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3rd WORKSHOP ON MECHANICS OF NANOMATERIALS

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3rd Workshop on Mechanics of Nanomaterials

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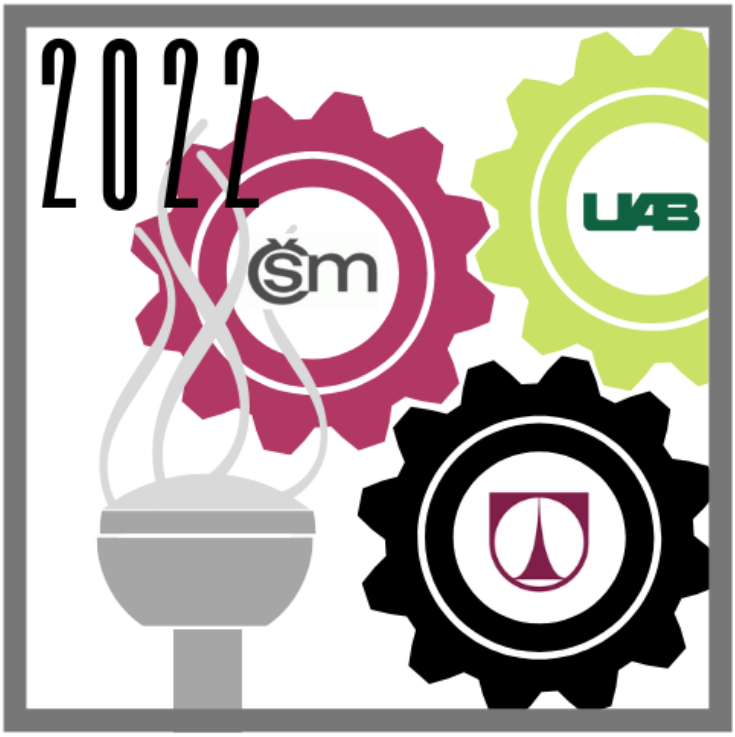

15th – 16th June 2022

Organizers: Hannah Lacy, Maxim Lisnenko, David Lukáš

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Workshop Agenda

June 15th

09:00 – 10:00	**Arrival and registration**
10:00-10:15	**Introduction** (Hannah Lacy and David Lukáš)
10:15-11:15	**First Session** Hannah Lacy, UAB Olivia Shivers, UAB Ranoah Holcomb, UAB Eva Kuželová Košťáková, TUL
11:15-11:35	**Coffee Break**
11:35- 12:35	**Second Session** Tabitha Berry, UAB Arielle Griffin, UAB Divyabharathi Madheswaran, TUL Ma Theresa Halog, UAB
12:35-13:45	**Lunch**
13:45- 18:30	**Trip to Ještěd**
18:30- 19:30	**Dinner**
19:30-22:00	**Closing Discussion**

June 16th

09:00-10:00	**Breakfast**
10:00-11:00	**Third Session** Philip Hyde, UAB Věra Hedvičáková, TUL Šárka Hauzerová, TUL Riley Yager, UAB
11:00-12:00	**Lunch**
13:00-14:00	**Fourth Session** Jacklyn Davis, UAB
14:30	**Transport of backpacks and luggage to Liberec**
15:00 -	**Trip to Machnín Railway station via transborder and ruins of the castle Hamrštein**

Ceramic electrospun nanofibers in B2O3-Al2O3-SiO2 system: structure versus composition

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Introduction: Boron Alumina ($Al_{18}B_4O_{33}$) and Mullite ($Al_6O_{13}Si_2$) are two main ceramic materials produced within a B_2O_3-Al_2O_3-SiO_2 reaction system. Boron Alumina ceramics, which are applied in high temperature insulation and composite material reinforcement, are known for having high temperature resistance and stability, low thermal expansion, and chemical inertness; however, they are also known for having low porosity and high thermal conductivity. Mullite ceramics, which are used in catalysis, as well as insulation and ceramic composite reinforcement, have low thermal conductivity, low thermal expansion, chemical stability, and low density.
Combination of these materials could potentially allow for improvement of the thermal conductivity and density in boron alumina-based ceramics, as well as reduce the temperature needed for mullite-formation in mullite fibers.

Materials and Methods: Alumina boron precursors were prepared using boric acid and alumina acetate. Tetraethyl Orthosilicate (TEOS) was added to the prepared precursor in different quantities to prepare 1%, 3%, 5%, and 7% weight concentration solutions. PVAc polymer was added to the solution to prepare a spinnable precursor. Nanofibers were spun using Alternating Field Electrospinning (AFES) and dried at 120°C to remove remaining solvent in preparation for annealing and X-Ray Diffraction (XRD) analysis. Fibers were annealed at 1000°C and above and have undergone XRD analysis to determine phase composition and crystallinity of B_2O_3-Al_2O_3-SiO_2 system fibers at this temperature. Thermal X-ray diffraction (T-XRD) and Thermogravimetric analysis (TGA) are used to determine when crystallization begins and what trends develop as fibers are further heated.

Results and Discussion: Samples annealed at 1000°C and 1200°C showed a primarily mullite-like structure. Mixed phase boron-mullite and classical mullite were observed to form after annealing at both annealing temperatures with all tested amounts of silica component. Partial decomposition of the initial $Al_4B_2O_9$ boron alumina phase into $Al_{18}B_4O_{33}$ and Al_2O_3 begins after sintering at 1200°C due to the loss of the boron at none or low silica content. When silica content increases, it compensates boron loss resulting in the mixed boron mullite-like structure and corresponding change seen in the crystalline lattice parameters (Fig.1). The substitution of boron with silica leads to the disappearance of Al_2O_3 phase (indicated by arrows in Fig.1) and the characteristic peak of

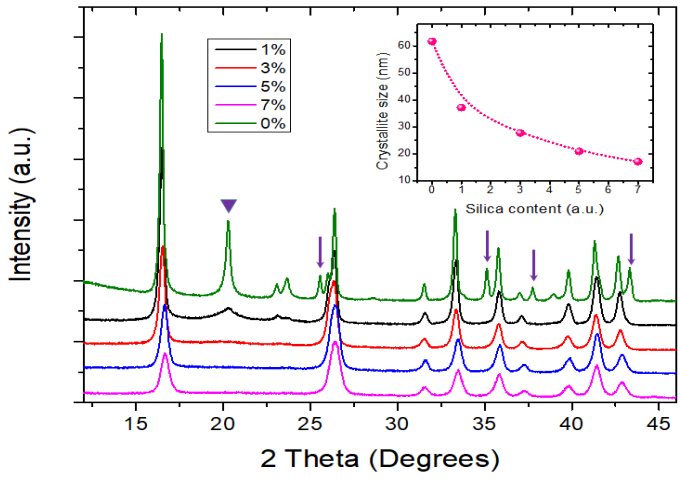

Figure 1. XRD patterns of B_2O_3-Al_2O_3-SiO_2 nanofibers with various SiO_2 content after sintering at 1200 °C. Inset shows the change in average crystallite size with % SiO_2.

$Al_{18}B_4O_{33}$ at 20.4º 2□ (labeled with a triangle). The changes in the intensity ratio of the most intense peaks at ~16.5 and ~26.4º 2□ indicate the formation of a mixed mullite-like structure gradually changing from $Al_4B_2O_9$ to "classical" mullite with the increasing silica content. Crystallite size also diminishes with increased silica content, leading to more mechanically and thermally stable nanocrystalline nanofibers with sub-20 nm crystallite sizes (Fig.1 inset).

Conclusion: Better understanding and knowledge of nanofibrous ceramic material properties is hindered by the lack of sustainable production of the nanofibers. This study used alternating field electrospinning (AFES), as a high-yield method to produce these materials. The addition of the SiO_2 precursor was observed to have little effect on the AFES process of the base B_2O_3-Al_2O_3 precursor material, which demonstrated high productivity. The addition of silica into the B_2O_3-Al_2O_3 system made the nanofibers thermally and mechanically more stable when compared to boron alumina nanofibers. Further studies will focus on the mechanical properties and application of these materials as catalyst supports in chemical reactions.

Acknowledgements: A.G. and T.B. have been supported by NSF International Research Experience for Students (IRES) award to UAB (Grant Number OISE-1852207). This study is supported by NSF Grant number DMR-1708600.

References:

Dong, Y., Dong, X., Li, L., Wu, J., Yan, L., Liu, J., Guo, A., *Lightweight and thermally insulating aluminum borate nanofibrous porous ceramics*, Ceram. Int., 47, 21029-21037 (2021).

Song L., Lui J., Wang J., Yao, S., Lui B., Ma Y., Lui W., Cai Q. *Non-isothermal crystallization kinetics for ceramic nanofibers prepared using different silica sources,* Ceram. Int., 45, 1392-1399 (2019).

Song X., Gao Y., Lui Q., Wang J., Yao S., Liu W., Ma Y. *Thermally stable boron-containing mullite fibers derived from a monophasic mullite sol*, Ceram. Int., 45, 1171-1178 (2019)

Song L., Lui W., Wang J., Xu S., Lui B., Cai Q., Ma Y., Highly *aligned continuous mullite nanofibers: Conjugate electrospinning fabrication, microstructure, and mechanical properties,* Material Letters, 212, 20-24 (2018).

Stanishevsky, A., Brayer, W. A., Pokorny, P., Kalous, T., Lukáš, D., *Nanofibrous alumina structures fabricated using high-yield alternating current electrospinning*, Ceram. Int.,42, 17154-17161 (2016).

Poly(ε-caprolactone) nanofibers produced by air-jet spinning

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Biodegradable nanofibrous materials are increasingly being used to produce materials for medical applications – scaffold for tissue engineering, drug delivery systems or wound dressings. Polymer nanofibers are usually produced by electrospinning technology. However, in addition to electrospinning, there are a number of other technologies that are not so much used or studied but offer certain advantages. These non-electrospinning technologies include, for example, centrifugal spinning, drawing, meltblowing and air-jet spinning.

Air-jet spinning or in other words solution blowing [1] is a technology for the production of polymer nanofibers by blowing a polymer solution. The force used to transform the polymer solution into the form of fibers is hydrodynamic force [2]. This technology does not use high electrical voltage and does not require an electrically active collector. For these reasons, this technology is also suitable for the application of nanofibrous materials in in-situ [3] medical applications mainly as wound dressing.

Solutions of poly(ε-caprolactone) (PCL) with molecular weight M_n=45 kDa (Merck) in different concentrations (6, 8, 10wt%) in dichloromethane (DCM) from Penta Chemicals were successfully air-jet spun by commercially available airbrush device (Fengda BD-180). Photos of air-jet spinning in the laboratory, schemes of the air-jet spinning, and scanning electron microscope images of selected air-jet spun and electrospun nanofibrous materials are presented in Fig. 1.

The equipment for the production of biodegradable nanofibers using air-jet spinning technology will be presented, the basic process parameters will be described and the resulting nanofibrous material structures from poly(ε-caprolactone) will be presented. Furthermore, the basic evaluation of chemical composition (FTIR), internal structure - arrangement of macromolecules (DSC) and in-vitro evaluation of cytotoxicity and biodegradation will be presented in comparison with electrospun material from the same polymer solution. Scanning electron microscope images are used for the structure evaluation of air-jet spun and electrospun nanofibrous materials and their comparison mainly with focus to fiber diameter measurements.

The vision of applying biodegradable nanofibrous wound dressings using air-jet spinning still requires many studies and testing. It is important to monitor the residual solvents in the formed nanofibers immediately after production. However, it would be best to avoid toxic solvents in the future and focus on aqueous or ethanol solutions. It is also necessary to study the cooling of the wound due to the application of nanofibers to its surface. Despite these obstacles, this technology seems very promising.

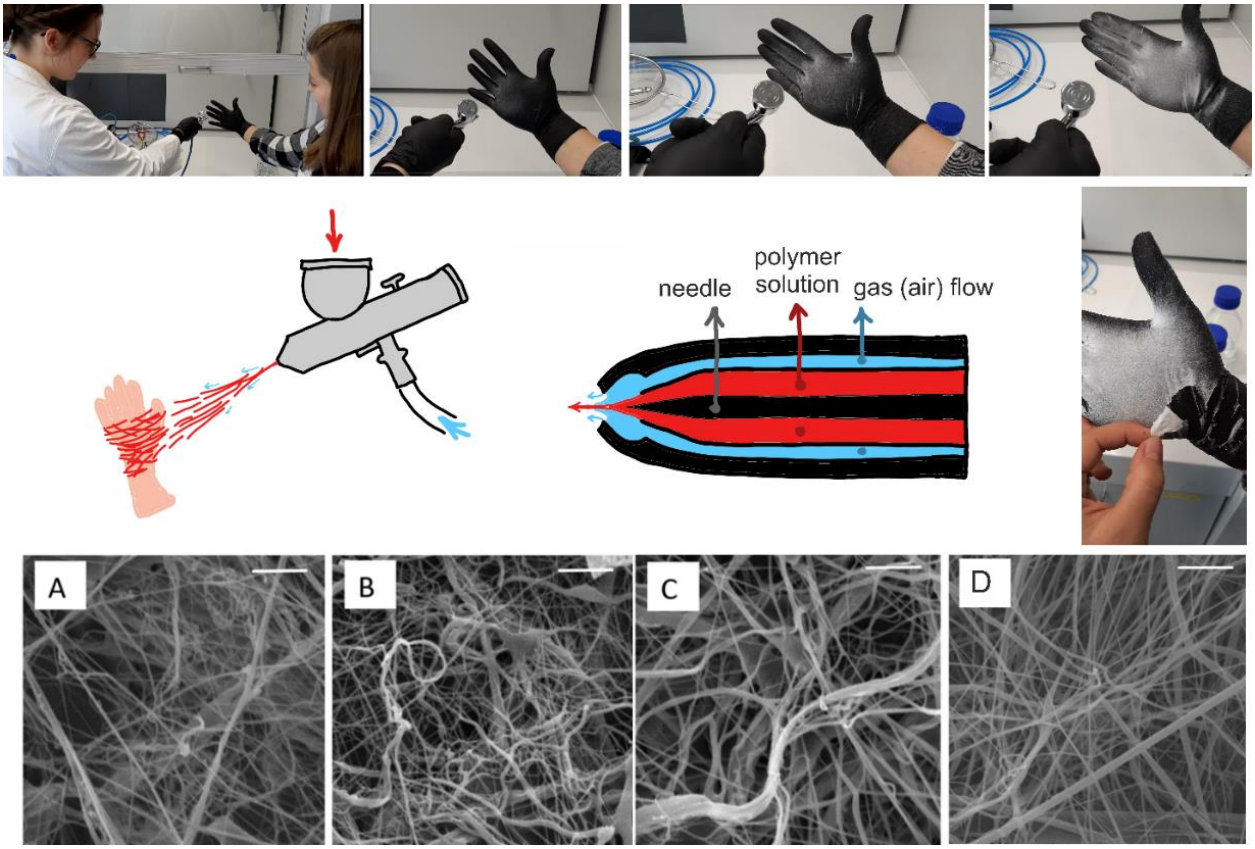

Fig. 1: *Photos of air-jet spinning, schemes of the air-jet spinning technology and of the used airbrush device and scanning electron microscope images of A) air-jet spun solution of 6wt% PCL in DCM; B) air-jet spun solution of 8wt% PCL in DCM; C) air-jet spun solution of 10wt% PCL in DCM; D) electrospun solution of 10wt% PCL in DCM. Scale bar presents 5 μm.*

Acknowledgements: The result was obtained through the financial support of the grant "Study of physical networks in polymer materials" of the Technical University of Liberec Grant Program „PURE“, No. PURE-2020-4007.

References:

1. Dias, G.C.; Cellet, T.S.P.; Santos, M.C.; Sanches, A.O.; Malmonge, L.F. PVDF Nanofibers Obtained by Solution Blow Spinning with Use of a Commercial Airbrush. *J Polym Res* **2019**, *26*, 87, doi:10.1007/s10965-019-1731-7.
2. Abdal-hay, A.; Sheikh, F.A.; Lim, J.K. Air Jet Spinning of Hydroxyapatite/Poly(Lactic Acid) Hybrid Nanocomposite Membrane Mats for Bone Tissue Engineering. *Colloids Surf B Biointerfaces* **2013**, *102*, 635–643, doi:10.1016/j.colsurfb.2012.09.017.
3. Behrens, A.M.; Casey, B.J.; Sikorski, M.J.; Wu, K.L.; Tutak, W.; Sandler, A.D.; Kofinas, P. In Situ Deposition of PLGA Nanofibers via Solution Blow Spinning. *ACS Macro Lett.* **2014**, *3*, 249–254, doi:10.1021/mz500049x.

Effects of increased poly(ε-caprolactone) (PCL) concentration in gelatin-based (GEL) nanofibrous scaffolds produced via alternating field electrospinning

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Introduction: Alternating field electrospinning (AFES, also referred to as alternating current electrospinning) continues to be a unique method for the creation of nanoscale materials. This high yield, free surface approach allows for many various solvent-polymer combinations to be employed while maintaining a wide range of motion for collection of the materials without the need for a grounded collector.[1-2] Included in the viable nanoscale materials possible to produce with AFES are biomaterials that exhibit biocompatibility, or "perform with an appropriate host response in a specific application," from both natural and synthetic sources.[3] Polycaprolactone (PCL) is a widely accepted synthetic polymer used in biomaterials, with desirable qualities such as biocompatibility, good mechanical characteristics, and biodegradability.[4-5] Similarly, Gelatin (GEL) is valued for its innate biocompatibility and biodegradability as a natural polymer.[6-7] When combined to make a blended material, the synthetic and natural polymers can be expected to form a more ideal blended biomaterial which assuages shortcomings of the individual polymers, such as extreme hydrophobicity/hydrophilicity or poor mechanical qualities.[4,6-8] To address this issue, various ratios of PCL/GEL polymer precursor solutions have been explored to determine the effect of increased PCL content in GEL nanofibrous scaffolds prepared via alternating field electrospinning.

Materials and Methods: Polycaprolactone (PCL, Sigma Aldrich) and cold water fish gelatin (GEL, Sigma Aldrich) were used to create spinnable precursors in glacial acetic acid. The resulting precursors were then blended at ratios of 1:5 to 2:1 (PCL:GEL). To further optimize precursor spinnability a salt additive was used, and viscosity and conductivity tests were conducted. Alternating field electrospinning of the PCL/GEL solutions was performed at RMS voltages ranging from 20-40 kV. The fibers were collected on a rotating cylindrical collector to form scaffolds with thicknesses ranging from 0.5-2.0 mm. Thermal treatment of the resulting scaffolds was performed to partially physically crosslink the GEL. Samples intended for cellular studies were simultaneously crosslinked and sterilized by the thermal treatment. Analysis of the scaffolds using SEM was performed to determine average fiber diameter and morphological changes. Fourier transform spectroscopy was used to analyze compositional changes. Cellular response to the blended materials was assessed by means of metabolic analysis, SEM imaging, and fluorescence imaging. Tensile tests for each scaffold composition in SBF to determine tensile strength changes have also been discussed.

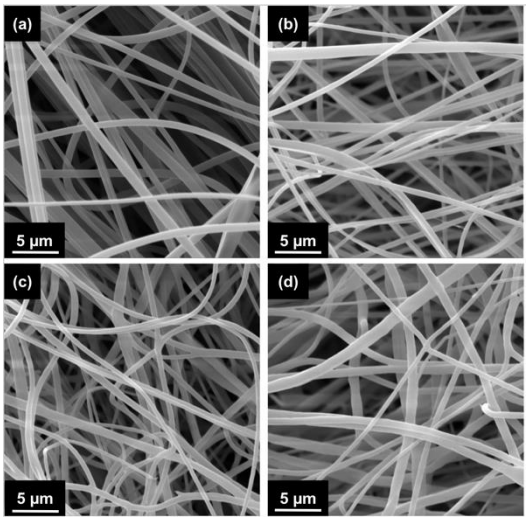

Figure 1. As-spun nanofibrous materials (a) pristine 30% GEL, (b) PCL/GEL 1:1, (c) PCL/GEL 1.5:1, (d) PCL/GEL 2:1 showing increased fiber diameter with increased PCL content

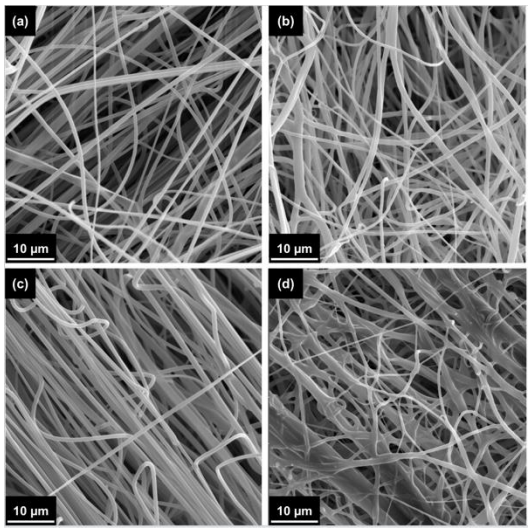

Figure 2. SEM images of as-spun (a) pristine GEL and (b) PCL/GEL 2:1 nanofibrous materials; and post-treated at 160oC for 4 h (c) pristine GEL and (d) PCL/GEL 2:1 material showing increased fiber diameter/bundling with increased PCL content and post-treatment morphological changes.

Results: The formation of beadless PCL/GEL nanofibers with diameters of 100-1000 nm was confirmed with SEM. Changes in fiber diameter and shape were dependent on the composition, with general trends of larger diameters consistent with increased PCL content (Fig. 1). Changes for the tested PCL/GEL compositions after thermal treatment followed the same trend, with higher PCL content corresponding to greater change in fiber morphology post-treatment (Fig. 2). Polymer precursors tested generally worked in the range of viscosities from 300 to 800 centiPoise. PCL/GEL precursors with electric conductivities of at least 100 microSiemens/cm allowed for adequate electrospinning. Preliminary results have shown that the addition of PCL strengthens the blended scaffolds and allows tunability of the degradation rate. The various compositions of PCL/GEL scaffolds were successfully seeded with 3T3 mouse fibroblasts, and cellular viability and proliferation were confirmed with SEM imaging, fluorescence imaging, and metabolic analysis. Initial results indicated that cellular activity was inversely related with PCL content within the scaffolds. Composition of the scaffolds appeared to have the greatest influence on *in vitro* testing, fiber diameter/morphology, and degradation. A similar trend is expected to be observed for mechanical testing of the scaffolds, such that increased PCL content is consistent with increased tensile strength.

Conclusion: Successful fabrication of various compositional ratios of PCL/GEL nanofibrous scaffolds was achieved via alternating field electrospinning using a “green” solvent system and post-fabrication treatment method. Cellular responses to the prepared scaffolds indicate promising use for potential dermal biomedical applications.

Acknowledgements: NSF International Research Experience for Students (IRES) award to UAB (Grant Number OISE 1852207), Department of Education GAANN (Grant Number P200A180001).

References: 1) Nealy, Sarah L., et al. “Nanofibrous TiO2 Produced Using Alternating Field Electrospinning of Titanium Alkoxide Precursors: Crystallization and Phase Development.” RSC Advances, vol. 10, no. 12, 13 Feb. 2020, pp. 6840–6849., doi:10.1039/c9ra10464j.
2) P. Pokorny , E. Koštáková , F. Sanetmik , P. Mikes , J. Chvojka , T. Kalous , M. Bilek , K. Pejchar , J. Valtera and D. Lukaš , Phys. Chem. Chem. Phys., 2014, 16 , 26816
3) dos Santos V., Brandalise R.N., Savaris M. (2017) Biomaterials: Characteristics and Properties. In: Engineering of Biomaterials. Topics in Mining, Metallurgy and Materials Engineering. Springer, Cham. https://doi.org/10.1007/978-3-319-58607-6_2.
4) Kim, Gyeong-Man, et al. “Electrospinning of PCL/PVP Blends for Tissue Engineering Scaffolds.” Journal of Materials Science: Materials in Medicine, vol. 24, no. 6, 2013, pp. 1425–1442., https://doi.org/10.1007/s10856-013-4893-6.
5) Chen, Shixuan, et al. “Fast Transformation of 2D Nanofiber Membranes into Pre-Molded 3D Scaffolds with Biomimetic and Oriented Porous Structure for Biomedical Applications.” Applied Physics Reviews, vol. 7, no. 2, 2020, p. 021406., https://doi.org/10.1063/1.5144808.
6) “Polycaprolactone/Gelatin Nanofibrous Scaffolds for Tissue Engineering.” Biointerface Research in Applied Chemistry, vol. 11, no. 4, 2020, pp. 11104–11115., https://doi.org/10.33263/briac114.1110411115.
7) Kong, Xiangqian, et al. “Chondroitin Sulfate/Polycaprolactone/Gelatin Electrospun Nanofibers with Antithrombogenicity and Enhanced Endothelial Cell Affinity as a Potential Scaffold for Blood Vessel Tissue Engineering.” Nanoscale Research Letters, vol. 16, no. 1, 2021, https://doi.org/10.1186/s11671-021-03518-x.
8) Perez-Puyana, V., et al. “Anisotropic Properties of PCL/Gelatin Scaffolds Obtained via Electrospinning.” International Journal of Fracture, vol. 224, no. 2, 2020, pp. 269–276., https://doi.org/10.1007/s10704-020-00460-4.

Sintering of Nanoceramics from Mixed Oxide Nanofibers

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Introduction: The main goal when sintering oxide nanofibers is to harness the ability to manipulate the microstructure of the resulting ceramic material. In doing so, one can potentially expand the applications of the finalized material giving it a broader range of use. This study advances the understanding of the fiber-fiber interaction during sintering and how the process can be optimized for the targeted product.[1]

Materials and Methods: The starting oxide nanofibers used in the experiments were composed of tetragonal ZrO_2 (t-ZrO_2), anatase TiO_2, and amorphous boron-Al_2O_3. In each experiment two types of nanofibers were crushed and mixed in 1:1 weight ratio and thermally processed at 1000 °C or 1200 °C to observe the behavior and composition outcome of the interaction. XRD patterns in a range of 5-90 two theta degrees were recorded to determine the crystalline structure and determine how the transition in composition was affected by the annealing temperature. SEM (25 kV accelerating voltage and x5k – 20k magnification) with EDS detector was used to characterize the fibers' surface morphology and elemental composition.

Results: SEM images indicate that the result of oxide nanofibers sintering depends on the composition of the mixture. For example, short nanofiber segments of TiO2 in ZrO_2/TiO_2 mixture show noticeable grain growth (Fig.1, top), whereas they seem to disintegrate in boron-alumina / titania mixture after partial sintering at 1200 °C while alumina nanofibers have increased porosity (Fig.1, bottom). On the other hand, the interaction between the fibers was restricted to the phase transformation of individual oxide materials and no chemical interaction between the different types of fibers was observed. For example, no formation of $Zr_xTi_{1-x}O_2$ phases were noted in ZrO_2/TiO_2 mixture, however some reduction of the grain size of the formed rutile TiO_2 and monoclinic ZrO_2 phases at 1200 °C may indicate the formation of a mixed interface layer between two types of fibers.

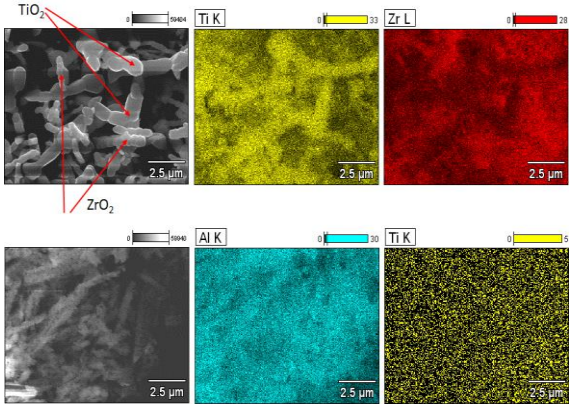

Figure 1: SEM and EDS element map of (top) zirconia/titania and (bottom) boronated alumina / titania mixtures after partial sintering at 1200 °C. Note the lack of TiO_2 fibrous structure in the boronated alumina / titania mixture.

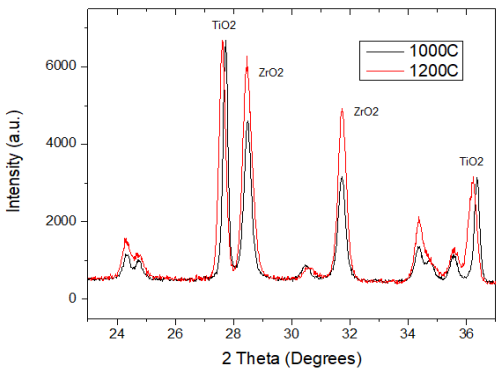

Figure 2: XRD analysis of ZrO_2/TiO_2 mixture at 1000 °C and 1200 °C. A shift in peak position of TiO_2 may be due to compressive stress reduction in TiO_2.

It has also been observed that the crystallite size in the oxide nanofibers was significantly larger when the individual oxide was annealed alone in comparison with the crystallite size of individual oxide fiber in the mixtures. Furthermore, the crystallite sizes depend also on the type of the materials in the mixture.

Conclusions: It has been found that the fiber shape, final phase composition, grain size, surface morphology, and other parameters of binary mixtures of short metal oxide nanofibers can be strongly affected by the composition and mixing procedure when using the same sintering procedure. Further studies will focus on the mixed oxide nanofibrous ceramics with the varying level of fiber-fiber interaction to further the understanding of the interactions during sintering.

Acknowledgements: This study is supported by NSF Grant number DMR-1708600. JD and TB thank the support from NSF Grant number OISE-1852207.

References:

[1]Handwerker, C.A., Blendell, J.E., Coble, R.L. (1989). Sintering of Ceramics. In: Uskoković, D.P., Palmour, H., Spriggs, R.M. (eds) Science of Sintering. Springer, Boston, MA. https://doi.org/10.1007/978-1-4899-0933-6_1

Alternating field electrospinning of Poly(ε-caprolactone)/Zein Nanofibers

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Introduction: Electrospinning of nanofibrous biomaterials is a relatively new development used to create a wide range of bio-scaffolding structures. Among the methods for biopolymer nanofiber fabrication, the emerging alternating field electrospinning (AFES, a.k.a. AC-electrospinning) method shows promising for high-yield, scalable production. This study focuses on AFES of zein and polycaprolactone (PCL) blended nanofibers. Zein based nanoparticles have been shown to contain bioactive components like antioxidants, fatty acids and carotenoids, which are ideal for biomaterials.[1] A recent study on polycaprolactone (PCL) with Zein nanofibers highlighted their potential for biological applications.[2] Desirable qualities of purified zein and polycaprolactone such as biodegradability, biocompatibility, non-toxicity, and wide availability support their potential for creating biomaterials that aid in tissue engineering.[3]

Materials and Methods: Precursors were synthesized using purified zein (Zein, purified powder, Scientific Polymer Products Inc.) and polycaprolactone (PCL, Sigma Aldrich) combined at mass ratios from 5:2 to 1:1 (PCL:Zein) in glacial acetic acid. Sodium acetate (NaAc, Lachema) was used as an additive to regulate the spinnability of the solution.[4] The viscosity of viable precursors was characterized using a rotational viscometer. AFES of the Zein/PCL precursors was carried out at RMS voltages within 20-40 kV and the spinnability range was determined. Bulk nanofibers were collected during electrospinning from each of the precursors and SEM imaging was performed to assess fiber morphology.

Results: Addition of zein leads to improved spinnability of blended precursors. However, the stability of blended PCL/Zein precursor remain relatively low and is determined by the PCL degradation rate in the solvent. When freshly prepared precursors were used, SEM imaging revealed that PCL/Zein nanofibers randomly aligned fibers with diameters ranging within 100-350 nm (Figure1). There was much less beading observed in PCL/Zein nanofibers (Fig.1b)

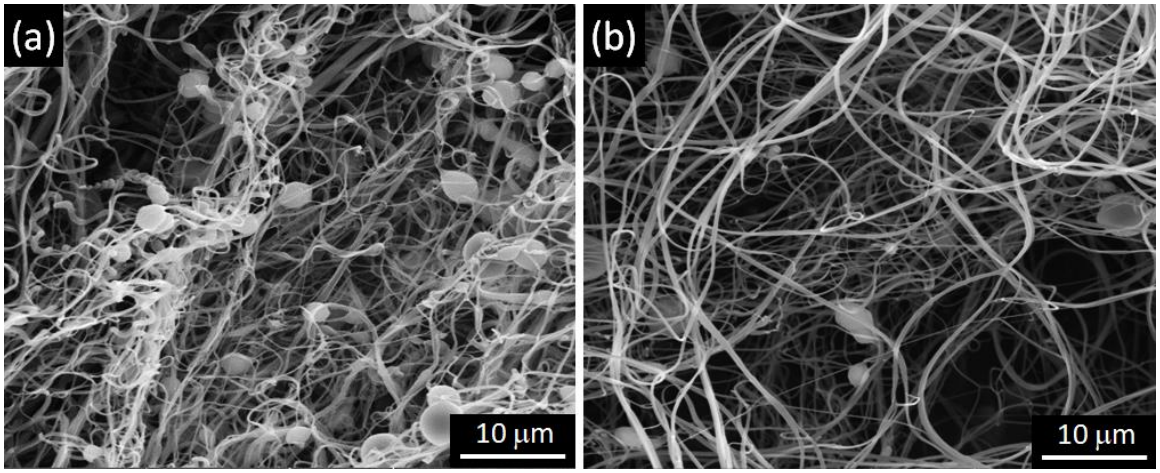

Figure 1. SEM images of (a) pristine PCL nanofibers, and (b) blended PCL/Zein nanofibers with 5:3 mass ratio using AFES process.

when compared to pristine PCL fibers (Fig.1a) spun at the same process parameters and

similar polymer concentration in the precursor. It has been found that the viscosity of tested PCL/Zein precursors was 250 – 280 mPa·s and about half of the viscosity of pristine PCL precursor. The addition of zein appears to decrease the average diameter of the nanofibers.

Conclusion: Successful alternating field electrospinning of several combinations of zein and polycaprolactone precursor solutions has been achieved such that viable nanofibrous materials were formed. The employed processes are considered “green”, as is ideal for biomaterial creation. Further characterization of the precursors, electrospinning process, and resulting fibrous materials will be conducted to improve the nanofibers quality and assess their potential for use as biomaterials in tissue engineering applications.

Acknowledgments: LJ and HL have been supported by NSF International Research Experience for students (IRES) award to UAB (Grant Number OISE-1852207).

References:

[1] M. Pascoli, et al. “Zein Nanoparticles and Strategies to Improve Colloidal Stability: A Mini-Review.” *Frontiers in Chemistry*, vol. 6, 2018, https://doi.org/10.3389/fchem.2018.00006.

[2] A. Martin, J. Cai, A.L. Schaedel, M. van der Plas, M. Malmsten, T. Rades, A. Heinz, Zein-polycaprolactone core–shell nanofibers for wound healing, Int. J. Pharmaceutics 621 (2022) 121809. https://doi.org/10.1016/j.ijpharm.2022.121809

[3] S. Tortorella, M. Maturi, V. Vetri Buratti, G. Vozzolo, E. Locatelli, L. Sambri, M. Comes Franchini, Zein as a versatile biopolymer: different shapes for different biomedical applications, RSC Adv. 11 (2021), 39004-39026. https://doi.org/10.1039/d1ra07424e

[4] C. Lawson, A. Stanishevsky, M. Sivan, P. Pokorny, D. Lukáš, Rapid fabrication of poly(ε-caprolactone) fibers using needleless alternating current electrospinning, *J. Appl. Polymer Scie.* 133 (2016) 43232. https://doi.org/10.1002/app.43232

Influence of physical crosslinking on the properties of nanofiber scaffolds based on PVA

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Introduction: Nanofibrous materials with incorporated growth factors have great potential for use in tissue engineering. The incorporation of proteins into nanofibers of water-soluble polyvinyl alcohol (PVA) prevents the loss of protein activity during the production of the material; however, the problem with these materials is their very rapid dissolution in the aqueous medium accompanied by the quick release of incorporated substances. PVA is a promising material for biomedical applications mainly due to its good biocompatibility, low cytotoxicity, high moisture retention and permeability for biologically active substances.

Materials and Methods: Therefore, this work focuses on the physical stabilization of materials made from PVA with a high degree of hydrolysis (98%) and high molecular weight (125,000 g / mol) with incorporated platelet-derived growth factors (PL). Unlike other cross-linking methods, which are not suitable due to the possible cytotoxic effects of the cross-linking agent, the F-T method is one of the gentler methods of physical cross-linking for incorporating biologically active substances. The principle of the technique is the strengthening of hydrogen bonds between PVA molecules due to repeated freezing and subsequent thawing. The number of applied F-T cycles, as well as the temperatures used, affect the crosslinking (in addition to the material parameters). The experiment was performed with 5 and 10 cycles of F-T, at freeze temperatures of -20 °C and thaw at 4 °C and 22 °C and 37 °C. Subsequently, the effect of applied F T on the change in crystallinity and solubility of PVA, as well as on the release rate of incorporated proteins was studied.

Results: Results show that materials produced by electrospinning with a fiber diameter of 150 to 700 nm (Fig. 1) due to F-T increase the crystallinity of PVA and at the same time reduce the solubility by up to 18%. A 17% delay in protein release was also observed.

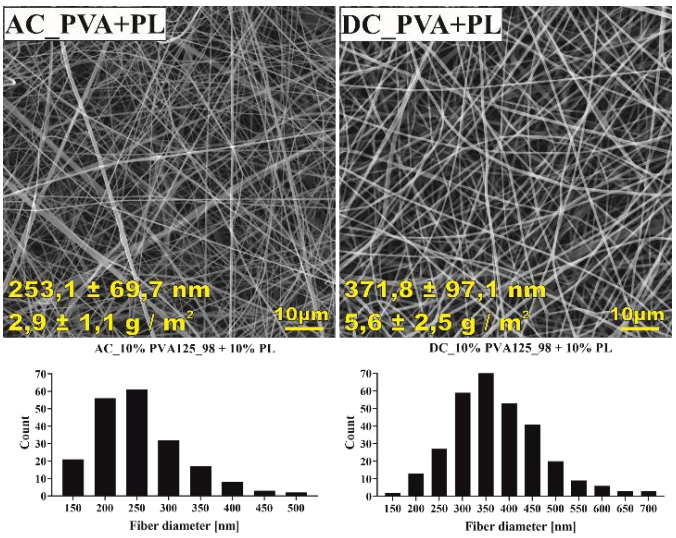

Figure 1: SEM images of materials from AC and DC electrospinning (magnification 5000x) and histograms of the distribution of fiber diameters

Conclusions: The reduced solubility of PVA and the more gradual release of incorporated native proteins from the stabilized F-T material have potential use, for example, in the healing of large and chronic skin wounds. Gradual release of incorporated proteins promotes both early wound healing and subsequent cell proliferation during subsequent healing phases.

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Alternate Current Electrospinning of Alkaline Lignin / Fish Gelatin Composite Nanofibers

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Introduction: With recent times of tissue engineering calling for more sustainable products and conscious practices, Fish Skin Gelatin (FSG) has become a promising polymer for creating such materials. It is a conscious alternative to bovine and porcine gelatins, which can be considered sacred animals [1]. FSG nanofibrous materials (NF) can be prepared by electrospinning from pure aqueous solutions using either DC-electrospinning [2] or more productive alternating field electrospinning (AC-electrospinning). However, FSG NF material alone does not promote strong enough mechanical properties or cell proliferation [3,4] and needs additives to match the targeted applications. Lignin is a biopolymer that is derived from wood and plant sources with great potential in biomedical applications and has properties of high biodegradability, biocompatibility, and low production costs with minimal environmental effects in production and usage [5]. In this study, the goals are to investigate the AC spinnability of precursors and textural properties of produced NF materials with different lignin and fish gelatin weight ratios.

Materials and Method: A range of solutions using alkaline or de-alkaline lignin (Tokyo Chemical Industry) prepared from needle-leaved trees and broad-leaved trees and gelatin from cold water fish skin (Sigma-Aldrich) were dissolved in different weight ratios in a mixture of distilled water (dH_2O) and glacial acetic acid (A.G. Penta Chemicals Unlimited). The solutions were bulk spun at 40kV rms AC voltage using an AFES electrospinning machine. The best spinnable precursors were characterized to determine their viscosity (Haake Rotovisco 1). Those precursors were then spun on an AFES machine for ~40 minutes to achieve a thickness of 0.35mm and analyzed with SEM (VEGA3 Tescan) to determine the fibers' average diameter and the diameter distribution along with the characterization of the fibers' surface morphology.

Results: AFES of lignin/FSG nanofibers was successful with both alkaline or de-alkaline lignin addition and lignin/FSG weight ratio up to 0.285. Uniform, continuous flows of nanofibers were generated from precursors containing 45-55 wt% of total polymer (Fig.1a). The fiber diameters were found in a range of 375±125nm and 220±80 nm when the total polymer concentration varied from 55 to 45 wt%. In a latter case, the fiber diameter was similar to that of pure FSG nanofibers produced at similar process parameters [2]. It was also noted that the addition of both types of lignin leads to larger fiber diameters at the same FSG concentration. It has been argued that the viscosity of the precursor solution is the main parameter that determines the fiber diameter in this material system. Representative SEM images of lignin/FSG nanofibers are shown in Fig. 1b,c. In all experiments with spinnable precursors, the produced fibers were almost beadless and had smooth surface morphology with both types of lignin. It appears that both types of lignin are well dispersible in the FSG precursor solution and do not form particle clusters.

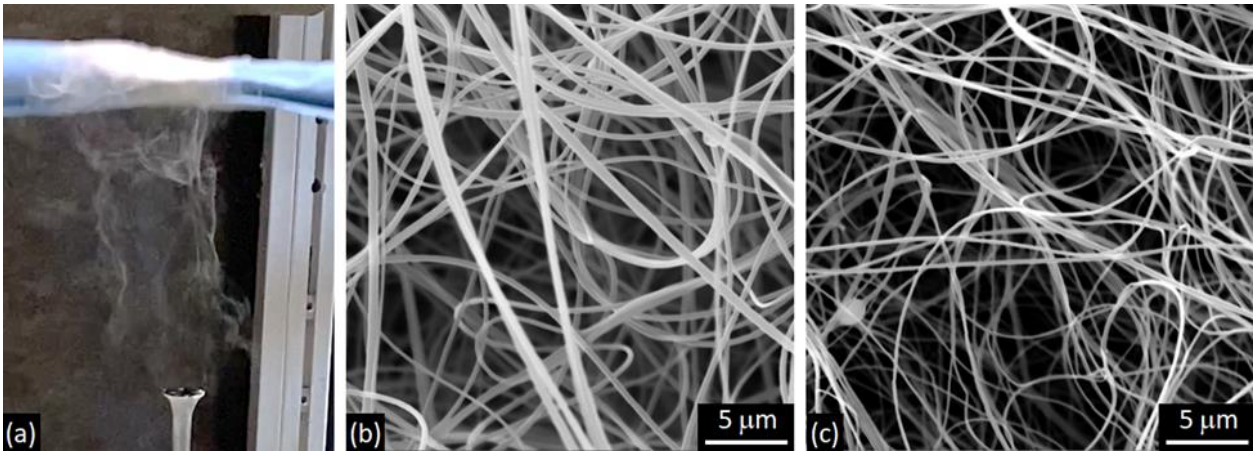

Figure 1. (a) A flow of lignin/FSG nanofibers generated from a well-spinnable precursor and exemplary SEM images of the produced FSG nanofibers with the addition of 10 wt% of alkaline (b) and 5 wt% dealkaline (c) lignin.

Conclusion: Successful AFES electrospinning of lignin/FSG composite nanofibers has been demonstrated with lignin loading up to 10 wt% with respect to FSG. Such material can be promising for use in numerous biomedical applications including skin patches and drug delivery, with minimal environmental effects. Future studies will determine the maximum level of lignin in addition to FSG and the composite material behavior in vitro.

Acknowledgements: MH and HL have been supported by the NSF International Research Experience for Students (IRES) award to UAB (Grant Number OISE-1852207)

References:

[1] A.A. Karim, R. Bhat. Fish gelatin: properties, challenges, and prospects as an alternative to mammalian gelatins. Food Hydrocolloids 23 (2009) 563-576. https://doi.org/10.1016/j.foodhyd.2008.07.002.

[2] H.W. Kwak , M. Shin , J.Y. Lee, H. Yun, D.W. Song, Y. Yang, et al. Fabrication of an ultrafine fish gelatin nanofibrous web from an aqueous solution by electrospinning. Int J Biol Macromol. 102 (2017) 1092–1103.

[3] A. Kennell, M. MacEwen, M. Armstrong, T. Nicola, B. Halloran, N. Ambalavanan, A. Stanishevsky, Fish skin gelatin nanofibrous scaffolds spun using alternating field electrospinning and in-vitro tested with tdTomato mice fibroblasts, Mater. Today Comm. 31 (2022) Art. # 103417 https://doi.org/10.1016/j.mtcomm.2022.103417

[4] S.R. Gomes, G. Rodrigues, G.G. Martins, C.M.R. Henriques, J.C. Silva. In vitro evaluation of crosslinked electrospun fish gelatin scaffolds. Mater Sci Eng C 33 (2013) 1219–1227.

[5] P. Figueiredo, K. Lintinen, J.T. Hirvonen, M.A. Kostiainen, H.A. Santos. Properties and chemical modifications of lignin: Toward lignin-based nanomaterials for biomedical applications. Progress in Mater. Sci. 93 (2018) 233-269. https://doi.org/10.1016/j.pmatsci.2017.12.001.

Postprocessing Methods of Electrospun Gelatin Nanofibers with N- Acetyl-D-glucosamine Additive for Potential Use as Vascular Grafts

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Introduction: Alternating Field electrospun (AFES) nanofibers hold great potential for many biomedical uses. These nanofibers have been developed for solutions to drug delivery systems, tissue-engineered scaffolds, medical implants, biosensors, and many others [1]. In addition, there exists the potential of utilizing nanofibers made of biocompatible materials as vascular grafts in surgical procedures, but the procedure and polymers that produce nanofibers best suited for in vivo use remains to be identified [2]. This research explores a nanofibrous scaffold with post-processing methods of freeze drying, thermal crosslinking, and glutaraldehyde treatment made with the sugar additive N- Acetyl-D-glucosamine (GCSM) and a base polymer of fish gelatin [3]. The GCSM additive was selected due to its previous success in increasing the crosslinking degree of nanofibrous scaffolds through means of the Maillard reaction during heat treatments [4]. The fish gelatin solutions with different sugar percentages effectiveness varied the degree of crosslinking, solubility in an aqueous solution, porosity, and cell proliferation which are all important factors to control for a biomedical nanofibrous scaffold.

Materials and Methods: Cold water fish gelatin (FG, Sigma Aldrich) was blended with N-Acetyl-D-glucosamine, 98 (GCSM, Alfa Aesar) in deionized water at room temperature with weight ratios of 35:100 to 45: 100 (FG: H_2O) to develop precursors for AFES. GCSM was first mixed in varying ratios in respect to the weight amount of gelatin and studied to determine the appropriate viscosity and ideal sugar concentration for spinnability. Precursors were spun using an AFES machine at RMS voltages between 26-39kV at 60 Hz AC frequency and environmental conditions of 21˚C and 40% humidity. Fibers were collected on a rotating collector as a sheet of nanofibrous material with ranges of 1-2mm thickness. The sheets were then crosslinked with different combinations of crosslinking methods including freeze drying (FD), thermal crosslinking (TX), and 50 wt% glutaraldehyde aqueous solution (GTA, Sigma Aldrich). The mechanical properties of the sheets were evaluated using tensile tests (ADMET eXpert 4000 microtester). Suitability of in-vivo application was further determined through degradation tests in synthetic body fluid (SBF), cell studies performed in-vitro, and SEM images of fiber morphology, diameter, and pore size.

Results: Optimal precursor concentrations of GCSM were determined through observational analysis of AFES spinning with parameters including flow rate, consistent fiber diameter, beading along fiber strands, buildup on electrode head, and width of precursor spray. The suitable concentrations of GCSM were determined to be 0.225:4.5:10 (GCSM 5% and 0.45:4.5:10 (GCSM 10%) weight ratios (GCSM: FG: dH_2O). Preliminary data collected from degradation tests of the scaffolds in SBF showed that FD+TX fibers had an average degradation of 27%, but FD+TX+GTA showed significant mass preservation with only a 10% degradation after 24 hours. SEM images of TX and TX+GTA for GCSM 5% and GCSM 10%

fibrous scaffolds showed nonaligned fiber morphology with no apparent beading, however those treated with GTA reveal a higher degree of crosslinking than TX or untreated as seen by significantly less pores and smaller pore size (Figure 1). MTT assay results showed that TX GCSM 5% scaffolds had the most cell attachment after 1 day while materials treated with GTA had smaller cell count values. Tensile tests indicated that GCSM 5% and GCSM 10% scaffolds could withstand a much higher stress (0.57MPa and 0.4 MPa) before failure with FD+TX treatment than untreated or FD treatments (<0.1MPa).

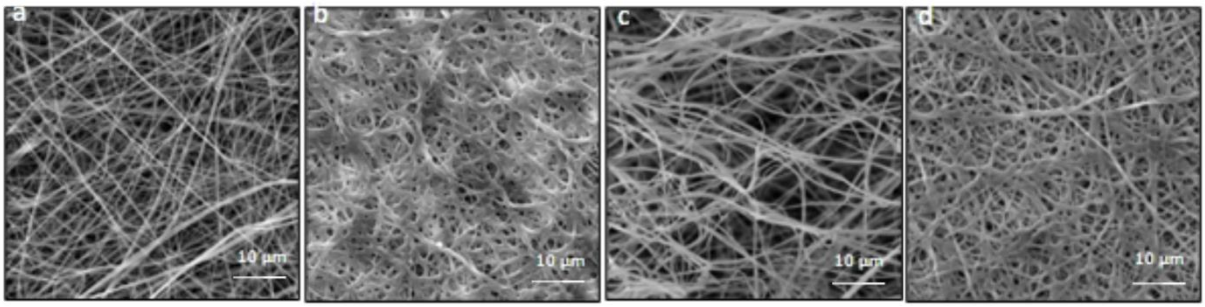

Figure 1.*GCSM 5% TX (a) GCSM 5% TX + GTA 1 (b) and GCSM 10% TX (c) GCSM 10% TX + GTA 1 (d) treatments at 5kx magnification*

Conclusion: Results from degradation tests and tensile tests show that fibers treated with freeze drying did not have the expected effects of decreasing the solubility/degradation of scaffolds or improving mechanical properties unless additionally treated with thermally crosslinking and potentially glutaraldehyde. GTA treatments had significant effects on the overall fiber morphology and decrease of solubility, however GTA also caused a decrease in cell viability. Therefore, alternative methods for removing glutaraldehyde after crosslinking serve as potential for future investigation to develop nanofibrous scaffolds for in vivo use.

Acknowledgements: O.S., R.H., and H.L. have been supported by NSF International Research Experience for Students (IRES) award to UAB (Grant Number OISE-1558268).

References:

[1] Aldana, A. A. and G. A. Abraham (2017). "Current advances in electrospun gelatin-based Scaffolds for tissue engineering applications." International Journal of Pharmaceutics 523(2): 441-453.

[2] Bružauskaitė I, Bironaitė D, Bagdonas E, Bernotienė E. Scaffolds and cells for tissue regeneration: different scaffold pore sizes-different cell effects. Cytotechnology. 2016;68(3):355-369.

[3] Alfaro, A.T., Balbinot, E., Weber, C.I. et al. Fish Gelatin: Characteristics, Functional Properties, Applications and Future Potentials. Food Eng Rev 7, 33–44 (2015). https://doi.org/10.1007/s12393-014-9096-5

[4] Kwak, H. W., et al. (2021). "Effect of crosslinkable sugar molecules on the physico-chemical and antioxidant properties of fish gelatin

nanofibers." Food Hydrocolloids 111: 106259.

Effect of the precursor composition on the structure of mixed zirconia-titania nanofibers

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Introduction: In many technological-based sciences, the use of mixed metal oxides has become an increasingly attractive strategy for producing materials with superior properties compared to their source binary oxides. Although known for its uses as a sensor and refractory ceramic, zirconium oxide is also an important catalyst support and is most often produced by the sol-gel process and has three stable crystalline phases, tetragonal, monoclinic, and cubic. The main challenge with ZrO_2 nanomaterials is the achievement of ZrO_2 grains with stable tetragonal phase (t-ZrO_2) due to low temperature degradation to monoclinic phase (m-ZrO_2). Literature suggests that the incorporation of Ti^{4+} into the ZrO_2 lattice would result in a lattice deformation which would stabilize the tetragonal phase. Similarly, titanium oxide is also attractive for its uses as a catalyst support as well as an efficient photocatalyst and has three polymorphs, brookite, anatase, and rutile. Titania is known commercially as the powerful photocatalyst due to its non-toxicity, low-cost, and resistance to acid, alkali, and organic solvents and, like zirconium oxide, it is often prepared through sol-gel processing. The photoactivity of nanocrystalline titania is highly dependent on its specific crystallinity and literature suggests that higher crystallinity shows higher photoactivity due to the large band gap (3.2 eV compared to rutile's 3.0 eV) in anatase phase. Studies have shown that doping TiO_2 with ZrO_2 results in a stable anatase phase up to 800°C. The present study focuses on the formation of nanocrystalline ceramic nanofibers from ZrO_2 and TiO_2 in different ratios from AC-electrospun precursor fibers.

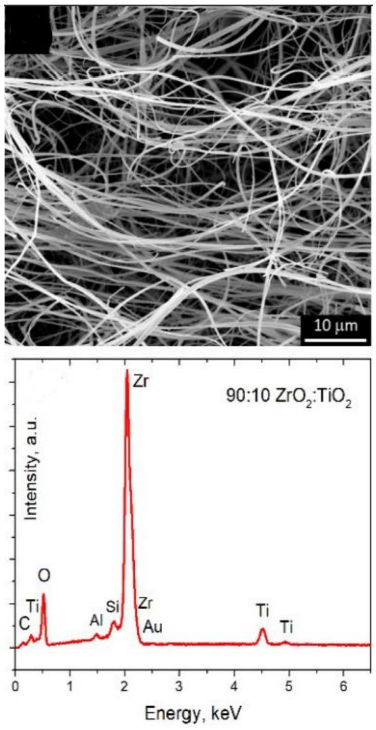

Figure 1: An example of SEM and EDS results for zirconia rich samples.

Materials and Methods: Alternating field electrospinning (AFES, a.k.a. AC-electrospinning) was used to prepare fibers from mixed titanium/zirconium alkoxides and polyvinylpyrrolidone (PVP)-based precursors with ethanol as a solvent. The molar ratios of Zr to Ti in the range from Zr-rich 0.9:0.1 to Ti-rich 0.1:0.9 were used in the experiments. Fibers were fabricated through alternating field electrospinning (AFES) with AC-voltages up to 40kV rms and at a current of 60 Hz. Collected fiber meshes were then calcined in a programmable furnace to temperatures up to 1200°C that resulted in flexible nanofibrous meshes with 0.1–5 mm thickness and porosity up to 99 %. The materials were characterized using Thermogravimetric (TG), differential thermal analysis (DTA) and differential thermogravimetric (DTG) curves which were recorded simultaneously at temperatures ranging from 20 to 1000°C. The size, shape, and surface morphology of the annealed ZrO_2/TiO_2 nanofibers were observed using field-emission scanning electron microscopy (SEM/EDS). The X-Ray Diffraction (XRD) patterns were obtained using a PANalytical Empyrean X-ray diffractometer to determine the crystalline phases in the annealed materials.

Results: Fabrication flow rate and overall productivity of the precursor fibers increase with increasing the content of titanium alkoxide in the precursor. Conductivity tests on the precursors showed that electrical conductivity is the

dominant factor for improving fiber flow and overall productivity. EDS data (Fig.1) for the targeted molar ratios shows that the precursor preparation, electrospinning, and annealing procedures were successful in achieving desired compositions. Analysis of the SEM images (Fig.1) showed a small increase in fiber diameter with the increased content of TiO_2. Further calcination and sintering of fibers at higher temperatures (800 – 1200°C) lead initially to further reduction of the fiber diameters due to the densification of the material. The formation of nanocrystalline zirconia fibers composed of single phase tetragonal ZrO_2 (t-ZrO_2) was observed at up to 28 mol% of TiO_2. The t-ZrO_2 phase was stable up to 1000 ^oC when the content of TiO_2 was 28 mol%. Single phase $ZrTiO_4$ nanofibers were formed from the ZrO_2/TiO_2 precursors with 1.0/1.0 molar ratio. This zirconium titanate phase starts to crystallize at 600 ^oC and was stable during sintering at 1200 ^oC for 2 h yet remaining a nanocrystalline material with the average crystallite size of 33±3 nm. The increase in titanium content led to precipitation of TiO_2 rutile phase although a zirconium titanate phase was still observed in the samples with up to 80 mol% titania.

Conclusions: From the results of this study, it has been suggested that the initially formed zirconia-titania crystalline phases, their stability, and transformations are determined by the atomic scale interactions of the precursor components, presence of carbonaceous residue during the decomposition of polymer fraction, surface energy and defect states (in particular oxygen vacancies) of initially formed crystallites with the dimensions less than 30 nm. This mixed sol gel and electrospinning method could be a great, consistent, and reasonably accurate method to obtain nanofibrous ceramic materials in zirconia-titania system with desired molar compositions in industrial or larger scale production.

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Reference: A. Stanishevsky, R. Yager, J. Tomaszewska, M. Binczarski, W. Maniukiewicz, I. Witońska, D. Lukáš. Ceram. Int. 45 (2019) 18672-18682. S. Nealy, C. Severino, A. Brayer, A. Stanishevsky. RSC Adv. 10 (2020) 6840-6849. A. Stanishevsky, J. Tchernov J. of Non-Cryst. S. 525 (2019). A. Stanishevsky, W.A. Brayer, P. Pokorny, T. Kalous, D. Lukáš. Ceram. Int. 42 (2016) 17154

Hemocompatibility of biodegradable polyester materials for tissue engineering

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Introduction: One of the main parameters for materials which are prepared for tissue engineering is the biocompatibility of these materials. The most used model for in vitro biocompatibility testing is monitoring the interaction and potential influence of a selected cell line with the tested materials. In these models, cell viability and potential adhesion and proliferation on materials are often monitored. One other method of monitoring the biocompatibility of materials in vitro is testing the materials in interaction with body fluids, specifically with human blood, native platelets (thrombocytes), and plasma. This method is called hemocompatibility (Horakova et al., 2018).

Materials and Methods: In this work biodegradable polyester nanofibers materials and their hemocompatibility were tested and evaluated in-vitro. The materials were produced by DC electrospinning. The materials for testing were prepared from polycaprolactone (PCL) and polylactic acid-caprolactone (PLCL) copolymer. Materials were incubated with full human blood, native platelets, and human plasma. Hemolytic effect (erythrocyte breakdown) was monitored after interaction with materials using spectrophotometry. Furthermore, thrombogenicity was monitored by cck-8 metabolic assay, which was incubated with materials and platelets and then absorbance of the solution measured at 450 nm. The effect of materials on coagulation pathways was evaluated by measuring coagulation times after the interaction of the materials with human plasma.

Results: The results show that the tested materials show almost zero hemolytic effect. Platelets viability after incubation with materials varied depending on the chemical composition of the materials and the resulting morphology of the tested layers. The PCL material showed higher thrombogenicity compared to the PLCL material. The evaluated coagulation times (aPTT and PT) were identical to the negative control for all materials (human plasma without material).

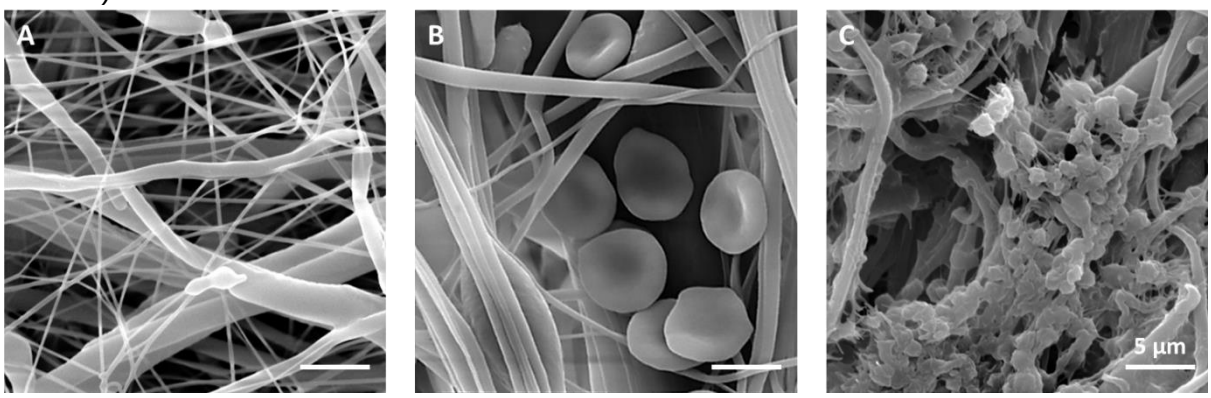

Figure 1: SEM images of PCL 45 after preparation of nanofibrous layers by electrospinning (A), after incubation of material with human blood (B), and after incubation of material with native platelets (C).

Conclusions: The test results show that the tested biodegradable polyester nanofiber materials are hemocompatible.

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References: Horakova, J., Mikes, P., Saman, A., Svarcova, T., Jencova, V., Suchy, T., Heczkova, B., Jakubkova, S., Jirousova, J., Prochazkova, R., 2018. Comprehensive assessment of electrospun scaffolds hemocompatibility. Mater. Sci. Eng. C 82, 330–335. https://doi.org/10.1016/j.msec.2017.05.011

Alternating current electrospinning and thermal processing for fabrication of boron-alumina nanofibers

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Introduction: Boron alumina with various compositions is part of a B_2O_3-Al_2O_3 system of ceramic materials, where the primary phase ($Al_{18}B_4O_{33}$) is most stable and useful for many structural, insulating, and filtering applications. In nanofiber form, the material exhibits exceptional mechanical properties and is stronger than pure alumina nanofibers. Various fabrication processes and material compositions have been investigated. This study explores the structure and morphology characteristics of boron alumina nanofibrous ceramic fabricated using alternating field electrospinning (AFES) followed by thermal processing of as-spun precursor fibers. The AFES method efficiently generates fibers that do not have electric charge, which makes the fibers easier to handle since the collector used does not have to be conductive as is required in other electrospinning methods.

Materials/Methods: The boron alumina precursor fibers were produced from aluminum acetate with boric acid using a carrier polymer solution. Salt/PVAc precursor mass ratios and concentrations were first optimized for maximum production and flow rate. AFES was then used to produce Aluminum salt/PVAC precursor fibers. The spun fibers were annealed at selected temperatures from 600 to 1200°C. XRD was used to determine the dependence of fiber crystallization on temperature, as well as phase composition and crystallite size at each temperature. SEM with EDS detector was used to determine the surface morphology and diameters of the fibers, as well as elemental composition.

Results: The electrospinning rate was 0.9-1.1mL/min has been observed in present experiments, producing about 35mg material (in terms of the resulting ceramic material) per mL solution. XRD and SEM showed that the produced alumina borate possessed quality structure, ~400 ±100 nm fiber diameter, and smooth surface morphology characteristics up to 1000 °C. The fibers maintained their shape but had a grainier and more porous appearance

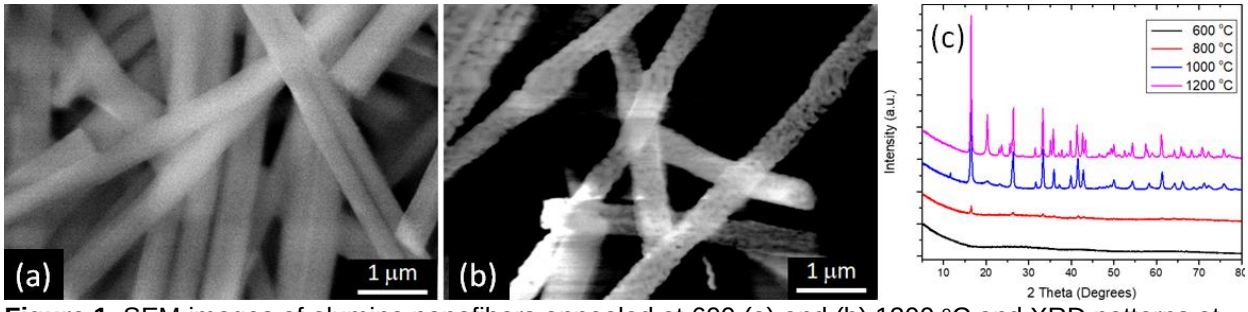

Figure 1. SEM images of alumina nanofibers annealed at 600 (a) and (b) 1200 °C and XRD patterns at of the material after thermal processing at different temperatures.

with ~60 nm crystallite size after 1200°C annealing, as determined from the SEM images and XRD patterns (see Fig.1). XRD patterns compared at each temperature indicated crystallization starts around 800 °C and the degree of crystallization increases with temperature and the sample was composed of mostly $Al_{18}B_4O_{33}$ phase at 1200°C along with some $Al_4B_2O_9$ at 1000°C. Small amounts of a-Al_2O_3 crystalline phase has been also observed at that temperature due to loss of boron, which has been confirmed by EDS analysis.

Conclusions: Boron alumina of usable quality has been successfully produced by AFES at promising and scalable production rates. It has been determined that using a single electrode, the AFES production rates of 4.2 g/h in terms of the resulting ceramic can be obtained. Future studies will be focused on further optimization of the electrospinning process and on the investigation of the mechanical properties of 3D structures composed of this ceramic material to evaluate the applicability potential in membranes and catalyst support.

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References:

Dong, Y., Dong, X., Li, L., Wu, J., Yan, L., Liu, J., Guo, A., *Lightweight and thermally insulating aluminum borate nanofibrous porous ceramics,* Ceram. Int., 47, 21029-21037 (2021).

Hernández, M., Suárez, G., Cipollone, M., Conconi, M., Aglietti, E., Rendtorff, N., *Formation, microstructure and properties of aluminum borate ceramics obtained from alumina and boric acid,* Ceram. Int., 43, 2188-2195 (2017).

Song, X., Liu, W., Wang, J., Xu, S., Liu, B., Liu, J., Ma, Y., *Microstructural differences between electrospun alumina borate nanofibers prepared by solutions with different PVP contents*, Ceram. Int., 43, 9831-9837 (2017).

Stanishevsky, A., Brayer, W. A., Pokorny, P., Kalous, T., Lukáš, D., *Nanofibrous alumina structures fabricated using high-yield alternating current electrospinning*, Ceram. Int.,42, 17154-17161 (2016).

Electric wind phenomenon in AC-electrospinning

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Introduction: Electric wind is formed by generating ions that can be accelerated by an electric field. Through this acceleration, the ions transfer momentum to surrounding neutral atoms and molecules. The electric wind phenomenon is very pronounced in the AC-electrospinning (a.k.a. alternating force electrospinning, AFES) process. The creation of a virtual counter electrode and effect on the electric wind in the presence of a nanofibrous plume during AC electrospinning have been investigated [1]. However, little is known on the effect of parameters such as AC voltage, frequency, and electrode shape on the electric wind in this process. This investigation is a part of an ongoing effort to advance the understanding of this vital component in the production of nanofibers using AC-electrospinning.

Materials and Methods: An experimental AC-electrospinning setup that operated at 50 Hz and up to 36 kV rms AC voltage with several electrode shapes has been used. A hot-wire anemometer was used to measure the electric wind ~250 mm above a rod, pin, and disk-shaped electrode. Experiments were run on all three electrodes at a 50 Hz frequency and various voltages (21, 28, and 35 kV). Another group of tests was done when a fish gelatin polymer solution with 80 wt% concentration was present. Additional experiments have also been planned by using a high-speed camera to capture the beginning and end of the process to visually observe the behavior of the nanofibrous plume at different voltage and frequencies, where possible.

Results: When AC voltage is applied, the electric wind develops and reaches its relatively steady velocity state within 1-2 seconds. Electric wind has been found to depend strongly on the voltage, electrode shape and the axial distance away from the electrode (Fig.1) but relatively little on the radial position within 10 cm radius.

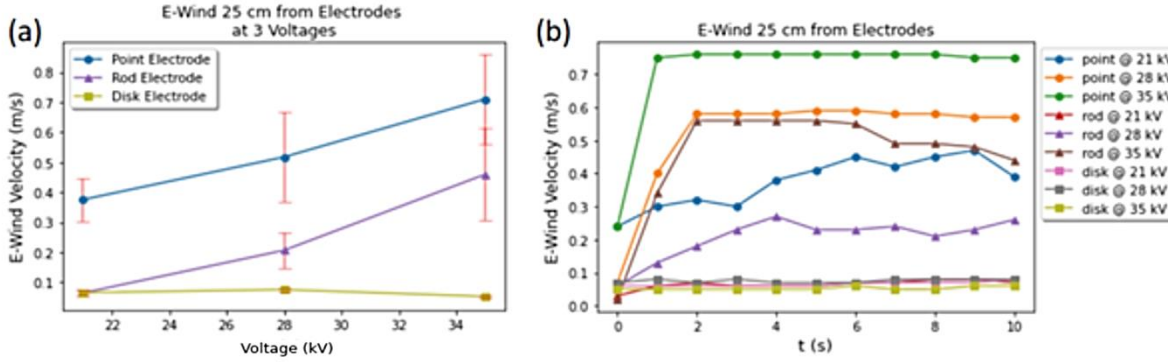

Figure 1: Effect of changing voltages on electric wind velocity (a) and effect of different electrode shapes on wind velocity over time (b).

For the disk electrode, velocity does not change much as a function of the voltage when measured above the axis. This contradicts the results obtained with pin and rod electrode shapes as well as the general trend established by Drews et al [2]. This can happen due to the increased surface area and sharp edge of the disk that pushes the wind at a much steeper angle compared to the point and rod electrodes. Further investigation is required to describe the wind velocity and geometry of the electric field for such electrodes. The wind speed at 25 cm axial distance above the rod-shaped electrode varied from 0.03 to 0.56 m/s and it was

noticeably impacted by the voltage and the stability of corona discharge around the electrode. When a layer of highly viscous, non-spinnable precursor was present on the electrode, the wind speeds were relatively close to their magnitudes measured without the liquid layer.

Conclusions: The results of present experiments indicate an obvious change in wind velocity when the shape of the electrode is changed. They also show the relative uniformity of electric wind at a given distance away from the electrode within a cylinder of the radius 4.5 mm. This uniformity is present regardless of the presence of a highly viscous solution even at differing AC voltages. More studies are planned to further the understanding of this key phenomenon in AC electrospinning process.

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References: [1] Pokorny P, Kostakova E, Sanetrnik F, Mikes P, Chvojka J, Kalous T, Bilek M, Pejchar K, Valtera J, Lukas D. Effective AC needleless and collectorless electrospinning for yarn production. Phys Chem Chem Phys. 2014 Dec 28;16(48):26816-22. doi: 10.1039/c4cp04346d. PMID: 25373725.
[2] Drews, Aaron & Cademartiri, Ludovico & Whitesides, George & Bishop, Kyle. (2013). Electric winds driven by time oscillating corona discharges. Journal of Applied Physics. 114. 143302. 10.1063/1.4824748.

Fish Gelatin and Dextran Composite Electrospun Nanofibers

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Introduction: In recent years, nanofibrous materials have shown promising potential in the field of biomedical engineering due to their high surface-area to pore ratio [1], which promotes cell growth and drug delivery [2]. One highly efficient but less explored method of producing nanofibrous materials for drug delivery and tissue scaffolding is Alternating Field Electrospinning (AFES, a.k.a. AC-electrospinning). Fish gelatin has recently been studied as a prospective material due to its biocompatibility, ease of spinnability, and natural sourcing [1, 3]. However, fish gelatin is easily soluble in water and requires an additional step of crosslinking to engineer the material for biological purposes. This research focuses on the effect of crosslinking fish gelatin nanofibrous material through the sugar additive dextran for the purpose decreasing the solubility of the material and enhancing the mechanical properties for cell proliferation and drug delivery.

Materials & Methods: Precursors were created by blending cold water fish gelatin (fGel, Sigma Aldrich) and dextran with molecular weight of 75,000 (DT75, Sigma Aldrich) or 500,000 (DT500, Sigma Aldrich) in deionized water at room temperature with weight ratios ranging from 35:100 to 45:100 (fGel:H2O) with 0.01–0.1 DT75 or DT500 to fGel ratio. Precursors were spun into nanofibers on an AFES machine at RMS voltages ranging from 26 to 39 kV at 60 Hz AC frequency. Optimized precursors were spun into sheets measuring 1-2 mm thick. Sheets were crosslinked with different combinations of crosslinking methods including freeze drying (FD), thermal crosslinking (TC), and 50 wt% glutaraldehyde aqueous solution (GTA, Sigma Aldrich). Tensile testing (ADMET eXpert 4000 microtester) was performed on crosslinked sheets to measure the mechanical properties of the nanofibers. Degradation tests and cell studies were performed *in-vitro* on the sheets to assess *in-vivo* capability.

Results: Criteria for selecting optimal precursors included a steady flow rate, consistent fiber diameter, and lack of buildup on the electrode during AFES. Optimal additive concentrations were determined by these criteria through observational analysis during AFES. The best spinnable precursor compositions of fGel and dextran were 45:2.7:100 (fGel:DT75:H_2O) and 45:2:100 (fGel:DT500:H_2O). SEM imaging of non-crosslinked sheets spun from the DT75 precursor show nonaligned nanofiber morphology with moderate beading and an average diameter of 177 nm (□=53 nm), while those from the DT500 precursor show non-aligned, beadless nanofiber morphology with an average diameter of 401 nm (□=107 nm) (Figure 1). Preliminary results on the SBF degradation of the cross-linked nanofibers with mentioned compositions indicate that thermally induced crosslinking followed by GTA treatment (TC+GTA) and freeze-drying of as-spun material followed by thermally induced cross-linking (FD+TC) outperformed other approaches of cross-linking for tested materials. These two crosslinking methods allowed the fGel fibers to retain the most mass –TC+GTA mass retention was 94.6% while FD+TC mass retention was 87.3%– after being in synthetic body fluid for

three days as compared to other methods. Tensile testing results also indicate FD+TC to be one of the best crosslinking methods for enhancing the mechanical properties of scaffolds as seen through higher elastic moduli in both DT75 and DT500 sheets.

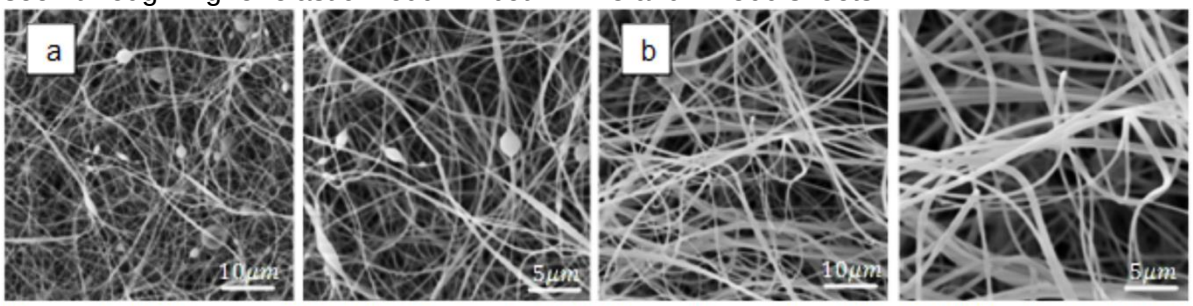

Figure 1. SEM image of fGel+DT75 untreated AFES nanofibers (a) and fGel+DT500 untreated AFES nanofibers (b).

Conclusion: Nanofibrous materials made from fish gelatin and dextran of different molecular weights were successfully spun using AFES, and when compared to pure fGel degradation tests were shown to degrade slowly enough to be able to be *in-vitro* tested to further validate it as a biomaterial. Preliminary results show the fGel materials as good potentials in applications such as tissue scaffolds and drug delivery. Further studies will be conducted to compare the effects of the different cross-linking methods and assess which method renders the best *in-vitro* capabilities of the materials.

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References:

[1] A. Kennell, M. MacEwen, M. Armstrong, T. Nicola, B. Halloran, N. Ambalavanan, A. Stanishevsky, Fish skin gelatin nanofibrous scaffolds spun using alternating field electrospinning and in-vitro tested with tdTomato mice fibroblasts, Mater. Today Comm. 31 (2022) Art. # 103417 https://doi.org/10.1016/j.mtcomm.2022.103417

[2] G. Sun, J. J. Mao, Engineering dextran-based scaffolds for drug delivery and tissue repair, Nanomedicine (Lond), 2012. https://www.ncbi.nlm.nih.gov/pmc/articles/PMC4620435/

[3] S. R. Gomes, G. Rodrigues, G. G. Martins, M. A. Roberto, M. Mafra, C. M. R. Henriques, J. C. Silva. In vitro and in vivo evaluation of electrospun nanofibers of PCL, chitosan and gelatin: a comparative study. Mater Sci Eng C Mater Biol Appl. 2015 Jan; 46:348-58. doi: 10.1016/j.msec.2014.10.051. Epub 2014 Oct 23. PMID: 25491997.


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