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Voronoi Tessellations in Thin Polymer Blend Films

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Introduction. Polymer films enjoy a wide range of biomedical and technological applications.[1−4] Polymer blending can yield materials with properties that cannot be provided by a single polymer.[5] Spin-coating is one of the most frequently used techniques for producing polymer blends, with film thicknesses down to the radius of gyration of the unperturbed ingredient homopolymer molecules. Studies on the domain structure and topography of the blend films are of current interest.[6] Understanding the mechanism that produces the final film morphology and how tailoring parameters, e.g. solvent type, influence the resulting structure is of prime concernment for tailoring films with desired properties. While significant advances have been made in understanding the processes leading up to final equilibrium morphology of polymer films,[7,8] an arrant apprehension of the spin-coating process has had only moderate success despite its importance. Lately, there has been heightened research activity in this area.[9,10]

Tessellations arise quite naturally in numerous applications. In some situations, e.g. in cell biology, physics, or geography,[11,12] one may wish to describe observed structures using models of tessellations. One way of generating them is to start with a set of discrete points in space, which are permitted to expand coetaneously in circular disks at the same rate. The disks are not allowed to overlap, so they must deform, and one finally gets polygons. Voronoi tessellations have been observed for dewetting thin film polymer bilayers.[13] Earlier on, such structures were chronicled as a stage of dewetting in homopolymer films prior to the formation of droplets.[7] Here we report the observation of such tessellations for unannealed polymer blend thin films. An exegesis of the phase separation process accounting for this observation is proposed.

The use of phase-sensitive acoustic microscopy (PSAM)[14] for characterizing polymer films has recently been reported.[15,16] The PSAM resolution here was about 1 μm. PSAM was employed together with a Dimension 3000 scanning probe microscope (Digital Instruments/Veeco Metrology Group) (AFM) operating in contact mode. Polymer blend films were spin-cast on silicon (111) substrates, from a solution containing polystyrene (PS, $M_w = 240\,000$) and poly(methyl methacrylate) (PMMA, $M_w = 106\,000$), with dichloromethane as the conjoint solvent. The PS/PMMA (50/50 w/w) blend film solution contained 3% of polymer by weight. The spin-coating time was 45 s. To check reproducibility, several samples were prepared using the same preparation conditions and parameters. The tessellation morphology discussed shortly was observed in each case. The average film thickness was obtained (using both AFM and PSAM) by applying scalpel scratches on the films and deducing the height difference between substrate and film from the AFM height analysis and PSAM phase images. For PSAM measurements, water was used as coupling fluid with no effect on the blend films.

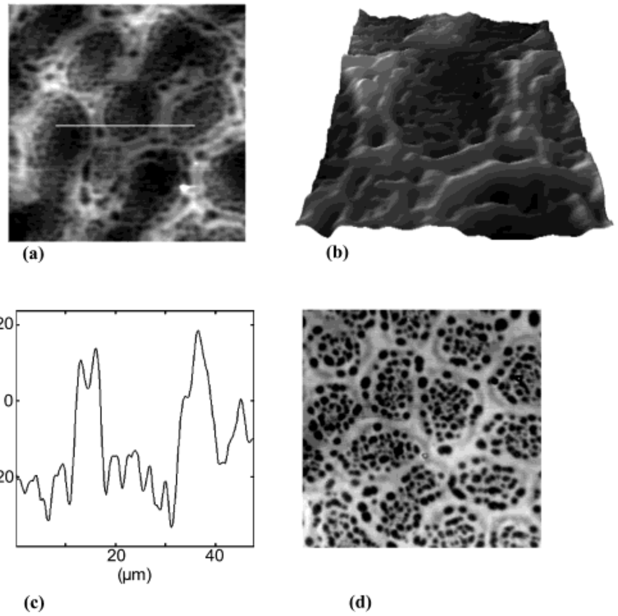

Figure 1. (a) 82 × 82 μm^2 AFM image of an unannealed 165 nm thick PS/PMMA blend film on silicon substrate. A Voronoi tessellation pattern is clearly visible. (b) Perspective view of single cell from (a). (c) Line profile from region marked with a line in (a). (d) 100 × 100 μm^2 PSAM maximum amplitude image showing tessellations of the unannealed blend film. The darker regions correspond to PS and bright regions to PMMA.

Results and Discussion. Figure 1a delineates an AFM image of the typically observed Voronoi tessellations of a 165 nm thick unannealed blend film. Figure 1b is a perspective image of a single cell extracted from the region with the line in Figure 1a. The line profile (Figure 1c) extracted from Figure 1a limns two levels of phase-separated domains. The observed valleys and hills are commensurate with expectations predicated on preferential solubility considerations for each homopolymer.[8] Although they can suggest a well-defined phase separation, AFM topographical features do not give an unambiguous picture of the phase composition. The film was thus examined with the PSAM technique and the morphology observed in Figure 1a confirmed. The PSAM maximum-amplitude image in Figure 1d shows bright PMMA regions and dark PS regions.

The crucial question is why these tessellations in blend films have eluded espial until now. A possible explanation lies in the concept of a critical point or regime that often escorts the idea of Voronoi tessellations.[7,11] During the first stage of the spin-coating process, most of the homogeneous fluid, composed in this case of PS and PMMA dissolved in dichloromethane, is

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spun off, leaving a uniform film. The second stage is characterized by the radial flow of the fluid, which is a balance between centrifugal and viscous forces, decreasing the film thickness and controlling its final average value. It is during this stage that phase separation takes place, initiated by decreasing solvent concentration.[17] During the third stage, the arrangement of phase domains is terminated for very low solvent concentration values, when one of the homopolymers is no longer mobile.[18] The last stage is where the solvent volatility factor comes into significant play: how fast the solvent concentration decreases and how quickly the termination takes place. This would account for our observations.

Quite recently, the consequential influence of the solvent volatility on the final film morphology of homopolymer films was reported.[9] In this study, this influence is ostensively borne out for polymer blend films. Dichloromethane is relatively much more volatile than the hitherto often used solvents. We suspect that within a critical regime the quenching process (termination time) during spin-coating can be so rapid (small) that it freezes the phase separation process, at a time that allows the observation of the Voronoi tessellation stage. For low vapor pressure solvents like toluene, the solvent evaporation time is long enough to achieve phase separation with the resulting morphology beyond the Voronoi tessellation stage. The critical regime of course depends on other parameters like the film thickness,[7] polymer concentration,[11] and a possible substrate-induced modification of the evaporation kinetics.[19] The phase-separation mechanism is apparently similar to that used for nonatomic solvent-driven Voronoi tessellations of proteins.[20]

Conclusion. We have presented an unusual polymer blend morphology of Voronoi tessellations, observed by AFM and PSAM. Our findings suggest that the congenitally entropy-driven phase separation process for polymer blend films may follow a “quasi-Voronoi tessellation” generation mechanism or, at the least, engender a Voronoi tessellation stage. This propounds a newfangled way for modeling the phase-separation process during spin-coating. A study of the critical role of the solvent volatility on the morphology of the spin-cast polymer blends analogous to that recently carried out for homopolymers,[9] or an extension of the investigations reported in ref 21, but also studies involving a variation of the molecular weight of one ingredient polymer, would further elucidate the observations reported here.

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