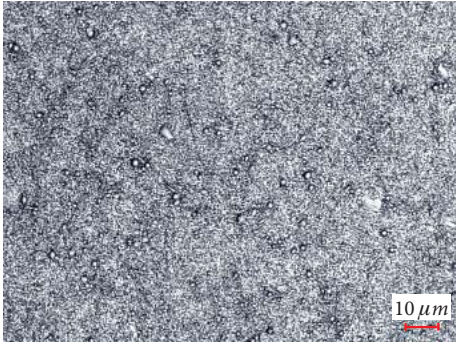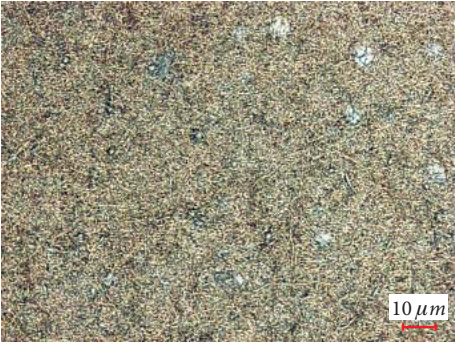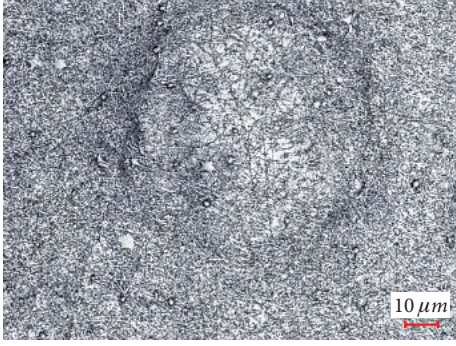
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	PAN 1.38 g	PAN 1.6 g
Casein 0.0 g	(370 ± 130) nm	(360 ± 90) nm
Casein 0.1 g	(370 ± 110) nm	(330 ± 80) nm
Casein 0.2 g	(470 ± 190) nm	(630 ± 320) nm
Casein 0.4 g	(780 ± 650) nm	

Figure 3: Nanofibrous mats with different amounts of PAN and casein after carbonisation at 500 °C (scale bars indicate 10 μm, fibre diameters are given as insets)
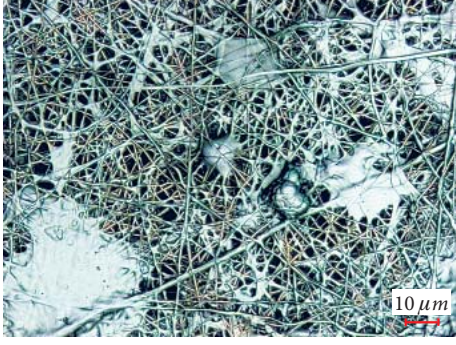
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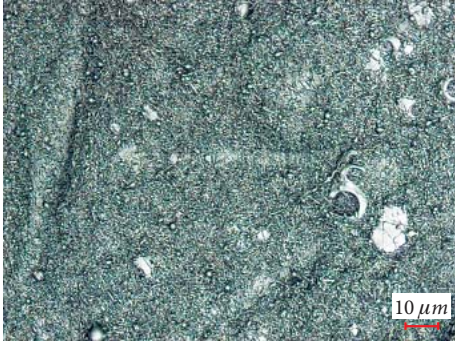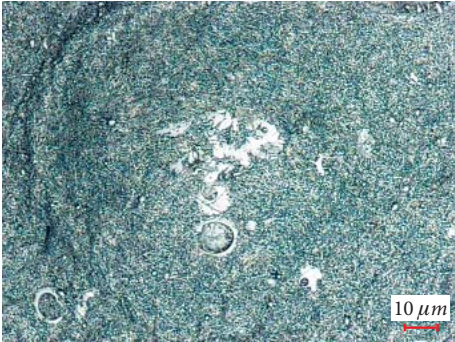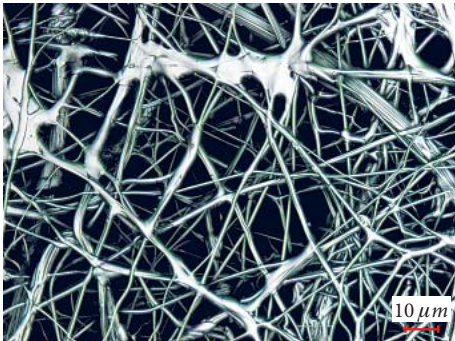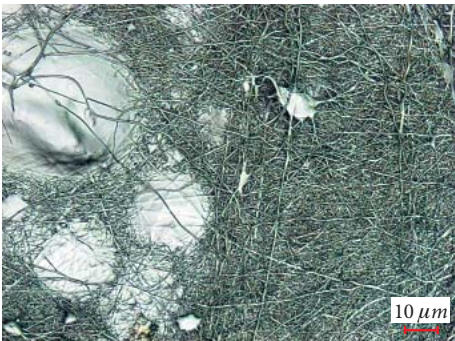|	PAN 1.38 g	PAN 1.6 g
Casein 0.0 g	(410 ± 80) nm	(380 ± 90) nm
Casein 0.1 g	(400 ± 80) nm	(360 ± 110) nm
Casein 0.2 g	(480 ± 130) nm	(820 ± 430) nm
Casein 0.4 g	(450 ± 130) nm	*Figure 4: Nanofibrous mats with different amounts of PAN and casein after carbonisation at 800 °C (scale bars indicate 10 μm, fibre diameters are given as insets)*

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after the carbonisation at 500 °C or 800 °C. Similarly to stabilised nanofibrous mats, the combinations of 1.38 g PAN with 0.2 g or 0.4 g casein again showed a combination of fibrous and membrane-like areas, hinting at casein/PAN agglomerations. The combination of 1.6 g PAN with 0.2 g casein, on the other hand, again showed relatively thick, straight fibres, the diameters of which remained similar to those of original fibres.

Macroscopically, a strongly increased mechanical stability of PAN/casein nanofibre mats was recognized. While the samples without casein or with 0.1 g casein were brittle after the carbonisation at 500 °C or 800 °C (cf. Figure 5b), the sample with 1.6 g PAN and 0.2 g casein was touchable without problems and even bendable to a certain degree without being destroyed (cf. Figure 5a) even after the carbonisation at 800 °C. Other samples were less brittle than pure PAN after carbonisation, but less elastic than the sample with 1.6 g PAN and 0.2 g casein. Nevertheless, it must be mentioned that further research is necessary to investigate how stable this effect is, whether small deviations from this material ratio or slightly different electrospinning conditions would retain similar results or modify them significantly. The very broad fibre diameter distribution suggests that the thicker fibres in the micrometre range would possibly remain intact, while the thinnest fibres may be more prone to breaking. This is going to be investigated in more detail in a follow-up study, using a defined bending process.
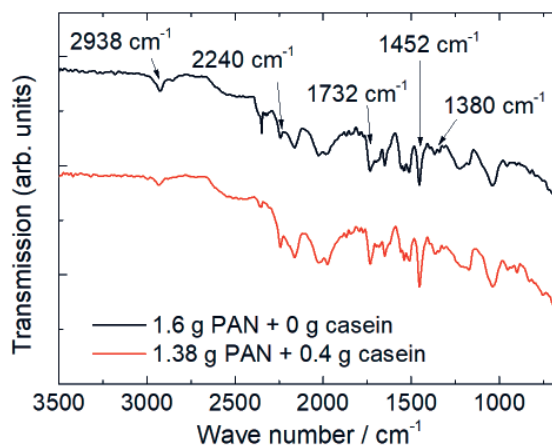
Figure 6: FTIR graphs of PAN and PAN/casein nanofibrous mats after electrospinning

Next, FTIR investigations were performed to investigate the influence of casein on the electrospun PAN nanofibrous mats (cf. Figure 6).

A few typical peaks which can be expected for pure PAN are stretching vibration of the $C\equiv N$ nitrile functional group at 2240 cm^{-1}, the carbonyl $(C=O)$ stretching peak at 1732 cm^{-1}, and the bending and stretching vibrations of CH$_2$ at 2938 cm^{-1}, 1452 cm^{-1} and 1380 cm^{-1} [37].

Casein should show amide bands at around 1659 cm^{-1} and 1539 cm^{-1}, respectively [38], which are here hidden in the PAN bands. Dong and Gu also reported about the missing amide bands for PAN/casein blends [39]. The measurements of stabilised and carbonised samples look similar to those visible

Figure 5: (a) Bending sample carbonised at 500 °C, electrospun from 1.6 g PAN and 0.2 g casein; (b) broken residues after the same bending test, performed on carbonised (500 °C) sample electrospun from 1.6 g PAN without casein

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in Figure 5 for the pure PAN nanofibrous mats, with the signals being slightly smaller, possibly due to slightly thinner fabrics.

Figure 7 shows a pure PAN nanofibrous mat after electrospinning, stabilisation and carbonisation at 500 °C and 800 °C, respectively, for comparison.

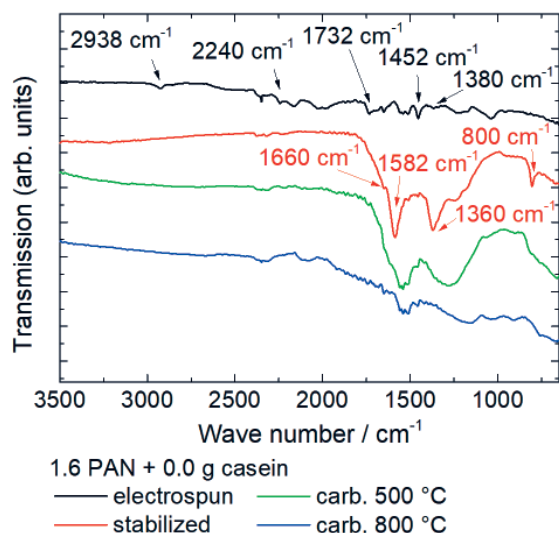1.6 PAN + 0.0 g casein

— electrospun   — carb. 500 °C
— stabilized   — carb. 800 °C

Figure 7: FTIR graphs of nanofibrous mats, electrospun from pure PAN, stabilised and carbonised at different temperatures

After the stabilisation, a new peak near 800 cm⁻¹ becomes visible due to aromatic C–H vibrations [40] as well as large peaks of C=N stretching vibrations at 1582 cm⁻¹ and C=C stretching vibrations at 1660 cm⁻¹ [37]. The second large peak at around 1360 cm⁻¹ can be explained by C–H bending and C–H_2 wagging [41].

After full carbonisation at 800 °C, typically only very few peaks are left due to the high absorbance of carbon [42]. The carbonisation at 500 °C, however, resulted in a spectrum between the stabilised and fully carbonised state, as it could be expected due to the relatively low temperature.

Finally, Figure 8 shows the results of FTIR investigations of the nanofibrous mats with the highest amount of casein. A comparison between Figures 8 and 7 shows that the general chemical process is apparently nearly identical with the one found for pure PAN, indicating that the increased fibre diameter does not influence the stabilisation and carbonisation process. Different peak heights may be attributed to different nanofibrous mat thicknesses.

1.38 PAN + 0.4 g casein

— electrospun   — carb. 500 °C
— stabilized   — carb. 800 °C
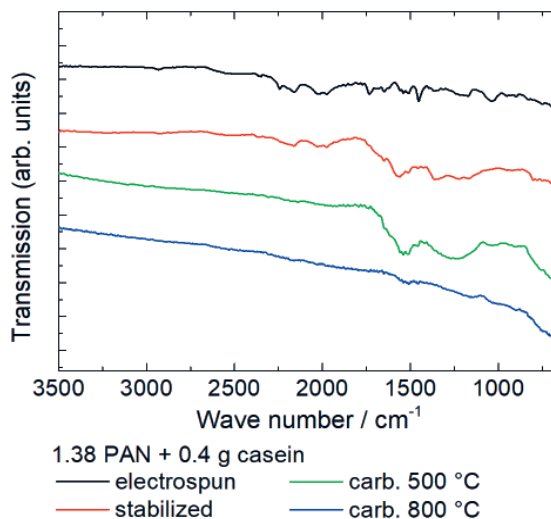
Figure 8: FTIR graphs of nanofibrous mats, electrospun from PAN with maximum amount of casein, stabilised and carbonised at different temperatures

4 Conclusion and outlook

Adding the biopolymer casein to a PAN electrospinning solution prepared in DMSO can be used to modify the nanofibrous mat morphology. By carefully tailoring the PAN : casein ratio, relatively thick fibres can be created, and unambiguously stabilised and carbonised. In this way, a new path may be offered to prepare PAN/casein or conductive carbon nanofibrous substrates for future cell growth experiments.

References

1. SUBBIAH, Thandavamoorthy, BHAT, G. S., TOCK, R. W., PARAMESWARAN, S., RAMKUMAR, S. S. Electrospinning of nanofibers. *Journal of Applied Polymer Science,* 2005, **96**(2), 557–569, doi: 10.1002/app.21481.
2. GREINER, Andreas, WENDORFF, Joachim H. Electrospinning: a fascinating method for the

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preparation of ultrathin fibers. *Angewandte Chemie International Edition,* 2007, **46**(30), 5670–5703, doi: 10.1002/anie.200604646.

3. JAHAN, Israt, JADHAV, Amit, WANG, Lijing, WANG, Xin. Electrospinning from a convex needle with multiple jet toward better controlling and enhanced production rate. *Journal of Applied Polymer Science,* 2019, **136**(40), 48014, doi: 10.1002/app.48014.

4. GROTHE, Timo, GROßERHODE, Christina, HAUSER, Thomas, KERN, Philip, STUTE, Kai, EHRMANN, Andrea. Needleless electrospinning of PEO nanofiber mats. In *Second International Conference on Mechanics, Materials and Structural Engineering (ICMMSE 2017). (Advances in Engineering Research).* Edited by D.K. Kim, J.W. Hu, J.K. Ahn. Paris : Atlantis Press, 2017, 54–58, doi: 10.2991/icmmse-17. 2017.9.

5. ALI, Usman, NIU, Haitao, KHURSHID, Muhammad Furqan, ABBAS, Amir, LIN, Tong. Electrospinning behavior of needleless spinneret with a popular mace shape. *Journal of the Textile Institute,* 2019, **110**(3), 349–357, doi: 10. 1080/00405000.2018.1480456.

6. BANNER, Jana, DAUTZENBERG, Maria, FELDHANS, Theresa, HOFMANN, Julia, PLÜMER, Pia, EHRMANN, Andrea. Water resistance and morphology of electrospun gelatine blended with citric acid and coconut oil. *Tekstilec,* 2018, **61**(2), 129–135, doi: 10.14502/ Tekstilec2018.61.129-135.

7. SANDRI, Giuseppina, ROSSI, Silvia, BONFERONI, Maria Cristina, MIELE, Dalila, FACCENDINI, Angela, DEL FAVERO, Elena, DI COLA, Emanuela, CORNAGLIA, Antonia Icaro, BOSELLI, Cinzia, LXBACHER, Thomas, MALAVASI, Lorenzo, CANTU, Laura, FERRARI, Franca. Chitosan/glycosaminoglycan scaffolds for skin reparation. *Carbohydrate Polymers,* 2019, **220**, 219–227, doi: 10.1016/j. carbpol.2019. 05.069.

8. SCHNELL, Eva, KLINKHAMMER, Kristina, BALZER, Simone, BROOK, Gary, KLEE, Doris, DALTON, Paul, MEY, Jörg. Guidance of glial cell migration and axonal growth on electrospun nanofibers of poly-ε-caprolactone and a collagen/poly-ε-caprolactone blend. *Biomaterials,* 2007, **28**(19), 3012–3025, doi: 10.1016/j. biomaterials.2007.03.009.

9. QIN, Xiao-Hong, WANG, Shan-Yuan. Electrospun nanofibers from crosslinked poly(vinyl alcohol) and its filtration efficiency. *Appl. Polym. Sci.,* 2008, **109**(2), 951–956, doi: 10.1002/app. 28003.

10. ROCHE, Roche, YALCINKAYA, Fatma. Electrospun polyacrylonitrile nanofibrous membranes for point-of-use water and air cleaning. *ChemistryOpen,* 2019, **8**(1), 97–103, doi: 10.1002/ open.201800267.

11. WEHLAGE, Daria, BÖTTJER, Robin, GROTHE, Timo, EHRMANN, Andrea. Electrospinning water-soluble/insoluble polymer blends. *AIMS Materials Science,* 2018, **5**(2), 190–200, doi: 10.3934/matersci.2018.2.190.

12. DE OLIVEIRA, Juliana Bovi, MÜLLER GUERRINI, Lilia, DOS SANTOS CONEJO, Luiza, REZENDE, Mirabel Cerqueira, BOTELHO, Edson Cocchieri. Viscoelastic evaluation of epoxy nanocomposite based on carbon nanofiber obtained from electrospinning processing. *Polymer Bulletin,* 2019, **76**(12), 6063–6076, doi: 10. 1007/s00289-019-02707-0.

13. LIU, Hua, SONG, Weiguo, XING, Aihua. *In situ* K_2S activated electrospun carbon nanofibers with hierarchical meso/microporous structures for supercapacitors. *RSC Advances,* 2019, **9**(57), 33539–33548, doi: 10.1039/c9ra06847c.

14. SABANTINA, Lilia, RODRÍGUEZ-CANO, Miguel Ángel, KLÖCKER, Michaela, GARCÍA-MATEOS, Francisco José, TERNERO-HIDALGO, Juan José, MAMUN, Al, BEERMANN, Friederike, SCHWAKENBERG, Mona, VOIGT, Anna-Lena, RODRÍGUEZ-MIRASOL, José, CORDERO, Tomás, EHRMANN, Andrea. Fixing PAN nanofiber mats during stabilization for carbonization and creating novel metal/carbon composites. *Polymers,* 2018, **10**(7), 735-1–735-11, doi: 10.3390/polym10070735.

15. BARZOKI, P. Kheirkhah, REZADOUST, A. M., LATIFI, M., SAGHAFI, H., MINAK, G. Effect of nanofiber diameter and arrangement on fracture toughness of out of autoclave glass/phenolic composites – Experimental and numerical study. *Thin-Walled Structures,* 2019, **143**, 106251, doi: 10.1016/j.tws.2019.106251.

16. KIAI, Maryann Sadat, EROGLU, Omer, KIZIL, Huseyin. Electrospun nanofiber polyacrylonitrile coated separators to suppress the shuttle effect for long-life lithium-sulfur battery. *Journal*

of Applied Polymer Science, 2019, **137**(17), 48606 doi: 10.1002/app.48606.

17. SARANYA, K., SUBRAMANIA, A., SIVAS-ANKAR, N., BHARGAVA, P. *In-situ* growth of cos nanoparticles onto electrospun graphitized carbon nanofibers as an efficient counter electrode for dye-sensitized solar cells. *Journal of Nanoscience and Nanotechnology,* 2017, **17**(1), 398−404, doi: 10.1166/jnn.2017.12542.

18. BASHIR, Z. A critical review of the stabilization of polyacrylonitrile. *Carbon,* 1991, **29**(8), 1081−1090, doi: 10.1016/0008-6223(91)90024-D.

19. DALTON, Stephen, HEATLEY, Frank, BUDD, Peter M. Thermal stabilization of polyacrylonitrile fibres. *Polymer,* 1999, **40**(20), 5531−5543, doi: 10.1016/S0032-3861(98)00778-2.

20. ISMAR, Ezgi, SARAC, A. Sezai. Oxidation of polyacrylonitrile nanofiber webs as a precursor for carbon nanofiber: aligned and non-aligned nanofibers. *Polymer Bulletin,* 2018, **75**, 485−499, doi: 10.1007/s00289-017-2043-x.

21. ALARIFI, Ibrahim, M., ALHARBI, Abdulaziz, KHAN, Waseem S., SWINDLE, Andrew, AS-MATULU, Ramazan. Thermal, electrical and surface hydrophobic properties of electrospun polyacrylonitrile nanofibers for structural health monitoring. *Materials,* 2015, **8**, 7017−7031, doi: 10.3390/ma8105356.

22. ARBAB, Shahram, TEIMOURY, Arash, MIR-BAHA, Hamideh, ADOLPHE, Dominique C., NOROOZI, Babak, NOURPANAH, Parviz. Optimum stabilization processing parameters for polyacrylonitrile-based carbon nanofibers and their difference with carbon (micro) fibers. *Polymer Degradation and Stability,* 2017, **142**, 198−208, doi: 10.1016/j.polymdegradstab.2017.06.026.

23. DHAKATE, Sanjay R., GUPTA, Ashish, CHAU-DHARI, Anurag, TAWALE, Jai, MATHUR, Rakesh B. Morphology and thermal properties of PAN copolymer based electrospun nanofibers. *Synthetic Metals,* 2011, **161**(5−6), 411−419, doi: 10.1016/j.synthmet.2010.12.019.

24. SABANTINA, Lilia, BÖTTJER, Robin, WEH-LAGE, Daria, GROTHE, Timo, KLÖCKER, Michaela, GARCÍA-MATEOS, Francisco José, RODRÍGUEZ-MIRASOL, José, CORDERO, Tomás, EHRMANN, Andrea. Morphological study of stabilization and carbonization of polyacrylonitrile/TiO₂ nanofiber mats. *Journal of Engineered Fibers*

and Fabrics, 2019, **14**, 1558925019862242, doi: 10.1177/1558925019862242.

25. SABANTINA, Lilia, Wehlage, Daria, Klöcker, Michaela, Mamun, Al, Grothe, Timo, GARCÍA-MATEOS, Francisco José, RODRÍGUEZ-MIRASOL, José, CORDERO, Tomás, FINSTER-BUSCH, Karin, EHRMANN, Andrea. Stabilization of electrospun PAN/gelatin nanofiber mats for carbonization. *Journal of Nanomaterials,* 2018, **2018**, 6131085, doi: 10.1155/2018/6131085.

26. WU, Meiyu, WANG, Qiaoying, LI, Kaina, WU, Yiqiong, LIU, Haiquing. Optimization of stabilization conditions for electrospun polyacrylonitrile nanofibers. *Polymer Degradation and Stability,* 2012, **97**(8), 1511−1519, doi: 10.1016/j.polymdegradstab.2012.05.001.

27. SANTOS DE OLIVEIRA JUNIOR, Mauro, MANZOLLI RODRIGUES, Bruno Vinícius, MARCUZZO, Jossano Saldanha, MÜLLER GUERINI, Lília, RIBEIRO BALDAN, Maurício, REZENDE, Mirabel Cerqueira. A statistical approach to evaluate the oxidative process of electrospun polyacrylonitrile ultrathin fibers. *Journal of Applied Polymer Science,* 2017, **134**(43), 42458, doi: 10.1002/app.45458.

28. TRABELSI, Marah, MAMUN, Al, KLÖCKER, Michaela, SABANTINA, Lilia, GROßERHODE, Christina, BLACHOWICZ, Tomasz, EHR-MANN, Andrea. Increased mechanical properties of carbon nanofiber mats for possible medical applications. *Fibers,* 2019, **7**(11), 98, doi: 10.3390/fib7110098.

29. BIER, M. C., KOHN, S., STIERAND, A., GRIM-MELSMANN, N., HOMBURG, S. V., RATTEN-HOLL, A., Ehrmann, A. Investigation of eco-friendly casein fibre production methods. *IOP Conf. Series: Materials Science and Engineering,* 2017, **254**, 192004, doi: 10.1088/1757-899X/254/19/192004.

30. DONG, Qingzhi, GU, Lixia. Synthesis of AN-g-casein copolymer in concentrated aqueous solution of sodium thiocyanate and AN-g-casein fiber's structure and property. *European Polymer Journal,* 2002, **38**(3), 511−519, doi: 10.1016/S0014-3057(01)00214-2.

31. TOMASULA, P. M., SOUSA, A. M. M., LIOU, S.-C., LI, R., BONNAILLIE, L. M., LIU, L. S. Short communication: Electrospinning of casein/pullulan blends for food-grade application.

Journal of Dairy Science, 2016, **99**(3), 1837–1845, doi: 10.3168/jds.2015-10374.

32. GROTHE, Timo, GRIMMELSMANN, Nils, HOMBURG, Sarah Vanessa, EHRMANN, Andrea. Possible applications of nano-spun fabrics and materials. *Materialstoday: Proceedings,* 2017, **4**(2), S154–S159, doi: 10.1016/j.matpr.2017.09.180.

33. WEHLAGE, Daria, BLATTNER, Hannah, SABANTINA, Lilia, BÖTTJER, Robin, GROTHE, Timo, RATTENHOLL, Anke, GUDERMANN, Frank, LÜTKEMEYER, Dirk, EHRMANN, Andrea. Sterilization of PAN/gelatin nanofibrous mats for cell growth. *Tekstilec,* 2019, **62**(2), 78–88, doi: 10.14502/Tekstilec2019. 62.78-88.

34. MOCANU, Anca Mihaela, MOLDOVEANU, C., ODOCHIAN, Lucia, PAIUS, Cristina Maria, APOSTOLESCU, N., NECULAU, R. Study on the thermal behavior of casein under nitrogen and air atmosphere by means of the TG-FTIR technique. *Thermochimica Acta,* 2012, **546**, 120–126, doi: 10.1016/j.tca.2012.07.031.

35. BLACHOWICZ, Tomasz, EHRMANN, Andrea. Conductive electrospun nanofiber mats. *Materials,* 2020, **13**(1), 152, doi: 10.3390/ma13010152.

36. SABANTINA, Lilia, RODRÍGUEZ-MIRASOL, José, CORDERO, Tomás, FINSTERBUSCH, Karin, EHRMANN, Andrea. Investigation of needleless electrospun PAN nanofiber mats. *AIP Conference Proceedings,* 2018, **1952**(1), 020085, doi: 10.1063/1.5032047.

37. MOLNÁR, Kolos, SZOLNOKI, Beáte, TOLDY, Andrea, VAS, Lázló Mihály. Thermochemical stabilization and analysis of continuously electrospun nanofibers. *Journal of Thermal Analysis and Calorimetry,* 2014, **117**, 1123–1135, doi: 10.1007/s10973-014-3880-6.

38. SZYK-WARSZYNSKA, Lilianna, RASZKA, Katarzyna, WARSZYNSKI, Piotr. Interactions of casein and polypeptides in multilayer films studied by FTIR and molecular dynamics. *Polymers,* 2019, **11**(5), 920, doi: 10.3390/polym11050920.

39. DONG, Qingzhi, GU, Lixia. Synthesis of AN-g-casein copolymer in concentrated aqueous solution of sodium thiocyanate and AN-g-casein fiber's structure and property. *European Polymer Journal,* 2002, **38**(3), 511–519, doi: 10.1016/ S0014-3057(01)00214-2.

40. GERGIN, Ilknur, ISMAR, Ezgi, SARAC, A. Sezai. Oxidative stabilization of polyacrylonitrile nanofibers and carbon nanofibers containing graphene oxide (GO): a spectroscopic and electrochemical study. *Beilstein J. Nanotechnol.,* 2017, **8**, 1616–1628, doi: 10.3762/bjnano. 8.161

41. CIPRIANI, E., ZANETTI, M., BRACCO, P., BRUNELLA, V., LUDA, M. P., COSTA, L. Crosslinking and carbonization processes in PAN films and nanofibers. *Polymer Degradation and Stability,* 2016, **123**, 178–188, doi: 10.1016/j.polymdegradstab.2015.11.008.

42. ARSHAD, Salman N., NARAGHI, Mohammad, CHASIOTIS, Ioannis. Strong carbon nanofibers from electrospun polyacrylonitrile. *Carbon,* 2011, **49**(5), 1710–1719, doi: 10.1016/j.carbon. 2010.12.056.