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Mesoscopic Patterns in POMA Spin-coated Films: a Systematic Study

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The surface morphology of poly(o-methoxy aniline) (POMA) films produced by spin coating was systematically studied using Atomic Force Microscopy (AFM). Initial solution concentrations, rotation speeds and relative humidity affected the final film structure and thickness. Particularly interesting is the unexpected appearance, at solution concentrations of 2% or higher, of regular patterns composed of characteristic nanometer sized holes. These patterns were caused by phase separation.

Keywords: POMA; AFM; mesoscopic pattern; polymer films

INTRODUCTION

Spin coating is widely employed for producing thin polymeric films over a flat substrate. Its mathematical description is complex as it requires considering a non-Newtonian flow, but several models have explained the experimental results [1,2]. Overall, final film thickness is insensitive to the amount of solution initially dispensed onto the substrate, the rate of dispensing, the rate of rotational acceleration and total spin time. On the other hand, it is strongly dependent on initial solution concentration and final rotation speed. Additionally, film thickness and film uniformity are not significantly sensitive to the radial distance (distance to the rotation axis). A variation of less than

2% on thickness across a 5 cm substrate [2] has been reported.

A spin-coated film surface comprises radial structures evidenced by optical microscopy, associated with standing waves formed in the fluid prior to the solvent evaporation. Formation of such waves in a fluid undergoing a vertical excitation has been studied since the pioneering work of Faraday in 1831 [3]. The more general study of pattern formation in fluids and in granular mixtures has received considerable attention recently [4]. These structures are referred to as "Faraday waves", i.e. parametrically forced surface waves. Mesoscopic structures on spin coated organic films [5-7] have been observed with powerful microscopic techniques. For instance, Wang and collaborators [5] found that poly(styrene-maleic anhydride) alternated copolymer form well arrayed and uniform sized surface hole patterns. The structure was attributed to traces of water droplets that would be emulsified by the polymer solvent system leading to the well-organized structures. Other polystyrene based systems formed regular structures, either by limitation of a minimum necessary thickness for obtaining a continuous film structure that depends on the polymer-solvent-surface combination [6], or by a process of rupture and dewetting induced by thermal treatment [7]. Curable polymer systems also form complex hole structures that were likewise shown to depend on the relative air humidity [8].

In this work we report a systematic AFM study carried out on POMA films produced by spin coating. Poly(o-methoxy aniline) (POMA) is a chloroform soluble derivative of polyaniline that can be easily processed as thin films by means of spin coating, casting or any other suitable thin film formation technique.

EXPERIMENTAL DETAILS

Poly(o-methoxy aniline) (POMA) was obtained according to reference 9. Solution was prepared by dissolving the proper amount of powder in chloroform (HPLC grade). After 24 hours stirring, the solution was filtered. Initial polymer concentrations ranged from 0.5 to 2.5% (w/v). Microscopic glass slides were employed as substrates. The surface was cleaned by immersion in KOH/alcohol 30g/l solution, followed by extensive rinsing in water, sonication in distilled water, acetone and bidistilled water baths. Films were obtained by spreading the solution

over the clean glass substrates until complete covering the surface area. The substrate was then rotated. Two distinct rotation speeds were employed (2250 and 4700 rpm). Relative air humidity was kept at 22%. Surface morphology was investigated using an Atomic Force Microscope AccurexIIL from Topometrix in ac mode and film thickness was measured by a profilometer Dektak IIA.

RESULTS AND DISCUSSION

Figure 1 shows the AFM topographic images of POMA films obtained from 1% and 1.5% (w/v) polymer solutions and rotation speed of 2250 rpm. The measured surface roughness (RMS) implies very smooth (RMS = 2 - 3nm) structures homogeneously distributed over the whole substrate with film thickness in the range between 2000 and 3000 Å. Higher rotation speed (4700 rpm) leads to an increase in RMS roughness. Films produced from 0.5% solution were rougher (RMS = 6nm) and not continuous, which is consistent with the mechanism of film formation by spin coating. Stange and coworkers [6] have shown that a continuous film occurs only after a critical solution concentration. At lower polymer concentrations, the molecules aggregate forming clusters with size depending on initial concentration, molecular weight and substrate.

A distinct and unexpected situation arises at solution concentrations of 2% or higher, when regular mesoscopic patterns composed of characteristic nanometer sized holes were formed. Figures 2(a) and (b) show the AFM topographic and phase contrast images of these structures. The depth of the holes was estimated as ca. 5nm, i.e. less than 2% of the total film thickness, therefore not exposing the substrate. The phase contrast image shows indeed that a similar arrangement is observed on film surface and inside the holes, indicating that the same film surface structure is also underneath the holes. We believe that the mesoscopic pattern is formed on a later stage of the spin coating process although a more detailed study has to be carried out to verify if similar hole structures are formed in the bulk of the film.

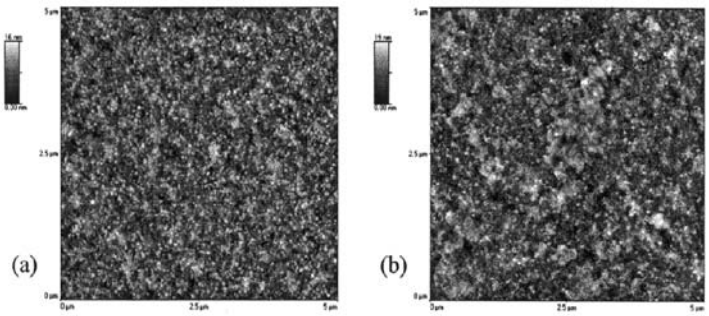

FIGURE 1 AFM images of films produced at different POMA concentrations (a) 1.0%; (b) 1.5%, and 2250 rpm.

The measured size of the holes does not depend on the distance from the rotation axis, in contrast to the roughness that was found to change significantly, indicating that the Faraday waves affect film roughness but not the hole structure or distribution. A systematic variation of the parameters known to affect film formation was performed. Table 1 summarizes the conditions of film production and their effect on film thickness, in addition to size and area occupied by the holes on the surface. Comparing films produced from the 2% solution, one observes that, as expected, films obtained at higher rotation speeds are thinner (about 60%) than the ones produced at 2250 rpm. Additionally, the size of individual holes is smaller and the total surface area occupied by holes are also proportionally smaller.

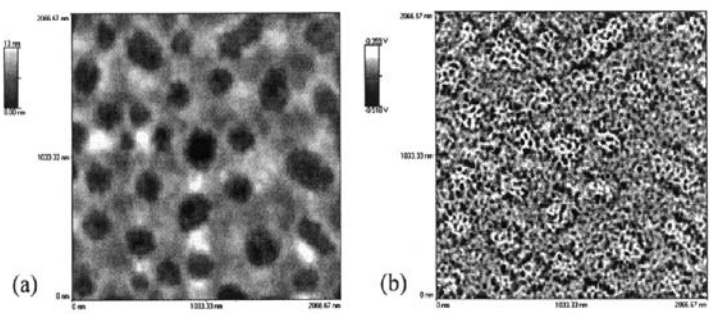

FIGURE 2 Topographic and corresponding phase contrast images of a 2.0% POMA film produced by spin coating.

Although water plays an important role on several systems where pattern formation is observed, we believe that in our case, the affinities of both POMA and chloroform with water are very low. Solubility of water in chloroform is as low as 806 ppm. We do not have the quantitative solubility data for POMA, but we observed that a higher relative air humidity does not affect significantly the dimensions of the mesoscopic structures. The details on this study will be published elsewhere. We attribute the formation of the holes in the POMA/chloroform system to demixing of the polymer/solvent due to temperature changes during the drying process. Demixing [10] is accomplished when a variation of solution temperature or addition of a non-solvent leads to an increase in the free energy of mixing. In order to minimize the energy, phase separation occurs. At least two phases are formed: one rich in polymer and another rich in solvent. The stable nucleus formed grows further in size by diffusion of the molecules from the continuous phase composition towards the new equilibrium phase until the viscosity effect stops the process. The type of structure after demixing by nucleation and growth mechanism depends on the initial polymer concentration.

TABLE 1 Characteristic dimensions of films presenting mesoscopic patterns

Solution Concentration	Speed (rpm)	Thickness (μm)	Area occupied by holes (%)	Individual hole size (μm^2)
2.0%	2250	0.23	21	0.028
2.0%	4700	0.14	11	0.016
2.5%	2250	0.29	18	0.037
2.5%	4700	0.16	11	0.013

For POMA films formed from chloroform solution, a reasonable variation of temperature is expected. For low polymer concentration, polymer rich regions are formed and coalesce during the solvent drying. For higher concentrations (2% or higher), solvent rich structures will be favored. As the polymer concentration grows, the demixing curve is shifted to lower temperatures and the demixing is delayed since the system will demand a large temperature variation to phase separate. This is corroborated by the rotation speed variation

experiments. Films produced at low speed are thicker and take longer to dry. In this case hole dimensions are bigger because the mass transfer process can last longer since the high viscosity state (freezing state) will be delayed. For films produced at high speed, the holes are smaller since the freezing state will occur sooner.

CONCLUSIONS

Mesoscopic structures have been observed on the surface of POMA films produced by spin coating. A strong role is played by the initial concentration of the solution, the structures only occurring at 2 % or higher. The presence of water absorbed from the air does not seem to be a relevant factor, rather suggesting that a phase separation process may be taking place.

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