ISSN 2348 – 7968

MWCNT-doped Nylon electrospun fibers as materials for increasing damage tolerance of CFRPs in structural applications

Alexandros Repanas[1#], Athanasios Kotrotsos[2#], Vassilis Kostopoulos[2] and Birgit Glasmacher[1]

[1] Institute for Multiphase Processes, Mechanical Engineering Department, Leibniz Universität Hannover, Hannover, 30167, Germany

[2] Department of Mechanical and Aeronautical Engineering, University of Patras, Rio, 26504, Greece

[#] These authors equally contributed to the paper

Abstract

Fibrous layers made by electrospinning are considered to be promising in the material science field, including aerospace composite structures. Electrospinning is an inexpensive technology that can create non-woven formulations. Nylon derivatives are polymeric materials that can be utilized in electrospinning. Carbon nanotubes (CNTs), have been studied as an additive element to enhance material properties, such as mechanical performance, electrical and thermal conductivity. Main aim of this work was to engineer and characterize Nylon electrospun fibers with and without MWCNTs doping and study whether the introduction of CNTs improved the properties of the fibers. The obtained results indicate that doping Nylon fibers with MWCNTs led to reduced apparent tensile properties, and provided thinner fibers with a more hydrophilic surface. Taken together, MWCNT doped nylon fibers can be further studied as candidates for incorporation into carbon fiber reinforced (CFRPs) structural composites in the form of interleafs for increasing damage tolerance characteristics.

Keywords: *Aerospace engineering, Electrospinning, Fibers, MWCNTs, Nylon.*

1. Introduction

During the last two decades, electrospinning has attracted worldwide attention in the material research community as a cutting-edge method for the fabrication of non-woven materials in the micro- and nanoscale. It involves the application of an electrical field to generate fibers from polymeric and other material blends. It is an inexpensive, versatile, top-down technique to generate formulations of different shape and size [1]. A typical electrospinning instrument consists of three basic parts: a power supply, a solution reservoir connected with a nozzle and a collector [2, 3]. Different process parameters, such as the applied voltage or the solution flow rate can determine the morphological, physical and mechanical properties of the fibers [4].Taken together, it has shown great potential in the fields of filtration, batteries, biomedicine and composite materials due to the wide range of materials that could be utilized [2 – 5].

Nylon is a polyamide polymer that has been used as material in textile and plastic industry. It can be dissolved in formic acid (FA) and has a high melting point (268.6^{o}C) [6]. Carbon nanotubes (CNTs) are cylindrical carbon structures with their length being significantly larger than their other dimensions that belong to the fullerene family [7]. Their properties (thermal conductivity, electrical properties) are affected by their nanostructure and have been used in various applications [8].They can be categorized in single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). Lately, on the focus of various researchers has been the enhancement of the mechanical properties of high performance structural composites. CNTs can be employed in order to enhance the mechanical properties (i.e. fracture and fatigue behavior) of polymers and composites [9, 10] because of their ability to act as a reinforcing phase at the nano-scale. Their superb properties (i.e. large aspect ratio, specific surface area, high longitudinal modulus) have attracted the attention of the researchers worldwide. To this end CNTs may be employed as fillers for polymeric matrices. The scope of the current investigation was the fabrication of pure and MWCNT doped Nylon electrospun fiber mats, using the electrospinning method. Finally the effect of the MWCNTs on fiber's structural, physical and mechanical properties was also assessed. In future work both types of fabricated electrospun mats are intended to be incorporated into CFRPs in the form of interleafs between the layers in order the fracture behavior of the composites to be improved.

ISSN 2348 – 7968

2. Materials and Methods

2.1 Materials

The pure Nylon that was utilized in the current investigation was the copolyamide Griltex D 1330A and was purchased from Emsgriltech, Switzerland. The Formic acid (FA) which played the solvent role was purchased from Sigma Aldrich. Finally the type of the MWCNTs that were utilized was the NC7000 and was supplied by Nanocyl, Belgium, produced via the Catalytic Chemical Vapor Deposition (CCVD) process. Typical MWCNTs diameter is in between 10-20 nm and their aspect ratio span was in between 50-100. All materials and reagents were used as received without any further purification or functionalization.

2.1 Solution preparation and electrospinning

Nylon and MWCNTs were dissolved in FA. The total concentration of both materials in the solution was 10 wt%. Three different solutions were created, one without MWCNTs, one with 2 wt% and a third one with 3 wt% MWCNTs. All blend solutions were constantly stirred for 48 h at room temperature in order to achieve homogeneity. Each solution was transferred into 10 ml syringes (Omnifix, B. Braun) for electrospinning. The solution flow rate for all samples was kept stable at 0.2 mL/h in order to achieve a stable process. The applied voltage was kept constant at 20 kV in order to achieve continuous jet formation. The distance between the tip of the nozzle and the collector was kept constant at 15 cm. Disposable blunt-tipped needles (Nordson EFD) of an inner diameter of 0.21 mm were used. A grounded, square aluminum collector (15×15 cm^2) was used to collect the samples. Electrospinning was performed at room temperature. The samples were removed from the collector and left to dry for 24 hours at room temperature.

2.2 Electrical conductivity

The electrical conductivity of all the different solutions with and without MWCNTs was measured using a conductometer (Seven Multi, Mettler Toledo AG). 3 mL of each solution were measured at room temperature (n=5).

2.3 Scanning electron microscopy (SEM) and transmission electron microscopy (TEM)

Square strips of 5×5 mm^2 were punched out from each electrospun specimen and were sputter coated with Au/Pd for 30s, before being placed inside the SEM instrument (S3400N, Hitachi) under high vacuum. An accelerating voltage of 15 kV, and magnification rates of 500x, 1000x, and 2000x were used for the morphological and structural analysis of the fibers. In order to determine the average diameter of the electrospun fibers, pictures obtained at 2000x magnification were processed using the image analysis software ImageJ (NIH) (n=50).
Circular carbon coated copper grids (200 mesh) with diameter 3.05 mm were utilized for the TEM characterization experiments for both the Nylon and MWCNT doped Nylon nano-fibers. These grids were positioned carefully on the collector's surface, in order the electrospun fibers to be deposited during the electrospinning process. The TEM instrument model was the JEM-2100/ HR-TEM which was produced by JEOL and operated at 200 kV.

2.4 Static water contact angle assay

Square strips of 5×5 mm^2 were punched out from each specimen to investigate the contact angles of water droplets on the surface of the fiber mats, using an optical contact angle apparatus (FM40 Easydrop, Krüss). Measurements were taken at 0s after a single droplet of bi distilled water (1μL) got in contact with the surface of the fiber mats. All measurements were performed at room temperature (n=5).

2.5 Tensile tests

Rectangular samples of 15 mm gauge length and 10 mm width were punched out from each specimen. The thickness of each specimen was measured with a thickness gauge (Quick mini, Mituotoyo). Duct tape was carefully placed at each edge of the samples to improve the mounting on the metallic grips of the testing device. Uniaxial tensile tests were conducted on an Electroforce Planar Biaxial tensile instrument with a 200 N load cell (TA Instruments). Ultimate tensile strength (UTS), strain at the maximum force and Young's modulus were measured and analyzed. All experiments were performed at room temperature until sample failure at a strain rate of 20 mm/min (n=6).

2.6 Statistical analysis

All data are expressed as mean ±standard deviation, unless mentioned otherwise. One-way analysis of variance (ANOVA) with post hoc Tukey means comparison tests were conducted and p values < 0.05 were considered significant.

3. Results and discussion

3.1 Structural and morphological analysis

As showcased in Figure 1, no fibers with beads were detected by SEM on the surface of the electrospun specimens. Figures 1A, 1B and 1C correspond to pure Nylon, 2 wt% MWCNT doped and 3 wt% MWCNT doped samples, respectively. In Figure 1D the formation of the Taylor cone at the tip of the needle is presented. In all cases, smooth, cylindrical, bead-less fibers were fabricated consisting of dense networks with no particular alignment (Figure 1). The average fiber diameter (and distribution of values) related with the concentration of MWCNTs in the solutions is depicted in Figure 1. The average fiber diameter decreased with the increase in MWCNTs concentration from 146.49±36.16 nm for pure Nylon fibers to 131.59±28.60 nm for the specimens with 2 wt% MWCNTs and to 107.39±19.65 nm for the 3 wt% MWCNTs specimens. All the obtained values followed a normal distribution and differed significantly to each other ($p<0.001$).

It can be expected that the addition of MWCNTs in the solution altered the solution parameters, such as the electrical conductivity which will be thoroughly discussed later [3, 4, 10, 11]. A possible explanation for this result could be that the MWCNT molecules inside the polymeric solutions contribute to the electrostatic charge build-up during electrospinning, due to the high electrical conductivity of MWCNTs. As the jet exits the tip of the nozzle, it reinforces the effect of the electric field, resulting in thinner fibers. Another possible explanation for the reduction in the average fiber diameter is that the addition of MWCNTs possibly lowered the surface tension of the polymeric solution, enhancing the bending instability during electrospinning [12].

Figure 2 contains TEM images for both the pure and MWCNT doped nanofibers. As it is shown TEM experiments validated the fiber diameter values which were calculated during the SEM examination tests as well as the behavior in which the fiber diameter trends to decrease with the increase in MWCNTs concentration. In Figure 2A the pure Nylon nanofibers is clearly distinguished while in Figure 2B the strong presence of the MWCNTs into the Nylon nanofibers is distinguished too. Additionally in Figure 2B a pulled out MWCNT is observed after the fracture of a doped Nylon nanofiber.

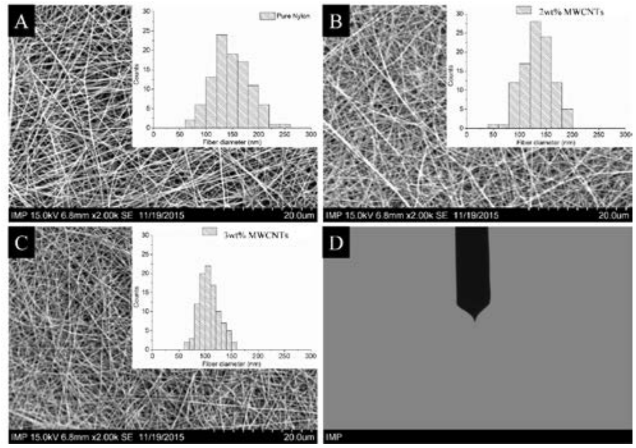

Fig. 1 . SEM pictures of electrospun Nylon fibers with different MWCNTs concentration (A = Pure Nylon), (B = 2wt% MWCNTs), (C = 3wt% MWCNTs); Taylor cone during electrospinning (D); magnification was set at 2000×; scale bars represent 20 μm; 15 kV accelerating voltage; Histograms of fiber diameter distribution; n=50.

3.2 Physical characterization

The addition of MWCNTs to the polymeric solutions significantly increased the electrical conductivity values. This property can be directly correlated with the decreased fiber diameter that was previously reported [4]. Increased electrical conductivity could have resulted in higher bending instability of the polymeric solution that is ejected towards the collector inside the electrical field, thus increasing the elongation of the jet and consequently resulting in thinner fibers. The electrical conductivity of the polymeric solutions was increased from 5.67±0.63 μS/cm in the absence of MWCNTs to18.37±1.21 μS/cm for a concentration of 2 wt% and to 35.82±1.54 μS/cm for 3 wt% ($p<0.001$). This significant increase in the conductivity values can be explained due to the sufficient transfer of charges into the jet [3, 11, 12].

A static water contact angle assay was conducted to study the influence of the addition of MWCNTs, on the surface hydrophilicity of the fiber mats. Results showed that when the concentration of MWCNTs in solution increased, there was also an increase in the hydrophilicity of the surface of the electrospun fibers (Figure 3). More specifically, the average static contact angle for the scaffolds without MWCNTs was 119.85±4.89^{o}. For the specimens with MWCNTs concentration 2 wt% and 3 wt%, the average contact angles were 104.49±2.67^{o} and 85.83±4.65^{o}, respectively. Statistically significant differences were observed between specimens ($p<0.001$) while the concentration of 3 wt% led to relatively hydrophilic fibers (contact angle < 90^{o}). This change could be very crucial

ISSN 2348 – 7968

for material applications that require the surface of a structure to be either hydrophilic or hydrophobic and thus the use of CNTs can be a very useful tool to regulate this property. Additionally, the average fiber diameter would play an important role in the hydrophilicity of the surface of the fibers since it affects the surface area-to-volume ratio [1, 3, 4, 12, 13]. Nevertheless, this property has to be further examined in the future and be correlated with other characteristics of the fibers for a more complete material profile.

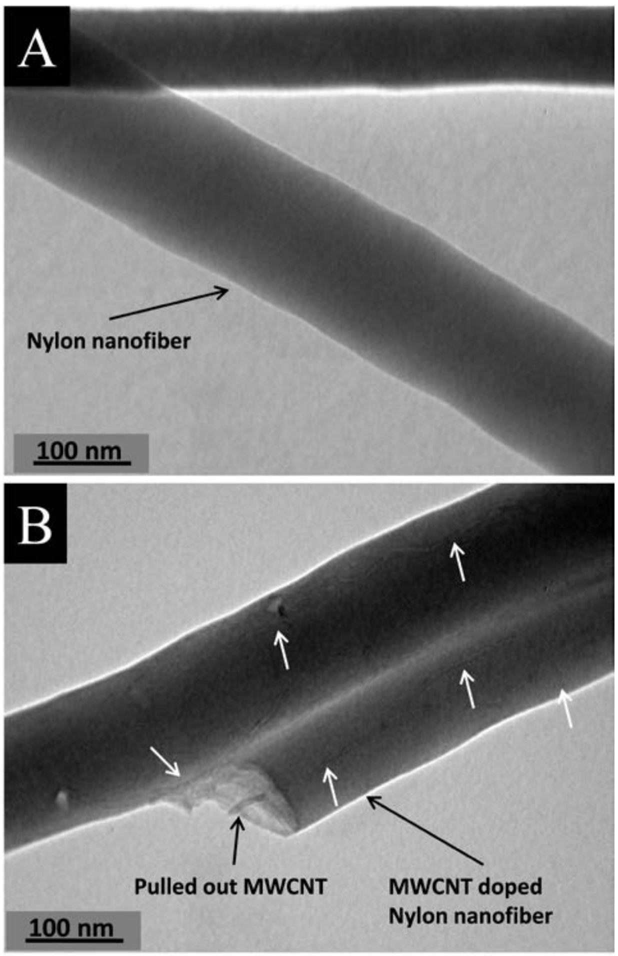

Fig. 2 TEM pictures of A) pure Nylon nanofibers and B) 2 wt% MWCNTs doped Nylon nanofibers in which the presence of the MWCNTs is clearly distinguished and marked (white darts); scale bars represent 100 nm.

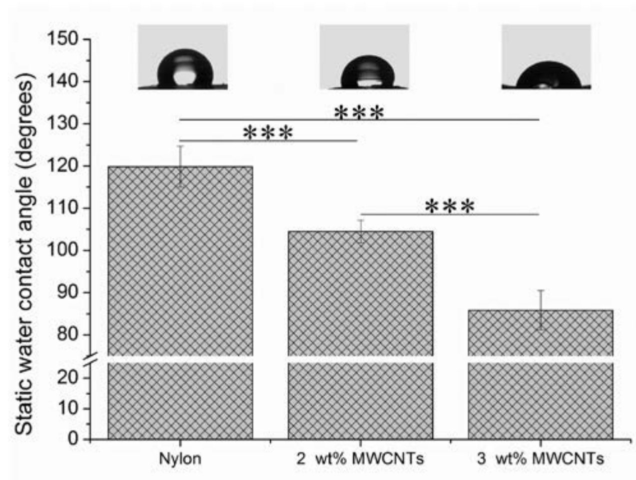

Fig. 3 . Influence of the concentration of MWCNTs on the average static contact angle of water droplets formed on the surface of the samples; n=5, mean ± SD.

3.3 Mechanical characterization

Figure 4 summarizes all mechanical testing data. It is worth to mention here that all the reported mechanical properties are apparent mechanical properties of the formed electrospun scaffolds. Increasing MWCNTs concentration led to decreased values of UTS, from 31.37±0.53 MPa for pure Nylon fibers to 9.22±0.80 MPa for 2 wt% MWCNTs and to 7.90±0.24 MPa for 3 wt% MWCNTs (Figure 4A). Tensile strain values at maximum load were within the range of 25-40% for all specimens. For Nylon fibers, tensile strain was 39.22±1.31%. In the case of MWCNT-doped fibers, the tensile strain reached the values of 36.37±2.90% and 26.80±3.02% for the 2 wt% and 3 wt%, respectively (Figure 4B). Young's modulus values calculated from the linear slope of the stress-strain curves exhibited similar trends with UTS (Figure 4C). More specifically, Young's modulus values dropped from 141.58±24.73 MPa for the Nylon specimens down to 45.50±8.04 MPa for the 2 wt% samples, down to 40.30±0.96 MPa for the 3 wt% samples, respectively. Other groups have also studied how parameters such as material concentration can influence fiber diameter and alignment and eventually the apparent mechanical properties of the resulted fiber mat [14 – 16].The decrease in the average fiber diameter has affected the mechanical properties, especially UTS and Young's modulus. For those two properties, no significant difference between the obtained values was observed ($p>0.05$). However, besides average diameter, fiber alignment is another parameter that needs to be carefully addressed, both qualitatively and quantitatively in order to precisely determine the influence of the scaffolds' micro-structure on the mechanical properties. Hence, it was crucial to determine if the architecture can be controlled sufficiently through parameter optimization. Furthermore, a crucial parameter that may affect the apparent mechanical properties of the resulted mat scaffolds is the affinity between the resulted fibers at the mat level. Low affinity leads to an internally sliding structure, and although at fiber level the presence of MWCNTs results to more brittle fibers, the overall apparent mat behavior keeps high strain to failure values. Another reason for the decrease of the apparent mechanical properties of the resulted mat structures in the presence of MWCNTs could be the miscibility of the solutions with MWCNTs. While the Nylon solution was fully homogenized, the solutions containing MWCNTs had the nature of a suspension rather than a solution. Therefore, during the electrospinning process the elongated jet was more prone in breaks and the process was less stable at times. Hence, a more careful study of the most appropriate MWCNT concentration as well as a more appropriate solvent system has to be studied in future research.

A comparison with values from the literature is difficult because of the nature of the testing processes and the different protocols that can be followed. Taken together, the introduction of MWCNTs in the polymeric solution led to lower UTS, tensile strain and Young's modulus. Therefore, the concentration of CNTs has to be considered when specific requirements in terms of mechanical properties are concerned. It could be another tool to modulate those properties.

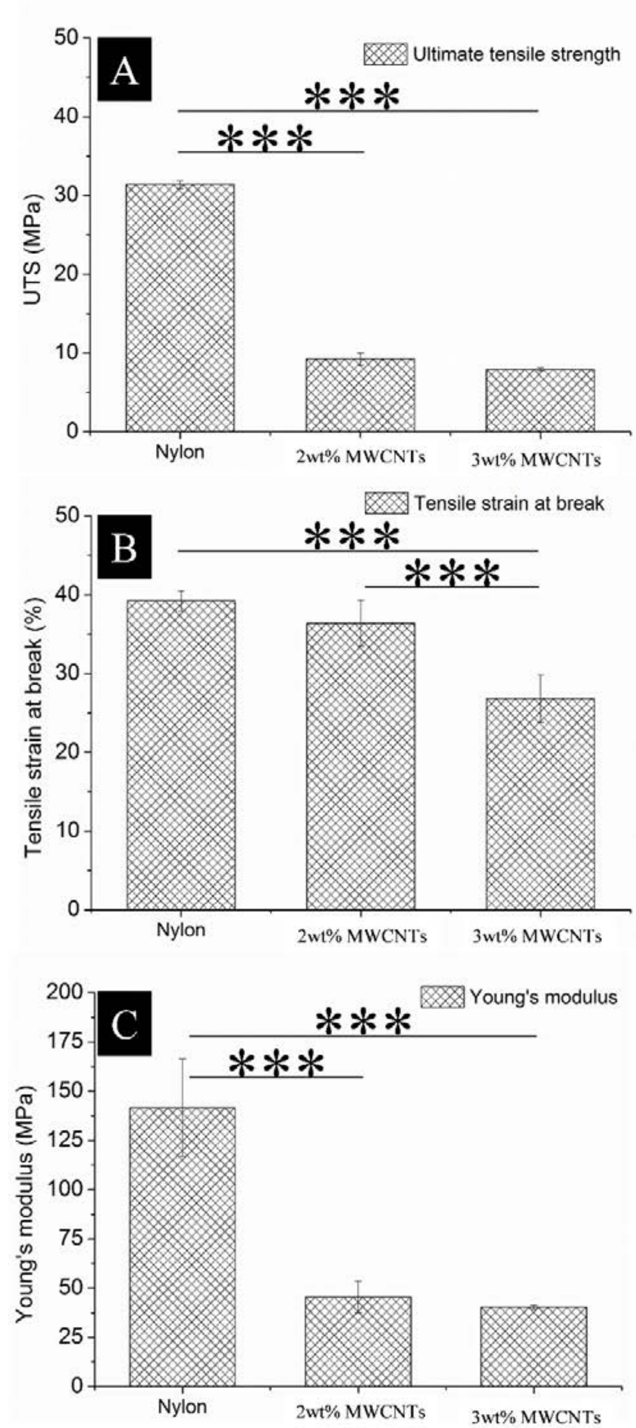

Fig. 4 Tensile properties of electrospun Nylon scaffolds at different MWCNT concentrations. Ultimate tensile strength (UTS) (A); Strain at break (B); and Young's modulus(C); n=6, mean ± SD.

4. Conclusions

In a nutshell, electrospun nylon fibers with and without MWCNTs were fabricated and characterized as promising candidates for materials used in the manufacturing process. Future research will focus on the use of different polymeric blends and the study of different electrospinning parameters in order to modify the fibers properties.

Acknowledgments

This research was granted (DFG EXC 62/1) by the German Research Foundation (Deutsche Forschungsgemeinschaft, DFG) and by the European Union within the frame of Erasmus placement programme (2015-2016).

References

[1] A. Szentivanyi, H. Zernetsch, H. Menzel, and B. Glasmacher, "A review of developments in electrospinning technology: New opportunities for the design of artificial tissue structures", Int J Artif Organs, 34, 10, 2011, pp. 986–997.

[2] B. Sun, Y.Z. Long, H.D. Zhang, M.M. Li, J.L. Duvail, X.Y. Jiang, and H.L. Yin, "Advances in three-dimensional nanofibrous macrostructures via electrospinning", Prog Polym Sci., 39, 5, 2014, pp. 862–890.

[3] T.J. Sill, and H.A. von Recum, "Electrospinning: Applications in drug delivery and tissue engineering", Biomaterials, 29, 13, 2008, pp.1989–2006.

[4] N. Okutan, P. Terzi, and F. Altay, "Affecting parameters on electrospinning process and characterization of electrospun gelatin nanofibers", Food Hydrocoll., 39, 2014, pp. 19–26.

[5] P. Akangah, S. Lingaiah, and K. Shivakumar, "Effect of Nylon-66 nano-fiber interleaving on impact damage resistance of epoxy/carbon fiber composite laminates", Composite Structures, 92, 2010, pp. 1432-1439.

[6] R.J. Palmer, "Polyamides, Plastics", Encyclopedia of Polymer Science and Technology, 2001.

[7] X. Wang, Q. Li, J. Xie, Jin Z, J. Wang, Y. Li, K. Jiang, and S. Fan, "Fabrication of Ultralong and Electrically Uniform Single-Walled Carbon Nanotubes on Clean Substrates", Nano Lett., 9, 9, 2009, pp. 3137–3141.

[8] S. Gullapalli, and M.S. Wong, "Nanotechnology: A Guide to Nano-Objects", Chemical Engineering Progress, 107, 5, 2011, pp. 28–32.

[9] V. Kostopoulos. P. Tsotra, P. Karapappas, A. Vavouliotis, S. Tsantzalis, and T. Tanimoto, "On the improvement of toughness of CFRPs with resin doped with CNF and PZT particles", Compos. Sci. Technology, 67, 2007, pp. 822-828.

[10] A. Vavouliotis, P. Karapappas, T. Loutas, P. Voyatzi, A. Paipetis, and V. Kostopoulos, "Multistage fatigue life monitoring on carbon fibre reinforced polymers enhanced with multiwall carbon nanotubes", Plastics, Rubber and Composites, 38, 2009, pp. 124-130.

[11] C.J. Thompson, G.G. Chase, A.L. Yarin, and D.H. Reneker, "Effects of parameters on nanofiber diameter determined from electrospinning model", Polymer, 48, 23, 2007, pp. 6913–6922.

[12] B. Cramariuc, R. Cramariuc, R. Scarlet, L.R. Manea, I.G. Lupu, and O. Cramariuc, "Fiber diameter in electrospinning process", J Electrost., 71, 3, 2013, pp. 189–198.

[13] C.K. Lee, S.I. Kim, and S.J. Kim, "The influence of added ionic salt on nanofiber uniformity for electrospinning of electrolyte polymer", Synth Met., 154, 1–3, 2005, pp. 209–212.

[14] A. Frenot, and I.S. Chronakis, "Polymer nanofibers assembled by electrospinning", Curr Opin Colloid Interface Sci., 8, 1, 2003, pp. 64–75.

[15] A. Saraf, G. Lozier, A. Haesslein, F.K. Kasper, R.M. Raphael, L.S. Baggett, and A.G. Mikos, "Fabrication of Nonwoven Coaxial Fiber Meshes by Electrospinning", Tissue Eng Part C Methods, 15, 3, 2009, pp. 333–344.

[16] T. Stylianopoulos, C.A. Bashur, A.S. Goldstein, S.A. Guelcher, and V.H. Barocas, "Computational predictions of the tensile properties of electrospunfibre meshes: Effect of fibre diameter and fibre orientation", J Mech Behav Biomed Mater., 1, 4, 2008, pp. 326–335.

Alexandros Repanas Dr. rer. nat. 2012-2016, M.Sc. 2010-2013, Dipl.-Pharm. 2005-2010; Institute for Multiphase Processes, Leibniz University Hannover, Germany, 2012-present; 8 papers published; Biomaterials, Electrospinning, 3D-printing

Athanasios Kotrotsos PhD candidate 2012-prsent, M.Sc. 2009-2011, Dipl.-Ing. 2002-2008; Department of Mechanical and Aeronautical Engineering, University of Patras, Greece 2005-present

Vasillis Kostopoulos is a Professor in University of Patras Greece and director of .the Laboratory of Applied Mechanics and Vibrations, University of Patras, Greece. He is also a Member of the Advisory Council for Aerospace Research in Europe (ACARE).

Birgit Glasmacher is a Professor in Leibniz University Hannover, Germany and head of the Institute of Multiphase Processes. She is also a former President of EAMBES / European Alliance for Medical and Biological Engineering & Science.