Atomic Force Microscopy Applied to the Study of Dewetting Patterns of Thin Films from Polymer Solutions

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Stable and defect-free films are required for many technological applications, while controlled dewetting processes are important for producing thin film microstructuring for microelectronics, optical devices and biochip technology. In this work, we study the dewetting features formed by drying an aqueous solution of a charged polymer deposited on a mica substrate. A rich variety of morphologies can be formed, including holes, polygonal networks, droplets and elongated structures. The dewetting behavior depends on film thickness and on the charge density on the polymer that can be controlled by surfactant addition. The various nanoscale morphological patterns that are formed may be applied as a potential method for surface nanostructuring.

Dewetting is a process that can occur in thin liquid films (< 100 nm) due to the deformability of the liquid-air interface. In this process, the free surface of an initially uniform film becomes unstable and deforms spontaneously to engender a microstructure spread over the substrate [1-2]. Much effort has been directed towards understanding the dewetting phenomena, both experimentally and theoretically [3-4]. The knowledge of rupture mechanism and of the underlying forces would enable us to predict stability conditions very useful in many practical situations. The behavior of thin films depends on various interactions within the film and between the film and the bounding media. In purely apolar systems, the film energy is dominated by long-range van der Waals forces while in polar systems, polar interactions also contribute to film stability, acting as either stabilizing or destabilizing forces [5].

Since dewetting process is closely related to the film thickness (h), atomic force microscopy is an appropriate technique for the investigation of thin film stability and breakdown due to the possibility of measuring the h value. Besides this, the technique allows not only the acquisition of topographic images from the sample but also surface properties like electrical, magnetic and elastic.

So far, studies on thin film behavior have concentrated on non-volatile, non-wetting apolar systems showing some classical dewetting steps with characteristic features such as emergence of holes, their expansion, coalescence and formation of a polygonal network of liquid rims that break up due to Rayleigh instability, leading to spherical droplets [1]. The system studied in this work is polar and presents charged species that make it relevant to the comprehension of real systems. Besides this, the system is volatile, with thinning and dewetting occurring simultaneously. Dewetting begins at regions with different thickness in the sample.

Solutions of poly (N-isopropylacrylamide) (PNIPAM) (M_w= 90K) and sodium dodecyl sulfate (SDS) were prepared by mixing the respective polymer and surfactant solutions to obtain the

required final polymer concentration and surfactant to polymer ratio. Native PNIPAM is a thermosensitive polymer with a lower critical solution temperature (LCST) around 32 °C. It interacts with SDS above its critical aggregation concentration to form a charged PNIPAM-SDS complex that exhibits polyelectrolyte behavior in water [6]. The polymer concentration was fixed in 10^{-4} g mL^{-1} while the surfactant concentration was varied within $5 \cdot 10^{-5}$, 10^{-4} and $2 \cdot 10^{-4}$ g mL^{-1}, giving surfactant to polymer mass ratio of 0.5, 1.0 and 2.0.

Films were prepared by depositing 10 µL of polymer solution on freshly cleaved mica and allowing it to dry at 20 °C. During drying, water evaporation and thinning of film occurred simultaneously and dewetting of the film was initiated on different regions of the film according to their thickness. This allows us to observe dewetting patterns on different regions of varying film thickness on the same sample. Images and the average thickness (h) of the dried films were acquired using atomic force microscopy in non-contact mode (Topometrix Discoverer and Shimadzu WET-SPM).

In the studied system, we have the following situation: the solvent wets the substrate while the polymer is repelled from it. Results previously published [8] for the polymeric aqueous solution deposited on mica show that, in the presence of a non-wetting polymer, short-range attractive forces in the film lead to the possibility of film instability within a narrow range of film thickness. A thick film can undergo dewetting via heterogeneous nucleation and for very thin films, instability takes place and spontaneous dewetting occurs by spinodal process when the second derivative of the excess free energy with respect to the film thickness is negative ($\delta^2 \Delta G / \delta^2 h^2 < 0$) [5].

Figure 1a-c shows AFM images of PNIPAM-SDS film at low charge density deposited on a mica substrate and dried at 20 °C. In Figure 1a, the film is partially ruptured with polydisperse holes formed due to the growth of polymer film surface deformations. Once a hole is formed, it grows on the substrate due to the conjoining pressure near to the contact line and because of the surface tension force that induces the liquid to flow away from the crater [7]. The higher population of holes at the edge of the film can be explained by the differences in thickness of the sample. During the drying process by evaporation, film thinning is uneven and thinner regions dewet ahead of the thicker regions. Here the unrupted region is about 20 nm and the edge region is 10 nm height. Under the same observation timescale, holes that have nucleated and grow in thinner regions may have fused to form larger holes while the hole nucleation stage is initiated in thicker regions.

As predicted by Sharma [5] and found in our previous study [8], a film formed from polymer solution is unstable within a thickness range of the order of a few nanometers. Another theoretical study [2] considers that when the film ruptures, the liquid accumulates in the rims or in the unruptured areas. Thus, we can expect that the patterns produced in this system fall within the instability range predicted by Sharma for the spinodal mechanism [5]. It is also possible to observe a wide range of morphologies for the same sample and the same drying condition, what is also in agreement with the theoretical predictions [2].

Figure 1b shows hole coalescence forming a polygonal network of rims. At this stage, further coalescence of larger holes slows down because the time for drainage depends on the hole diameter [7]. As the hole size grows and the drainage from polymer ridges slows down, the coalescence rate also vanishes, and the Rayleigh instability engendered by the cross-section curvature of long ribbons leads to their break-up into droplets arranged in roughly polygonal arrays. In Figure 1c and also in

the line profiles traced in different regions of the image (Figure 1d), it is possible to observe thicker rims around the holes, formed by the polymer displaced from the growing hole and accumulated in the hole rim. Sharma and Reiter explained the occurrence of this phenomenon as a consequence of two mechanisms occurring simultaneously: viscous resistance that hinders polymer flow, and the surface tension that prevents the rim from growing indefinitely [7].

Figure 2a-b shows a dewet film of a polymer at increased charge density. Here, the dewetting has proceeded to a more advanced stage, and a different film morphology is observed. Patterns of aligned droplets can be seen, reminiscent of the polygonal forms. They are formed by rupture of the previous rims due to Rayleigh instability. In Figure 3 a-b, at a higher charge density, we observe a pattern approximately similar to that shown in Figure 2, but the droplets are elongated forming almost parallel lines. The formation of more elongated structures has been attributed to an increase in viscosity due to increased stiffness of polymer at very high charge density [2]. The viscosity effect counters capillary forces in the fragmentation of the rims, and thus favors anisometric shapes.

We have shown that dewetting of thin films of aqueous charged polymer solutions deposited on freshly cleaved mica produces patterns that depend on the film thickness and on the polymer charge density. Macromolecular conformations change with surfactant addition in different concentrations and so do the features formed. By controlling simple parameters in the dewetting system, a rich variety of morphologies, ranging from holes to polygonal network, droplets and elongated structures, can be obtained. The control of dewetting behavior can thus produce various nanoscale morphological patterns and it may be applied as a potential method for surface nanostructuring. [9]

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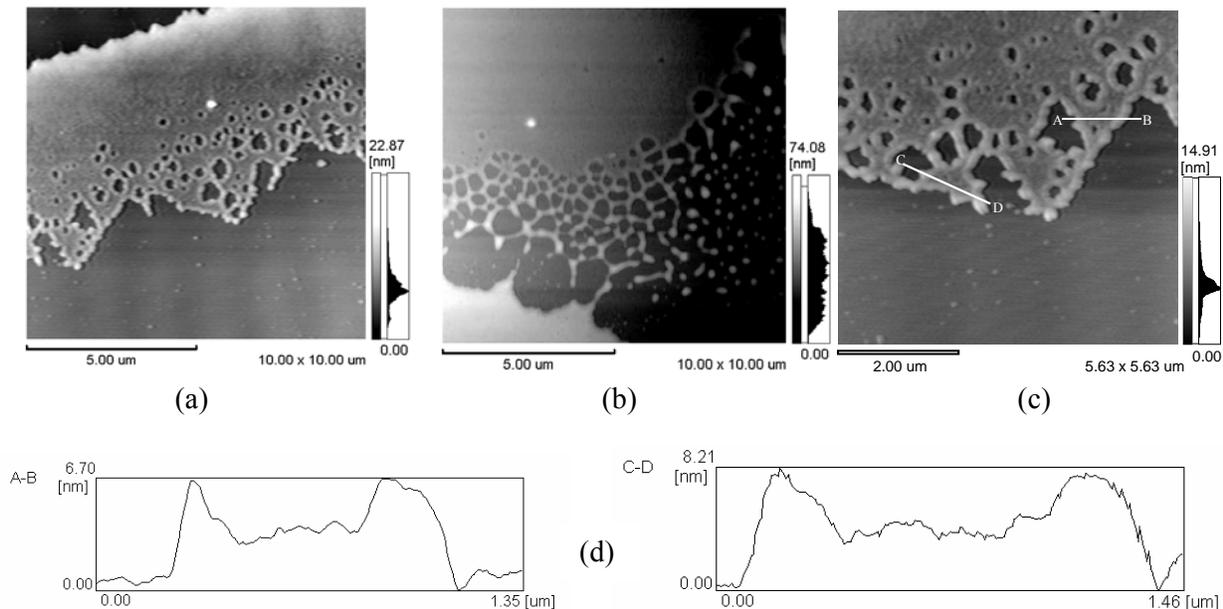[9] The authors acknowledge Fapesp, CNPq and Instituto do Milênio de Materiais Complexos.

Fig. 1. (a-c) AFM images of dewetting patterns of PNIPAM-SDS films at low charge density; (d) line profiles (A-B and C-D), showing polymer accumulation in the holes rim.
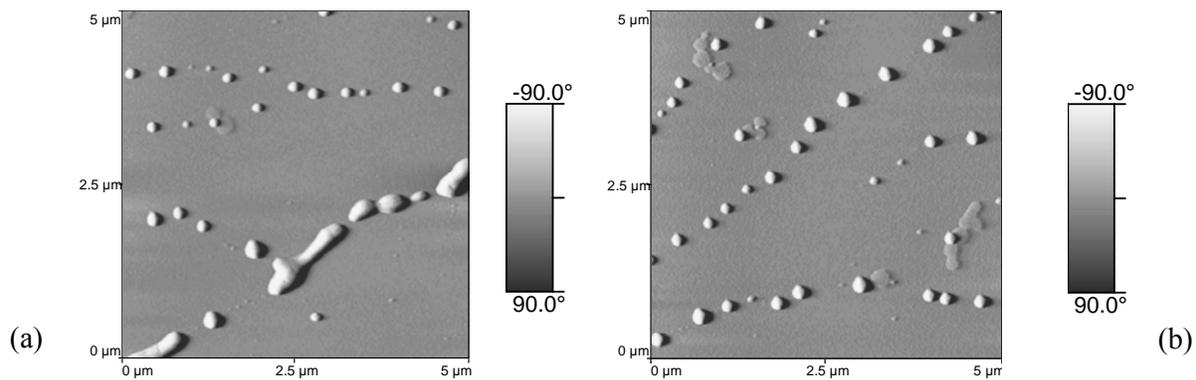

Fig. 2. AFM images of dewetting patterns of PNIPAM-SDS films at high charge density.
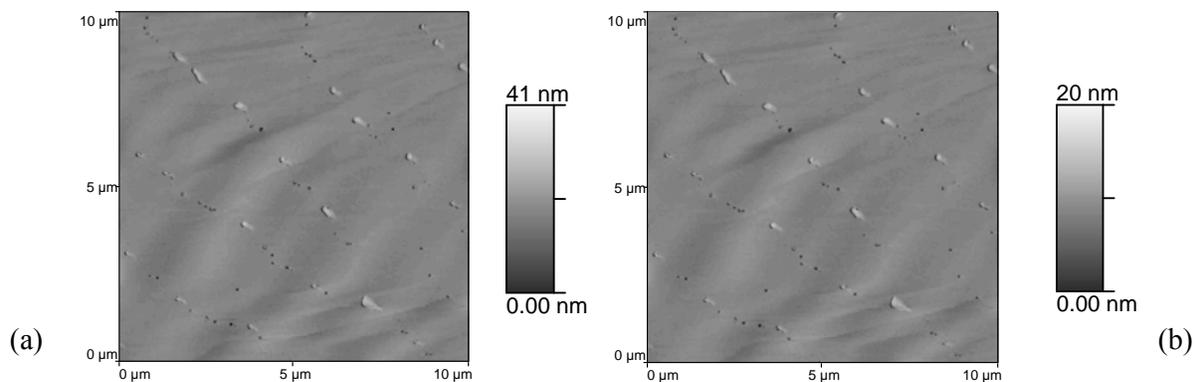

Fig. 3. AFM images of dewetting patterns of PNIPAM-SDS films at high charge density.