October 21-22, 2021 Online
TEX TEH X
INTERNATIONAL CONFERENCE ON TEXTILES AND CONNECTED R&D DOMAINS

PREDICTIVE MATEHMATICAL MODEL FOR ABSORBANT SUBSTRATE ACHIEVEMENT, THROUGH ELECTROSPINNING PROCESS

DOI: 10.35530/TT.2021.59

C. Mihai[1], A.G. Ene[1], R.-G. Hertzog[2], D. Popescu[2], A.F. Vladu[1]

[1]IT Research Department in Industrial Engineering, National Research Development Institute for Textiles and Leather, Romania
(E-mail: carmen.mihai@incdtp.ro)
[2]Biological Research Department, "Cantacuzino" National Institute of Research, Bucharest, Romania
(E- mail: office.cantacuzino@mapn.ro)

Abstract: *The new generations of wound dressings aim to create an optimal environment that allows epithelial cells to move easily in order to support regeneration. Such optimal conditions include a humid environment around the wound bed, efficient oxygen circulation to help regenerate cells and tissues, and low bacterial contamination. Composite matrices have several layers and can be used as primary or secondary dressings. Most composite dressings have three layers, respectively a semi-adherent or non-adherent layer, an absorbent layer, and a bacterial barrier layer. A method to obtaining these materials, which can be assimilated to layer-by-layer deposition, or which can be operated in this regime, is represented by electrospinning. However, the deposition technique by electrospinning on textile surfaces (fabrics or nonwovens) raises some problems related to the electrostatic behaviour of textile fibres with dielectric properties. In this case, the characteristics of the jet are affected directly proportional with the thickness of the textile material, resulting in defects of nano- or micro-fibrillar deposition, such as unevenness and/or sputter (formation of drops, which are deposited in mixture with electro spun fibres). The article presents a mathematical model that predicts the diameter of the fibres in the composition of the absorbent layer of the multilayer matrix structure for the treatment of burns or gunshot wounds, taking into account the nonlinear relationships between the parameters explained above and specific theories of electrodynamics for thin profiles (for instance, those used in aeronautics) for the prediction of the behaviour of the electrospinning jet.*

Keywords: *cellular matrix, electrospinning, mathematical modelling, textile substrate, skin regeneration*

1. INTRODUCTION

Studies worldwide have shown that for biomedical applications, in case of the development of multilayer matrices for the treatment of wounds caused by burns or by shooting, the adhesion of fibroblast cells and their migration depends on the diameter of the fibres in the textile structure [1]. A method that can be assimilated to layer-by-layer deposition, or that can be operated in this regime, is represented by electrospinning. The resulting irregular layer of nanofibers can then be further processed by compration/fusion in the form of extremely thin films, or by physico-chemical functionalization (for instance in cold plasma), followed by the continuation of deposition by the same technique, but using a different composition, or by any other technique [2,3].

However, the technique of deposition by electrospinning on textile surfaces (fabrics or nonwovens) raises some problems related to the electrostatic behaviour of textile fibres with dielectric properties. In their case, the characteristics of the jet are affected in directly proportional to the thickness of the textile material, resulting in defects of nano- or micro-fibrillar deposition, such as unevenness and/or sputter (formation of drops, which are deposited in mixture with electro spun fibres) [1,4].

It is possible to reach the complete collapse of the micro-nano-fibrillar layer and the formation of non-homogeneous, interrupted films. [4].

The article presents a mathematical model that predicts the diameter of the fibres in the composition of the absorbent layer of the multilayer matrix structure for the treatment of burns or gunshot wounds, taking into account the nonlinear relationship between the parameters explained above and specific theories of electrodynamics for thin profiles (for instance, in aeronautics) for the prediction of jet behaviour. Specifically, it has been proposed to explain, from a mathematical point of view, the interaction of the electric field with the properties of the fluid to predict the diameter of the final jet.

2. MATERIALS AND METHODS

The absorbent layer of the multilayer matrix, made by multilayer electrospinning must: have a moderate hydrophilic surface, dimensional stability (especially for deep burns), adequate microstructure, proper porosity, controllable biodegradability, allow adhesion and cell population growth [2].

i. Materials used to make the absorbent layer in case of burn wounds: natural polymers-collagen, gelatine, chitosan, fibrin, and their combinations (e.g., PLGA and collagen, to increase cell proliferation and the rapid development of extracellular matrix).

ii. Materials used to make the absorbent layer in case of gunshot wounds (blood vessels and bone tissue regeneration): chitosan, hyaluronic acid, collagen hydrolysed and colloidal silver.

Electrospinning is performed with a single nozzle; multiplication of the primary jet not been taken into account. After the formation of the Taylor cone, the molecular cohesion of the liquid is high and constant enough to prevent the flow from breaking (the electrospray phenomenon does not occur), generating the charged liquid jet [5].

The current flow changes from ohmic (linear) to convective (turbulent) as the load migrates to the fibre surface. The elongation of the jet takes place due to the whipping process caused by the electrostatic rejection initiated in the curved areas of the fibre. The visco-elastic behaviour of the polymer solution is described using the nonlinear model used in aerodynamics, considering the motion of the jet fluid element, and the mass transport of the solvent between the liquid jet and the gaseous medium is described by Frick's first law (stationary diffusion).

Fluid motion is defined by diffeomorphism $x=\aleph(t,X)$, with X being the position vector of a particle in the initial configuration, x is the position vector of the same particle at time t. Consequently, the velocity and acceleration of the particle are given by the equation 1 [3-5]:

$$v(t,X) = \frac{d}{dt}\aleph(t,X) \quad a(t,X) = \frac{d}{dt}v(t,X) \tag{1}$$

The fluid is a continuous medium, so the image through diffeomorphism is also a domain [6-8] and the intervening functions are of class $C_2(\mathfrak{D}_0)$ with the Jacobian 2:

$$J = \frac{\partial(\aleph_1, \aleph_2, \aleph_3)}{\partial(X_1, X_2, X_3)} \neq 0 \tag{2}$$

The equations of motion: the mass conservation principle 3, the continuity equation 4, the impulse variation principle 5, the energy balance equation 6 are the well-known ones, not insisting on the specific conditions of the studied case:

$$\frac{d}{dt}\int \rho dv = 0\,,\ \forall D \subset \mathfrak{D} \tag{3}$$

$$\dot{\rho} + \rho div v = 0 \tag{4}$$

$$\frac{d}{dt}\int \rho v dv = -\int p n da + \int \rho f dv\,, \forall D \subset \mathfrak{D} \tag{5}$$

In this case, from (5) si $a = \frac{\partial v}{\partial t} + (v \cdot \nabla)v$ is result in the Euler equation:

$$\rho\left[\frac{\partial v}{\partial t} + (v \cdot \nabla)v\right] = \rho f - grad\, p$$
$$\frac{d}{dt}\int \rho(e + \frac{1}{2}v^2)dv = -\int pv \cdot n da + \int \rho f \cdot v da - \int q \cdot n da\,, \forall D \subset \mathfrak{D} \tag{6}$$

It is considered that the basic state of the environment in which the jet operates is undisturbed, so it can be considered that it is at rest, in uniform motion or with a given speed distribution. It is well known that the problem of determining perturbations can be solved only in cases where they are small, because only in these cases e the methods of classical analysis or the methods of distribution theory can be approached.

Taking into account that the order of magnitude of the disturbance is given by the basic movement and the shape of the body, for this case study the theory of thin bodies will be applied, with low incidence.

The validation conditions of the linear theory cannot be established before, this following to be established after determining the solution of the linearized equations, but making the condition that the result does not lead to physical impossibilities.

The systems of equations will be linear and with constant coefficients if the basis state is constant and will be linear with variable coefficients if the basis motion is uneven.

Taking into account the previously imposed conditions, for modelling the characteristics of nanofibers according to process parameters, the phenomenological model described in figure 1 was considered, where the liquid jet is replaced by rectilinear linear segments, subjected to a convective field, the jet being connected in a "Viscoelastic chain".

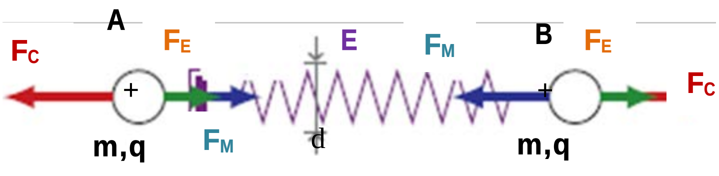

Figure 1. Force analysis for a rectilinear linear segment of the jet placed in the electrostatic field [4]: F_C - Coulomb repulsive force; F_E - electrostatic field strength; F_M - viscoelastic force; η - dynamic viscosity; E - modulus od elasticity; d - diameter; l - length; m - mass; q - loading

2.1 Mathematical modelling of the main descriptive parameters of the jet:

The mass loss of the solvent is calculated by equation 7:

$$\frac{dm_{si,i+1}}{dt} = h_m \pi d_{i,i+1} l_{i,i+1} \rho (c_{s,eq} - c_{s,\infty}) \tag{7}$$

where: $m_{si,i+1}$, $d_{i,i+1} l_{i,i+1}$ represents the instantaneous mass of the solvent, the instantaneous diameter and the instantaneous length relative to the rectilinear and linear segment (i, i + 1) of the electrically charged jet between the element i and i + 1 at time t, h_m is the mass transfer coefficient, ρ is the density of the polymer solution, $c_{s,\infty}$ represents the concentration of the solvent saturated vapor.

The mass transfer coefficient can be written according to the Sherwood criterion 8:

$$Sh = \frac{h_m d_{i,i+1}}{D_{S,a}} = \text{const.}Re^a Sc^b \tag{8}$$

where $D_{S,a}$ is binary diffusion coefficient, Re, Sc - Reynolds and Schmidt numbers, respectively, a, b - exponents, which can take 1/3 values, ½ respectively [5].

It's resulting that equation 9:

$$h_m = \frac{0.495 Re^{1/3} Sc^{1/2} D_{S,a}}{d_{i,i+1}} = \frac{0.495 \sqrt[3]{\frac{\rho_a l_{i,i+1} \left|v_{ni,i+1}^i\right|}{\eta_a}} \sqrt{\frac{\eta_a}{\rho_a D_{S,a}}} D_{S,a}}{d_{i,i+1}} \tag{9}$$

Using a few transformations, the equation governing the evaporation of the solvent becomes equation 10:

$$\frac{dm_{si,i+1}}{dt} = 0.496 v_a^{\frac{1}{6}} D_{S,a}^{\frac{1}{2}} \pi \rho (c_{s,eq} - c_{s,\infty}) l_{i,i+1}^{4/3} \sqrt[3]{\left|v_{ni,i+1}^i\right|} \tag{10}$$

Simple, it can also be determined the volume loss factor, using relationships 11:

$$\Lambda_{i-1,i} = \frac{V_{i-1,i}}{V_0} \qquad \Lambda_{i,i+1} = \frac{V_{i,i+1}}{V_0} \tag{11}$$

Friction force - caused by the friction of the jet with the gaseous medium. Considering that the current lines depend on the shape of the body and the Reynolds number, it can be written successively in equations 12-17:

$$F_{Di-1,i}^i = C_f S_{fi-1,i} \frac{\rho_a (v_{ni-1,i}^i)^2}{2} + C_p A_{pi-1,i} \frac{\rho_a (v_{ti-1,i}^i)^2}{2} \tag{12}$$

$$F_{Di,i+1}^i = C_f S_{fi,i+1} \frac{\rho_a (v_{ni,i+1}^i)^2}{2} + C_p A_{pi,i+1} \frac{\rho_a (v_{ti,i+1}^i)^2}{2} \tag{13}$$

where C_f is friction coefficient and C_p - pressure coefficient.

$$S_{fi-1,i} = \frac{1}{2} \pi d_{i-1,i} l_{i-1,i} \qquad S_{fi,i+1} = \frac{1}{2} \pi d_{i,i+1} l_{i,i+1} \tag{14}$$

$$A_{pi-1,i} = \frac{1}{2} \pi d_{i-1,i} l_{i-1,i} \qquad A_{fi,i+1} = \frac{1}{2} \pi d_{i,i+1} l_{i,i+1} \tag{15}$$

$$v_{ni-1,i}^{i} = \frac{v_i \cdot n_{i,i-1}}{n_{i,i-1} \cdot n_{i,i-1}} \frac{r_{i-1} - r_i}{|r_{i-1} - r_i|} \qquad v_{ni,i+1}^{i} = \frac{v_i \cdot n_{i+1,i}}{n_{i+1,i} \cdot n_{i+1,i}} \frac{r_i - r_{i+1}}{|r_i - r_i + 1|} \tag{16}$$

$$v_{ti-1,i}^{i} = v_i - v_{ni-1,i}^{i} \qquad v_{ti,i+1}^{i} = v_i - v_{ni,i+1}^{i} \tag{17}$$

where $n_{i,i-1} = r_{i-1} - r_i$ si $n_{i+1,i} = r_i - r_{i+1}$.

From $c_f = f(Re_l)$ and $c_p = f(Re_d)$ is resulting equations 18 and 19:

$$Re_l = \frac{\rho_a l_{i-1,i} \left| v_{ni-1,i}^{i} \right|}{\eta_a} \qquad Re_l = \frac{\rho_a l_{i,i+1} \left| v_{ni,i+1}^{i} \right|}{\eta_a} \tag{18}$$

$$Re_d = \frac{\rho_a d_{i-1,i} \left| v_{ti-1,i}^{i} \right|}{\eta_a} \qquad Re_d = \frac{\rho_a d_{i,i+1} \left| v_{ti,i+1}^{i} \right|}{\eta_a} \tag{19}$$

For laminar flow, take into account that $c_f = 24/Re_l$ and $c_p = 24/Re_d$.

It's resulting:

$$F_{Di} = 6\eta_a \pi d_0 l_0^{\frac{1}{2}} \left[\left(\frac{\Lambda_{i-1,i}}{l_{i-1,i}} \right)^{\frac{1}{2}} \frac{(v_{ni-1,i}^{i})^2}{\left| v_{ni-1,i}^{i} \right|} + \left(\frac{\Lambda_{i,i+1}}{l_{i,i+1}} \right)^{\frac{1}{2}} \frac{(v_{ni,i+1}^{i})^2}{\left| v_{ni,i+1}^{i} \right|} \right] + 6\eta_a \left[l_{i-1,i} \frac{(v_{ti-1,i}^{i})^2}{\left| v_{ti-1,i}^{i} \right|} + l_{i,i+1} \frac{(v_{ti,i+1}^{i})^2}{\left| v_{ti,i+1}^{i} \right|} \right] \tag{20}$$

The viscoelastic behaviour of the jet (constitutive relation) is described by the equation 21:

$$\frac{d\sigma_{i,i+1}}{dt} = \frac{\eta_{i,i+1}}{\tau_{i,i+1}} \frac{(r_i - r_{i+1}) \cdot (v_i - v_{i+1})}{l_{i,i+1}^2} - \frac{\sigma_{i,i+1}}{\tau_{i,i+1}} \tag{21}$$

where: $\sigma_{i,i+1}, \eta_{i,i+1}$ *si* $\tau_{i,i+1}$ represents the normal stress, the instantaneous dynamic viscosity and respectively the instantaneous relaxation time of the polymer solution.

The motion equation becomes equation 22:

$$\frac{dp_i}{dt} = m_i \frac{dv_i}{dt} - \left| \frac{dm_i}{dt} \right| v_i = F_{Ei} + F_{Ci} + F_{Mi} + F_{Si} - F_{Di} \tag{22}$$

It is easy to notice that the second order differential equation for the position of the mass point can be rewritten as a system of first order equations 23 and 24:

$$\begin{cases} \frac{dr_i}{dt} = v_i & (23) \\ m_i \frac{dv_i}{dt} = \left| \frac{dm_i}{dt} \right| v_i + F_{Ei} + F_{Ci} + F_{Mi} + F_{Si} - F_{Di} & (24) \end{cases}$$

The solvent evaporation equation 10, the constitutive relationship 21, the kinematic equation 23 and the motion equation 24 form the system of equations that describe the behaviour of an ideal linear jet segment moving in an electrostatic field.

The numerical solution for the equations determined above is based on the Euler method (for the predictor) and the Adams-Moulton method (for the corrector), respectively.

The group of dimensionless parameters were determined using scale factors as follows: (equations 25 - 31): normal tension:

$$\sigma_{i,i+1}^{*} = \frac{\sigma_{i,i+1}}{E_0} \tag{25}$$

- dynamic viscosity:

$$\eta^*_{i,i+1} = \frac{\eta_{i,i+1}}{\eta_0} \tag{26}$$

- diameter:

$$d^*_{i,i+1} = \frac{d_{i,i+1}}{d_0} \tag{27}$$

- vector components of the radius:

$$x^*_i = \frac{x_i}{L}, \quad y^*_i = \frac{y}{L}, \quad z^*_i = \frac{z}{L} \tag{28}$$

- mass:

$$m^*_{i,i+1} = \frac{m_i}{m_0} \tag{29}$$

- electrostatic charging:

$$q^*_{i,i+1} = \frac{q_i}{q_0} \tag{30}$$

- time:

$$t^*_{i,i+1} = \frac{t}{t_0} \tag{31}$$

where $E_0 = \eta_0/\tau_0$ = Young's modulus of the polymer solution
m_0, q_0 = initial mass and initial electrostatic charge
$L = \sqrt{\frac{\tau_0 q_0^2}{\varepsilon_0^2 \varepsilon_r \pi^2 \eta_0 d_0^2}}$ = characteristic length

Dimensional equations 32 – 42:

$$\frac{dm^*_{si,i+1}}{dt^\#} = C^*_m (l_{i,i+1})^{\frac{4}{3}} \left|v^i_{ni,i+1}\right|^{\frac{1}{3}} \tag{32}$$

$$\frac{d\sigma^*_{i,i+1}}{dt^*} = \frac{\eta^*_{i,i+1}}{\tau^*_{i,i+1}} \frac{(r^*_i - r^*_{i+1}) \cdot (v^*_i - v^*_{i+1})}{(l^*_{i,i+1})^2} - \frac{\sigma^*_{i,i+1}}{\tau^*_{i,i+1}} \tag{33}$$

$$\frac{dr^*_i}{dt^*} = v^*_i \tag{34}$$

$$m^*_i \frac{dv^*_i}{dt^*} = \left|\frac{dm^*_i}{dt^*}\right| v^*_i + C^*_E q^*_i E^* + C^*_c q^*_i \sum_{j=1}^{n} \frac{q^*_i}{\left|r^*_i - r^*_j\right|^2} \frac{r^*_i - r^*_j}{\left|r^*_i - r^*_j\right|} + C^*_M \left(\sigma^*_{i-1} d^{*2}_{i-1,i} \frac{r^*_{i-1} - r^*_i}{|r^*_{i-1} - r^*_i|} + \sigma^*_{i,i+1} d^{*2}_{i,i+1} \frac{r^*_{i-1} - r^*_i}{|r^*_{i-1} - r^*_i|}\right) + C^*_S \left(d^*_{i-1,i} \frac{r^*_{i-1} - r^*_i}{|r^*_{i-1} - r^*_i|} + d^*_{i,i+1} \frac{r^*_{i-1} - r^*_i}{|r^*_{i-1} - r^*_i|}\right) + C^*_S \left(d^*_{i-1,i} \arcsin \frac{l^*_{i-1,i}}{2R^*_i} + d^*_{i,i+1} \arcsin \frac{l^*_{i,i+1}}{2R^*_i}\right) \frac{r^*_c - r^*_i}{|r^*_c - r^*_i|} + C^*_{Df} \left(d^*_{i-1,i} \frac{(v^i_{ni-1,i})^2}{|v^i_{ni-1,i}|} + d^*_{i,i+1} \frac{(v^i_{ni,i+1})^2}{|v^i_{ni,i+1}|}\right) + C^\#_{Dp} \left(l^*_{i-1,i} \frac{(v^i_{ti-1,i})^2}{|v^i_{ti-1,i}|} + l^*_{i,i+1} \frac{(v^i_{ti,i+1})^2}{|v^i_{ti,i+1}|}\right) \tag{35}$$

where:

$$C^*_m = \frac{0.495 \pi \nu_a^{\frac{1}{6}} \tau_0^{\frac{2}{3}} D_{S,a}^{\frac{1}{2}} L^{\frac{5}{3}} (c_{s,eq} - c_{s,\infty})}{m_0} \tag{36}$$

$$C^*_E = \frac{\tau_0^2 q_0^2}{\varepsilon_0 m_0 L^3} \tag{37}$$

$$C_c^* = \frac{\tau_0^2 q_0^2}{4\pi\varepsilon_0\varepsilon_r m_0 L^3} \quad (38)$$

$$C_M^* = \frac{\pi\eta_0\tau_0^2 d_0^2}{4m_0 L} \quad (39)$$

$$C_S^* = \frac{\pi\gamma\tau_0^2 d_0^2}{m_0 L} \quad (40)$$

$$C_{Df}^* = -\frac{6\pi\eta_a\tau_0 d_0}{m_0} \quad (41)$$

$$C_{Dp}^* = -\frac{6\eta_a\tau_0 L}{m_0} \quad (42)$$

Based on these theoretical hypotheses, the established input data and the numerical discretization, the equations that describe the motion of the jet in the convective zone (the so-called whipping phenomenon) can be solved. These will highlight which of the process parameters decisively influences the characteristics of the obtained nanofibers.

The further development of the mathematical model could lead to the prediction of the breaking strength and elongation of the nanofiber.

3. RESULTS AND DISCUSSIONS

The mathematical modelling performed in this stage show the following:

- a particularly important parameter in the electrospinning process is the initial dynamic viscosity, η_0; the decrease of the values of this parameter determines the increase of the whipping area and the decrease of the linear part of the jet, which implies an elongation of the liquid jet and implicitly a decrease of the nanofiber diameter.
- the initial relaxation time τ_0 observed in the previous equations is another very important parameter of the process. As the relaxation time increases, the Young's modulus of the polymeric liquid decreases, the width of the whipping area increases and the length of the linear area decreases, in other words the normal surface tension is responsible for the length of the linear area of the jet.

4. CONCLUSIONS

Electrostatic spinning is a complex process that involves diffusion/evaporation/ cooling, heat transfer, water condensation and polymer diffusion, all these stages of the process being accompanied by their associated variables, such as jet initiation, laminar and turbulent motion, solidification and deposition of nanofibers.

The control of the morphology and the mechanical behaviour of the nanofibers is still at the beginning, the mathematical models obtained so far predicting these parameters specifically for the field of use.

It is necessary to deepen the specific phenomenology of this process for future modelling routes, especially regarding the evolution of nanoscale structures and parameter control.

ACKNOWLEDGEMENTS

The authors would like to express appreciation for the support of the Project Number 496PED/2020.

REFERENCES

[1] Yarin, A.L., Koombhongse, S., Reneker, D.H., *Bending instability in electrospinning of nanofibers*, In: J Appl Phys, 2011, 5, 89, 18-26

[2] Casper, C.L,, Yang, W., Farach-Carson, M.C., Rabolt, J.F., *Coating electrospun collagen and gelatin fibers with perlecan domain I for increased growth factor binding*, In: Biomacromolecules, 2007, 4, 8, 1116-23

[3] Kenawy, R., Layman, J.M., Watkins, J.R., Bowlin, G.L., Matthews, J.A., Simpson, D.G., *Electrospinning of poly(ethylene-co-vinyl alcohol) fibers*, In: Biomaterials, 2013, 6, 24, 907-13

[4] Zhong, S., Teo, W.E., Zhu, X., Beuerman, R.W., Ramakrishna, S., Yung, L.Y., *An aligned nanofibrous collagen scaffold by electrospinning and its effects on in vitro fibroblast culture*, In: J Biomed Mater Resarch, 2016, 3, 79, 456-63

[5] Yarin, A.L., Koombhongse, S., Reneker, D.H., *Bending instability in electrospinning of nanofibers*, In: J. Appl. Phys., 2011, 5, 89, 3018-3026

[6] Fisher, A.C., De Cossart, L., How, T.V., Annis, D., *Long term in-vivo performance of an electrostatically-spun small bore arterial prosthesis: the contribution of mechanical compliance and anti-platelet therapy,* In: Life Support Syst, 1985, 1, 3 Suppl, 462-465

[7] Doshi, J., Reneker, D.H., *Electrospinning process and applications of electrospun fibers*, In: J Electrostatics, 1995, 35, 2-3, 151-160

[8] Song, J.H., Kim, H.E., Kim, H.W., *Production of electrospun gelatin nanofiber by water-based co-solvent approach*, In: J Mater Sci Mater Med, 2017, 19