# Experimental and Theoretical Investigations in Polyamide Spin-Coated Thin FIlms

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*Thin films of polyamide 6 (with various concentrations) were deposited by spin-coating method (at various rotation speeds) and surface morphology of these films was analyzed by scanning electron microscopy. Following this analysis it was revealed that deposited film thickness depends on solution density, its viscosity, rotation speed and rotation time. In the context of multi-scale type theories, a theoretical model which explains our experimental results is established.*

*Keywords: spin-coating, polyamide, thin film, multi-scale theory*

In the context of society development, theoretical and practical interest of researchers was drawn to the important role that organic compounds have gained in everyday life through their applications in electronics and telecommunications, medicine and genetic engineering, in computer science, biophysics, etc. Displays, photo-detectors, solar cells, field effect transistors with organic channel, organic light emitting devices, photovoltaic cells based on organic thin films, organic lasers, gas and moisture sensors, biosensors, are just some of the multiple applications of the organic semiconductors with an extremely wide presence in today's industry [1,2].

Particular emphasis is given to the possibility of manipulating the structures of these materials in order to obtain products with certain properties.

Through this study we try to explain some of the exotic effects that could be observed at polyamide 6 thin film surfaces, obtained by spin-coating method. Thin films were prepared by varying the solution concentration and the rotation speed, both contributing to modification of surface structures. This modification and the effects produced were analyzed both in terms of empirical and theoretical point of view, in order to establish a predictability of their occurrence.

## Experimental part

### *Thin film preparation by spin-coating method*

The spin coating method is an extensively used process, especially in the electronics industry, and is applied when a planar substrate needs to be coated. Shortly, the polymer solution is deposited on a substrate which is then rotated at high speeds, causing dispersion and evaporation of the fluid. In order to obtain homogeneous films must be taken into account the following factors: viscosity and solution concentration, solvent evaporation rate, rotation speed and rotation time [3,4].

For preparation of the solution it is necessary to use a solvent that evaporates quickly at room temperature. Evaporation affects the flow of the solution. If solvent evaporation happens very quickly, the flow of the solution is becoming smaller due to solution viscosity. In the spin-coating process, the interactions between substrate and solution are higher than those between solution and air [5]. During centrifugation, the solvent evaporates, leading to an increase in concentration and, therefore, in the solution viscosity, which changes its rheology [5, 6]. Film thickness is dependent on fluid viscosity and concentration. The more concentrated the solution, the thicker the film. Reverse option is valid for thickness dependence of angular velocity. The same dependence is obtained also with the rotation time. The higher the rotation time, the film becomes thinner – for a constant rotation speed.

The polymer used for preparing the solution is polyamide 6. It was purchased from Sigma – Aldrich (France), as pellets with medium size of 3 mm. Polyamides are thermoplastic resins, tasteless, colourless, transparent to translucent and non-toxic. The polyamide 6 was dissolved in formic acid (90%), purchased from Fisher Scientific (France). Formic acid is a liquid with unpleasant odor, colourless and with the boiling point of 101° C.

Experimental equipment was specially designed and build for this study in the "Laboratoire de physique et Mécanique Textiles", ENSISA - Mulhouse (France) and consists of a plate onto which a glass lamella is fixed, a motor that rotates the plate, a dispenser for deposition of the polymer solution and a variable voltage source for controlling the rotation speed.

In order to obtain thin films by spin-coating method, two solutions of polyamide 6 and formic acid were prepared, with the following concentrations: 0.05 g/mL and 0.15 g/L. The glass lamella of the apparatus were washed and dried before the process. For each solution concentration, the following voltages were set: 4 V, 8 V and 12 V, corresponding to the following rotation speeds of the plate: 1000 rpm, 3000 rpm and 5000 rpm. For fabricating a film, a quantity of 1 mL of polymer solution was placed drop by drop onto the glass slide, during rotation. Polymer solution was deposited at an 90° C angle with the spin-coater support. Rotation speed determines the spreading of the solution on the glass surface, removing the excess of liquid and forming a thin film. By solvent evaporation, the film thickness decreases further, resulting in a solid layer. After

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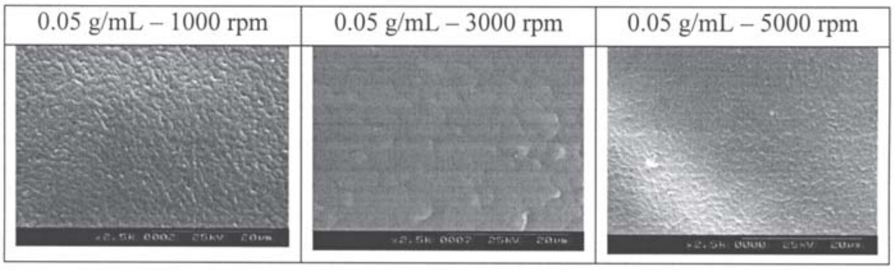
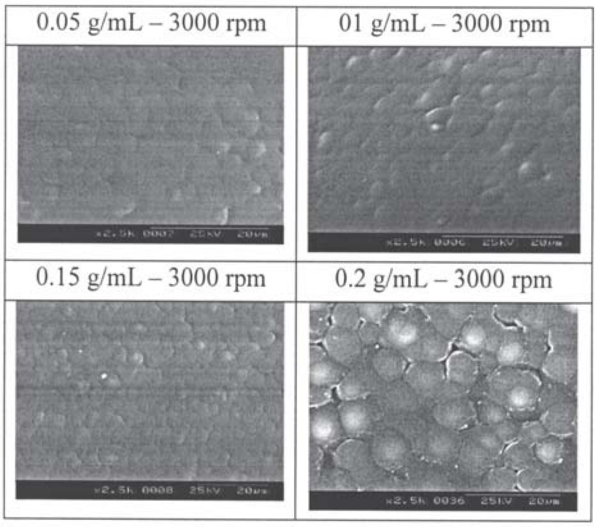


0.05 g/mL – 1000 rpm | 0.05 g/mL – 3000 rpm | 0.05 g/mL – 5000 rpm

**Table 1**
SEM MICROGRAPHS OF THIN FILMS OBTAINED FROM THE SAME SOLUTION CONCENTRATION (0.05 g/mL POLYAMIDE 6 IN FORMIC ACID) SUBJECT TO DIFFERENT ROTATION SPEEDS (1000 rpm, 3000 rpm, 5000 rpm)

**Table 2**
SEM MICROGRAPHS OF THIN FILMS OBTAINED FROM DIFFERENT CONCENTRATIONS OF SOLUTION (0.05 g/mL; 0,1 g/ mL; 0,15 g/mL; 0.2 g/mL POLYAMIDE 6 IN FORMIC ACID) SUBJECTED TO THE SAME ROTATION SPEED (3000 rpm)



0.05 g/mL – 3000 rpm | 01 g/mL – 3000 rpm
0.15 g/mL – 3000 rpm | 0.2 g/mL – 3000 rpm

30 s of rotation, the apparatus is stopped and the film is left for several minutes so that any remaining solvent evaporates. Resulting film thickness depends on the concentration of the solution used, the rotation speed of the plate and the evaporation rate of the solvent.

## Results and discussions

### *Thin film characterization*

In order to characterize the thin films obtained by spin-coating method from a structural point of view, scanning electron microscopy was used. This allows the analysis of surface morphology of thin films and helps us to understand the correlations between varying the working parameters during the fabrication process and characteristics of thin films.

Scanning electron microscopy reveals morphological characteristics of polyamide 6 thin films, as shown in the SEM micrographs in tables 1-2. These were taken at a high voltage of 25 kV. From these images it can be observed that thin films have a irregular surface consisting of spherical-looking formations (bubbles), distributed approximately uniformly. At some films, bubbles formed are not well defined but, in dimensional terms, we can see that they are relatively the same size.

Spherical formations (bubbles), is assumed to be formed during the solidification of the polymer film by evaporation of the solvent (formic acid). From theoretical studies it is known that solvent evaporation is accelerated as the applied rotation speed is higher and the solution concentration is smaller [7,8]. Therefore, acid evaporation creates the capillarity effect in the film, leading to bubbles formation. At the same time, the solvent evaporation changes the flow capacity of the solution. This affects the elasticity and the plasticity of the films.

In table 1, images of the surfaces of thin films obtained from solution concentration of 0.05 g/mL polyamide 6 in formic acid and for different rotation speeds (1000 rpm, 3000, rpm, 5000 rpm) are shown. Analysis of these images allows us to state that the rotation speed significantly influences the surface morphology of films, in that they become smoother as the rotation speed increases. Thin film surface obtained at the lowest speed presents small and dense spherical formations whose diameter is increased for 3000 rpm rotation speed, eventually the film becoming almost smooth (fine ribbed) for the higher speed (5000 rpm). Therefore, if the speed is high, the solution of polyamide 6 covers sooner the surface of the glass slide, leading to film formation before complete evaporation of formic acid. Since the films obtained at higher speeds are thinner than those obtained at lower speeds, they are more elastic, the bubbles formed due to solvent evaporation having the capacity to deflate and uniform the surface. This capacity decreases as the speed is lower.

In table 2, images of the surfaces of thin films obtained from different solution concentrations (0.05; 0,1; 0.15; 0.2 g/mL polyamide 6 in formic acid) subject to the same rotation speed (3000 rpm) are shown. It is noted that the surface morphology is influenced by varying the solution concentration, meaning that spherical formations are becoming larger and well-defined with increasing concentration. Increasing solution concentration causes a slower solvent evaporation, which leads to the formation of thicker films (for the same rotation speed). The thicker the film is, the more it loses its elasticity, bubbles formed by acid evaporation solidifies (for the film obtained from the higher solution concentration – 0.2 g/mL – there is a well-defined globular morphology).

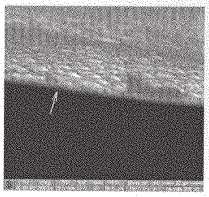
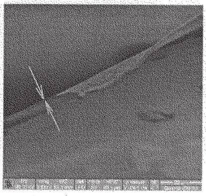
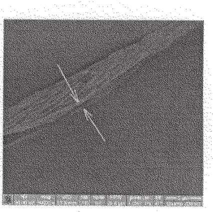
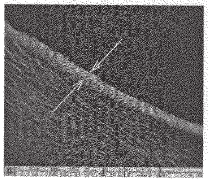
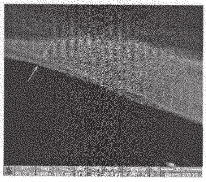
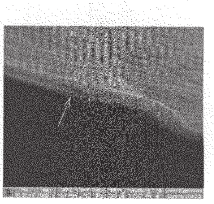
Moreover, it was observed that the film thickness is closely related to solution concentration and rotation speed: the higher the rotation speed, the thinner the film and the higher the solution concentration, the film is more thicker. This results also from the images presented in table 3.

### *Theoretical modeling of spin-coating process through multiscale type theory*

Theoretical analysis of spin-coating process based on hydrodynamic principles is relatively difficult to perform because of physical and mathematical complexity of the system, despite the ease of obtaining empirical data. However, even partial analysis may provide some insight into the effectiveness and limitations of the process [3,6].

In what follows, we develop a hydrodynamic theory of spin-coating process, assuming that generation and evolution of this process is of multi-scale type [7-10]. This means that quantities describing physics of process are simultaneously dependent not only on the coordinates and time, but also on the scales of interaction (physical quantities are continuous and non-differentiable functions [11]). We can distinguish the following specific scales of interaction associated with evolutionary sequences of spin-coating process [13]: i) due to radial directed flow the solution thickness decreases. Moreover, due to solvent evaporation perpendicular to the surface, the gradient of

**Table 3**
SEM IMAGES SHOWING THE DEPENDENCE OF THIN FILM THICKNESS ON ROTATION SPEED AND SOLUTION CONCENTRATION

| Rotation speed / Solution concentration | 1000 rpm | 3000 rpm | 5000 rpm |
|---|---|---|---|
| 0.05 g/mL | 2.47±0.01 μm  | 1.53±0.01 μm  | 0.87±0.02 μm  |
| 0,15 g/mL | 3.68±0.02 μm  | 2.45±0.03 μm  | 1.75±0.02 μm  |

the solution concentration appears; ii) the concentration of the layer surface reaches a critical value, so that the solution behaves like a elastic crust: has two overlapped phases, both solid and liquid; iii) the crust thickness increases and that of the diluted solution decreases; iv) the radial flow ceases, since the diluted solution on the support runs out. The solution layer dries as the support rotates; v) the layer is completely dry.

Mathematically, this situation can be described using the Navier – Stokes equations set which contains momentum conservation law:

$$\frac{\partial v}{\partial t} + v\nabla v - \eta\Delta v = \sum_i \mathbf{f}_i \qquad (1)$$

and density conservation law:

$$\frac{\partial \rho}{\partial t} + \nabla\rho v = 0 \qquad (2)$$

In previous relationships, ν define velocity field, ρ the density field, $\sum_i f_i$ external force field per unit volum and η viscosity. The scale dependences of physical quantities describing the spin-coating process, are introduced assuming that for a given interaction scale, the structure parameters of the physical system (either η, ρ or β=η/ρ ) allow dependencies:

$$\eta = \eta(\lambda_i, \tau_i)\ ,\ \rho = \rho(\lambda_i, \tau_i)\ ,\ \beta = \beta(\lambda_i, \tau_i) \qquad \text{(3a-c)}$$

where $\lambda_i$ is a specific length scale and $\tau_i$ is a characteristic time scale. Now gathering the scale dependences with the substitution "principle" (natural consequence of non-differentiability of physical quantities associated with the evolutionary sequences of spin-coating process – for details see the references [6,11,13,14]), which allow identifications like $\lambda_i \equiv \lambda$ or $\tau_i \equiv \tau$, the „dynamics" of the spin-coating process are drastically simplified. Thus additional "complications" are avoided (solving the specific equations set of evaporation, various empirical dependences of the structure coefficients [14], etc). Other applications of multi-scale type theories are given in [15-17].

We study the "dynamics" of spin-coating process based on the following simplifying assumptions conditional on a viscous liquid on a rotating disk: i) the plane of rotation is horizontal, so there is no radial gravitational component; ii) the liquid layer is so thin that differences in the gravitational potential normal at the surface have negligible effects; iii) radial velocity is sufficiently small that Coriolis forces may be neglected; iv) the plane of rotation is infinite; v) the liquid layer is symmetrical on radial direction; vi) the liquid is Newtonian; vii) the resistance to flow is only considered in horizontal plane; viii) the surface is fully wet.

Using cylindrical polar coordinates (r, θ, z), with origin at the rotation center, *z* perpendicular to the plane, *r* and θ axes rotating with the plane with angular speed Ω, equation (1), based on simplifying assumptions i) – viii) lead to:

$$-\eta\frac{d^2v}{dz^2} = \rho\Omega^2 r \qquad (4)$$

where *υ* is the velocity in the *r* direction. Integrating twice by *z*, it can be obtained:

$$v = \frac{1}{\eta}\left(-\frac{\rho}{2}\Omega^2 z^2 r + c_1 z + c_2\right) \qquad (5)$$

Integration constants $c_1$ and $c_2$ are determined by the boundary conditions

$$v(z=0) = 0\ ,\ \frac{dv}{dz} = (z=g) = 0 \qquad \text{(6a,b)}$$

The first condition (6a) implies $c_2=0$ and the second (6b) $c_1=\rho\Omega^3 gr$. Finally, the relation (5) becomes

$$v(z) = \frac{1}{\eta}\left(-\frac{\rho}{2}\Omega^2 z^2 r + \rho\Omega^2 grz\right) \qquad (7)$$

The velocity field described by equation (2), admitting the dependence (7), based on given symmetry and on simplifying assumptions i) – viii), becomes:

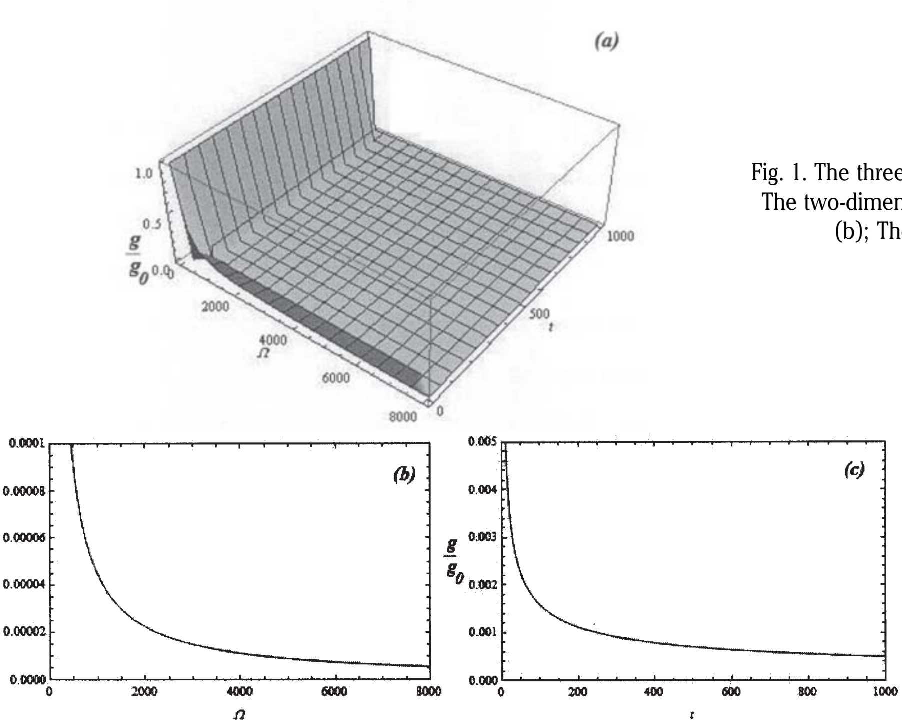


Fig. 1. The three-dimensional dependence g=g(Ω,t) (a); The two-dimensional dependence g=g(Ω) for given t (b); The two-dimensional dependence g=g(t) for given Ω (c)

$$r\frac{\partial g}{\partial t} = -\frac{\partial}{\partial r}(rq) \qquad (8)$$

where $q$ is the radial flow per unit length of circumference,

$$q = \int_0^g v(z)dz = \frac{1}{\eta}\int_0^g\left(-\frac{\rho}{2}\Omega^2 z^2 r + \rho\Omega^2 grz\right)dz = \frac{\rho\Omega^2 r g^3}{3\eta} \qquad (9)$$

If we consider a special solution that depends only on time, the relation (8) becomes:

$$r\frac{dg}{dt} = -\frac{d}{dr(rq)} \qquad (10)$$

or again, substituting (9) in (10)

$$\frac{dg}{g^3} = -\frac{2\rho\Omega^2}{3\eta}dt \qquad (11)$$

Hence, by integration, it results

$$\frac{1}{g^2} = \frac{4\rho\Omega^2}{3\eta}t + c_3 \qquad (12)$$

The integration constant value is determined by the condition

$$g(t=0) = g_0 \qquad (13)$$

It is found that $c_3 = 1/g_o$, which implies the solution

$$g = \frac{g_0}{\left(1 + \frac{4\rho\Omega^2 g_0^2}{3\eta}t\right)^{1/2}} \qquad (14)$$

The following conditions are evident: i) for given $t$, $g$ decreases continuously and monotonically with Ω (fig. 1a,b); ii) for given Ω, $g$ decreases continuously and monotonically with $t$ (fig. 1a,c); iii) removing the interaction scales $\lambda_i$ and $\tau_i$ from relations (3a,b) implies a functional dependence $\eta = \eta(\rho_i)$ which specifies the viscosity dependence of density. As viscosity increases with density [12], it follows that g increases.

An example is given by [31]:

$$\eta = \frac{a}{1-\rho b} \qquad (15)$$

where $a$ and $b$ are constants, situation in which the relation (14) becomes:

$$g = \frac{g_0}{\left[1 + \frac{4\Omega^2 g_0^2(1-\rho b)}{3a}t\right]^{1/2}} \qquad (16)$$

Such a result is verified experimentally as shown in the SEM images (table 3) that presents the thickness of polyamide 6 thin films obtained by spin-coating method. From that images results that the film thickness decreases as the rotation speed increases and the films are thicker as the solution concentration is higher.

The theoretical model can be validated based on our experimental results. For example, for the parameters used in the experiment: $g_0$ = 1.64 ±0,01μm, Ω = 3000 rpm (50 rot/s), $\rho_{(0,05\ g/ml\ PA6/HCOOH)} \sim 1.12$ kg/m$^3$; $\eta_{(0,05\ g/ml\ PA6/HCOOH)} \sim 8\cdot 10^{-3}$ Ns/m$^2$, $t$=30 s, using the relation (14), it results $g \sim 1.55$ μm, close to that found experimentally.

## Conclusions

The main conclusions of the present paper are:

-Characteristics of polyamide 6 thin films obtained by spin-coating method are strongly dependent on the parameters used during the manufacturing process (solution concentration and rotation speed), influencing both surface morphology and thickness.

-The theoretical model developed based on the multi-scale type theories regarding the thin film thickness dependence on the parameters of the spin-coating process describes well our experimental results.

In a next paper, a new multi-scale type model will be developed, taking into consideration the evaporation process.

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