Morphological and Optical Properties of Polyamide Thin Films Obtained by Spin-coating Method

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This paper presents some morphological properties of polyamide 6 thin films obtained by spin-coating method. These properties were investigated by scanning electron microscopy and atomic force microscopy. It results that the thin film thickness is influenced both by rotation speed and solution concentration. Finally, some aspects between morphological and optical properties (structural colours) were considered.

Key words: polyamide thin films, spin-coating method, scanning and atomic force microscopy, structural

A thin film is a layer of material whose thickness varies from several nanometers to several micrometers and its optical properties are strongly dependent on the thickness and morphology. For example, it was found that, from an experimental point of view, there are a number of empirical correlations between the thin film thickness and varying the working parameters [1-7]. Considering the parameters that can be varied, rotation speed has the greatest influence on the final layer, which means the higher the speed, the thinner the film [2,3]. Other parameters involved in spin-coating process is viscosity, solution concentration and rotation time. Of these, viscosity and solution concentration significantly influence deposited film thickness, which is lower as the concentration is lower [5,6]. Rotation time can have negligible effect when the substrate is entirely covered with solution [8].

By this study we are trying to develop spin-coated thin films, whose morphological properties determine its coloristic behaviours.

The technique by which a thin film of material is applied onto a surface (substrate), or other deposited layers is called „thin film deposition". Layer thickness can be controlled within a few tens of nanometers.

The method used in our experimental study to obtain thin films is spin-coating. This is one of the most commonly used method for thin film fabrication from polymers. In brief, the polymer solution is deposited on a substrate which is then rotated at high speeds, causing dispersion and evaporation of the fluid. Being a method relatively easy to use, safe and without involving high costs, it is applied in many fields where high quality layers are required. Layers produced by spin-coating method are used especially for fabricating microcircuits, CDs and DVDs, magnetic disks coatings and electronic devices from polymers [9-12].

In order to obtain homogeneous films must be taken into account the following factors: viscosity and solution concentration, solvent evaporation rate, rotation speed of substrate and rotation time. For preparing the solution is necessary to use a solvent that evaporates quickly at room temperature. Evaporation process affects the solution flow. If solvent evaporation happens very quickly, the solution flow is becoming smaller due to solution viscosity.

In spin-coating process, the interactions between substrate and solution are higher than those of the solution and air. During centrifugation, the solvent evaporates, leading to an increase in concentration and, therefore, an increase in viscosity of solution, that changes its rheology. Film thickness is dependent on fluid viscosity and concentration. The concentrated the solution, the thicker the film. Reverse option is valid for film thickness dependence of angular velocity. The same dependence is obtained also for rotation time. The higher the rotation time the thinner the film – for a constant rotation speed.

The advantage of this method is that thin films can be made from a great variety of polymers at room temperature and on different substrates (silicon, mica, glass, including plastic – if it does not react with the solvent in the solution).

Depending on the desired colour effect, spin-coating method also offers the possibility of deposition of multiple layers from various solutions, thus obtaining multilayer structures of different polymers. Necessary condition for obtaining these layered structures is related to the nature of solvents involved (they must not react with adjacent layers).

Experimental part

Materials

The polymer used in this study is polyamide 6, purchased as pellets with medium size 3 mm from Sigma-Aldrich (France). Polyamides are thermoplastic resins, transparent to translucent, colourless, tasteless and non-toxic.

The solvent used to dissolve the polyamide is formic acid (90%), purchased from Fisher Scientific (France). Formic acid is a colourless liquid, with unpleasant odor, with the melting point of 80^{o} C and the boiling point of 101^{o} C (decomposition).

In order to achieve thin films by spin-coating method, two solutions of polyamide 6 and formic acid were made, with the following concentrations: 0,05 g/mL and 0,15 g/mL. For each solution, voltages were set as follows: 4 V, 8 V, 12 V, corresponding to the following approximate speeds of the rotating support of thin film fabricating equipment: 1000 RPM, 3000 RPM, 5000 RPM. Experimental equipment was designed and built in the "Laboratoire de physique et

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Mécanique Textiles”, ENSISA - Mulhouse (France) and comprises: a rotary plate onto which the glass support is placed, a dispenser for deposition of the polymer solution and a variable voltage source for controlling the rotation speed.

Thin film manufacturing

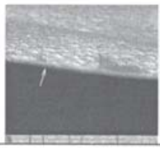
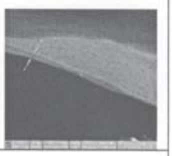
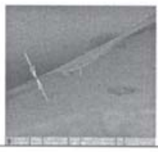
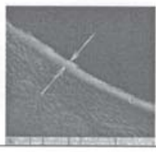
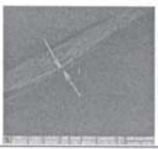
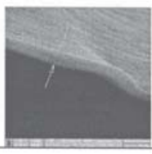
For fabricating a film, a quantity of 1 mL of polymer solution was placed onto the glass lamella, during rotation, drop by drop. Polymer solution was deposited at an angle of 90° with the rotary plate of the equipment. The rotation speed determines the spreading of the solution on glass slide surface, removing the excess material and forming a thin liquid film. By evaporation of the solvent, the film thickness decreases further, resulting in a solid layer. After 30 s of rotation, the machine is stopped and the film is left at rest for several minutes so that any remaining trace of solvent evaporates. The thickness of the fabricated films depends on the concentration of the solution used, the rotation speed of the support and the evaporation rate of the solvent.

Results and discussions

Thin film thickness

In order to determine thin film thickness a Quanta 200 3D scanning electron microscope was used. The average thickness measured (50 measurements / film) for each film obtained from different solution concentrations and at different rotation speeds are summarized in table 1. According to these values, the rotation speed used influences the film thickness obtained, namely, the higher the speed is, the thinner the film. Also, concentration of the solution subject to centrifugation determines obtaining thicker films if the concentration increases.

Table 1
POLYAMIDE 6 THIN FILM THICKNESS

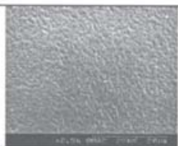
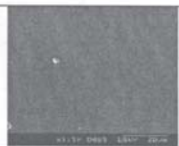
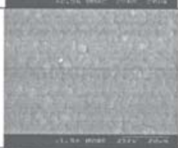
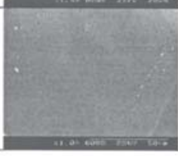
Rotation speed (RPM)	Solution concentration (g/ml)	
	0,05 g/ml	0,15 g/ml
1000 RPM	2,74±0,01 μm 	3,33±0,02 μm 
3000 RPM	2,01±0,01 μm 	2,45±0,03 μm 
5000 RPM	0,87±0,02 μm 	1,40±0,02 μm 

SEM

Surface morphology analysis of polyamide 6 thin films was performed using a scanning electron microscope Hitachi S-2360N, at „Laboratoire de Physique et Mécanique Textiles”, ENSISA – Mulhouse (France). For examination by scanning electron microscopy, thin films of polyamide 6 are required a special treatment, in advance, in order to achieve a good quality image. Since organic materials are almost transparent to electrons because their low electron density, samples were first coated with a thin gold layer. The method used for sample preparation before analysis at electron microscope was deposition by evaporation in vacuum (sputtering). This conductive layer of gold is capable of scattering the electrons, preventing the accumulation of charge on the sample surface, thus helping to improve image contrast.

As can be seen from table 2, SEM images obtained reveal the presence of polymeric clusters on thin film surface. These clusters are outlined at lower rotation speeds and as the speed increases, the films became more uniform. Moreover, the film uniformity increases as the concentration of the solution increases. This means that, initially at low speeds and low concentrations the distributions of structural units of the polymeric chain are different. As speed and concentration increases these distributions are more uniform.

Table 2
SEM IMAGES OF THE POLYAMIDE 6 THIN FILM SURFACE

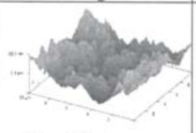
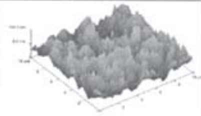
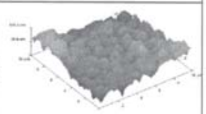
Rotation speed (RPM)	Solution concentration (g/ml)	
	0,05 g/ml	0,15 g/ml
1000 RPM		
3000 RPM		
5000 RPM		

AFM

For the analysis of surface roughness of polyamide 6 thin films, atomic force microscopy has been used. The analysis was performed at „Laboratoire de Physique et Mécanique Textiles”, ENSISA – Mulhouse (France) on a model of microscope Nanoscope IIIa. Topographic images obtained are summarized in table 3. Notice that the rotation speed and solution concentration influence on the roughness of films as follows:

- the higher the rotation speed, the higher the roughness of the surface (eg for solution concentration of 0.05 g/mL, roughness values for 1000 RPM are Rq=26,1 nm and Ra=21,5 nm, while for 5000 RPM they become Rq=31,7 nm; Ra=22,1 nm);
- the higher the solution concentration, the denser the surface roughness.

Table 3
SURFACE TOPOGRAPHY OF POLYAMIDE 6 THIN FILMS

Rotation speed	Solution concentration (g/ml)	
	0,05 g/ml	0,15 g/ml
1000 RPM	 Rq=26,1 nm; Ra=21,5 nm	 Rq=39,4 nm; Ra=31,4 nm
5000 RPM	 Rq=31,7 nm; Ra=22,1 nm	 Rq=43,4 nm; Ra=33,1 nm

Conclusions

Analysis of thin film morphology of polyamide 6 obtained by spin-coating method specifies the following:

-SEM analysis indicates that the layer thickness decreases with increasing the rotation speed, and their smoothness increases also with speed and solution concentration;

-AFM analysis confirms the results of SEM analysis, namely that the surface roughness is higher with increasing solution concentration and rotation speed.

The polymer solution concentration influences the mechanical properties (elongation, compression etc.), that is increasing the concentration determines decreasing of elasticity and increasing of plasticity. This study requires a detailed analysis according to [13-15]

On the other hand, morphological properties of thin films strongly influence their optical behaviour (emergence of structural colours for films with nanometer thickness and high surface roughness). From studying the structure of thin films it was found that they are similar to photonic crystals, guiding wavelengths of light in the same way and presenting structural colours from different observing angles [16-18].

Through this study we could show that many natural structures displaying structural colour can be reproduced by spin-coating thin film manufacturing. This shows that the fundamental physical phenomena of light that generates structural colour have been understood and can be manipulated so that to result in obtaining new materials with special optical properties. Mimicking biological structures with submicron dimensions through polymeric thin films opens new ways for exploration and characterization of complex structures in nature. The results obtained from analysing the thickness and thin film morphology of polyamide 6 are in agreement with their structural colours, showing that the more intense and diverse colours are obtained from the lowest solution concentration and the higher rotation speed.

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