

RUPTURING OF POLYMER FILMS WITH RUBBING-INDUCED SURFACE DEFECTS*

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Abstract It has been a long-standing question whether dewetting of polymer film from non-wettable substrate surfaces wherein the bicontinuous morphology never forms in the dewetting film is due to spinodal instability or heterogeneous nucleation. In this experiment, we use a simple method to make the distinction through introduction of topographical defects of the films by rubbing the sample surface with a rayon cloth. Spinodal dewetting is identified for those films that dewet by a characteristic wavevector, q^* , independent of the density of rubbing-induced defects. Heterogeneous nucleation, on the other hand, is identified for those with q^* increasing with increasing density of defects. Our result shows that PS films on oxide coated silicon with thickness less than ≈ 13 nm are dominated by spinodal dewetting, but the thicker films are dominated by nucleation dewetting. We also confirm that spinodal dewetting does not necessarily lead to a bicontinuous morphology in the dewetting film, contrary to the classic theory of Cahn.

Keywords Dewetting, Polymer thin films, Spinodal instability, Heterogeneous nucleation

INTRODUCTION

It is an everyday experience that liquid films on non-wetting surfaces may dewet and break up into liquid beads. Despite its being commonplace, there has been much debate on the physics of thin film dewetting, namely it cannot be resolved whether the thin film rupture is initiated by a spinodal mechanism or heterogeneous nucleation. According to Cahn^[1], if the second derivative of a system's free energy as a function of the order parameter is less than zero (*i.e.* $G''(h) < 0$), the system is unstable towards spinodal decomposition, and spontaneous fluctuations in the system order parameter will grow exponentially with time^[1]. Amongst all the fluctuation modes that are growing, the one with wavevector, q , equals $q_m = \sqrt{G''(h)/\gamma}$ will grow the fastest, resulting in a characteristic wavevector $= q_m$ in the sample morphology at the initial stage of phase separation. In later stage, however, coarsening of the morphology will occur due to renormalization of the free energy by the fluctuations so the characteristic wavevector will shift to smaller q ^[2]. In apolar liquid films on a substrate, if the film thickness is less than ≈ 100 nm, the free energy is mainly due to non-retarded van der Waals interactions^[3] and is of the form $-A/12\pi h^2$ per unit area. Here, A is the Hamaker constant, and h is the film thickness, which is also the system order parameter. From the foregoing discussion, liquid films with $A < 0$ will have $G''(h) < 0$ so are unstable against spinodal decomposition, whereby inhomogeneity in the film thickness will take place by exponential growth in the amplitude of surface undulations in the film. Correspondingly, the phase-separating state is a distribution of ridges and valleys. However, if $G''(h)$ is positive, so long as $G'(h)$ is not zero (*i.e.* $G(h)$ has not yet reached its minimum), the film may still undergo phase separation through heterogeneous nucleation.

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It is important to note that the two mechanisms being discussed concern only the initialization of film rupturing. Once the surface undulations have grown to touch the substrate surface, the hence nucleated holes from either mechanism always widen according to hydrodynamics of dewetting until adjacent holes touch each other, whereupon the thin polymer ribbon connecting neighboring holes either coalesces to produce one single bigger hole, or breaks up into small polymer beads through the Rayleigh instability.

In distinguishing spinodal and nucleation dewetting in liquid (mostly polymer) films, current practice makes use of the known characteristics of the spinodal mechanism. Two characteristics have been frequently used, including the appearance of the bicontinuous structure in the phase separating morphology, as Cahn had found in his simulation result^[1], and the $q_m \sim h^{-2}$ scaling, which results from applying $G(h) = -A/12\pi h^2$ to Cahn's theory^[1]. While the occurrence of a bicontinuous structure does provide unequivocal evidence for spinodal dewetting, cases in which the bicontinuous structure did not occur, but instead holes were formed, are controversial. In these samples, the characteristic wavevector is determined from either the areal density of holes, N_H , appearing in the initial stage of rupturing or the areal density of droplets, N_d , or polygons, N_p , formed in the final stage. Compliance of $N_H(h)$ or $N_p(h)$ with the h^{-4} scaling has been taken as evidence of spinodal dewetting (Reiter, 1992), equivalent to the $q_m \sim h^{-2}$ characteristic. On the other hand, Jacobs *et al.*^[4] pointed out that the holes had no spatial correlation and hence were unlikely due to spinodal growth of surface undulations. They further showed that the $N_H(h) \sim h^{-4}$ scaling could be erroneously taken from an exponential dependence.

In this paper, we report a simple experiment by which one can resolve this controversy unambiguously. In our approach, small height fluctuations were artificially introduced to the thin film samples by mechanically rubbing the film surface with a rayon cloth before dewetting takes place. Since the characteristic length of the dewetting pattern of polymer films that dewet by nucleation should depend on the density of surface defects introduced, but that of the films dewetting by a spinodal process should be relatively unaffected, one should be able to unambiguously identify which of the two dewetting mechanisms has in fact dominated in the rupturing of a given film simply by comparing its dewetting morphologies with and without the rubbing-induced defects.

EXPERIMENT

The system chosen for this study is polystyrene (PS) (molecular weight, $M_w = 13.7$ K Da and polydispersity index = 1.1) spin-coated on silicon covered with a layer of ≈ 100 nm thick thermal oxide. The PS, purchased from Scientific Polymer Products (Ontario, NY), has a glass transition temperature, $T_g \approx 99^\circ\text{C}$ from differential scanning calorimetry. To prepare the substrates, 4" diameter Si (100) wafers were subject to wet oxidation before being cut into 1×1 cm² pieces, then cleaned as reported in an earlier publication^[5]. Upon spin-coating with the PS, the samples were annealed at 100°C under a 10^{-2} torr vacuum for 5 h to remove the residual solvent. No sign of dewetting could be found in the polymer films after annealing. To engrave the topographical fluctuations, a piece of rayon cloth was rubbed against the film surface at a constant speed of 1 cm/s under a normal pressure of 10 g/cm². The density of surface defects was controlled by changing the number of rubbings. The surface morphology of the films was characterized by a model SPA-300HV atomic force microscope (AFM) from Seiko Instruments (Chiba, Japan). Figure 1(a) shows the topographical image obtained from a PS film freshly rubbed 15 times, from which parallel corrugations from rubbing are clearly evident. The Fourier spectra of this sample and those rubbed by 3 and 10 times are shown in Fig. 1(b). Evidently, the spectra due to different numbers of rubbings appear to be the same. This strongly suggests that surface structures added to the films by individual rubbing are independent. It thus follows that the density of rubbing-induced surface defects should increase linearly with increasing N .

Dewetting experiments were carried out at 180°C from 10 to 60 min. We deduce the characteristic wavevector, q^* , of the final dewetted patterns from the Fourier spectra. When the initial holes do not coalesce to form a network of polygons before breaking up into droplets, the dewetted patterns often display uniformly distributed liquid droplets (Fig. 4, for example). In that case, the square of the characteristic wavevector, $(q^*)^2$ is proportional to the areal density of the final liquid droplets, N_d . On the other hand, if the holes do coalesce before they break up into liquid droplets, the dewetted patterns are composed of a network of polygons^[6]. Then the

square of the characteristic wavevector will instead be proportional to the areal density of the polygons, N_p . The change in physical meaning of q^* simply reflects the different dewetted morphologies that were found in samples of different thickness. However, with either interpretation, q^* serves to provide a measure of the characteristic length scale of the sample morphology for which we will compare between samples subject to different number of rubbings.

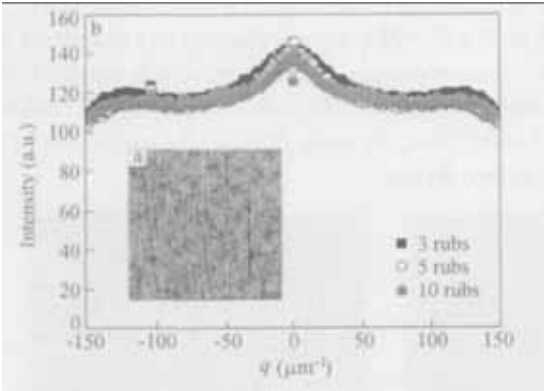


Fig. 1 (a) AFM topographical image of a PS film subjected to 15 rubbings
(b) Fourier spectra of PS films rubbed different number of times from 3 to 15 times

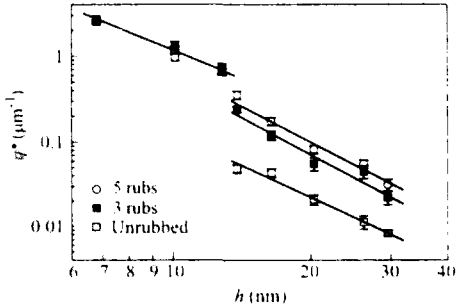


Fig. 2 Characteristic wavevector, q^* versus h for PS films subject to different numbers of rubbings from 0 to 5

RESULTS AND DISCUSSIONS

Figure 2 shows q^* versus h for PS films subject to different numbers of rubbings, N ($= 0$ to 5). As seen, q^* increases with decreasing h , consistent with previous results^[4, 6]. We further note that q^* of the samples with h

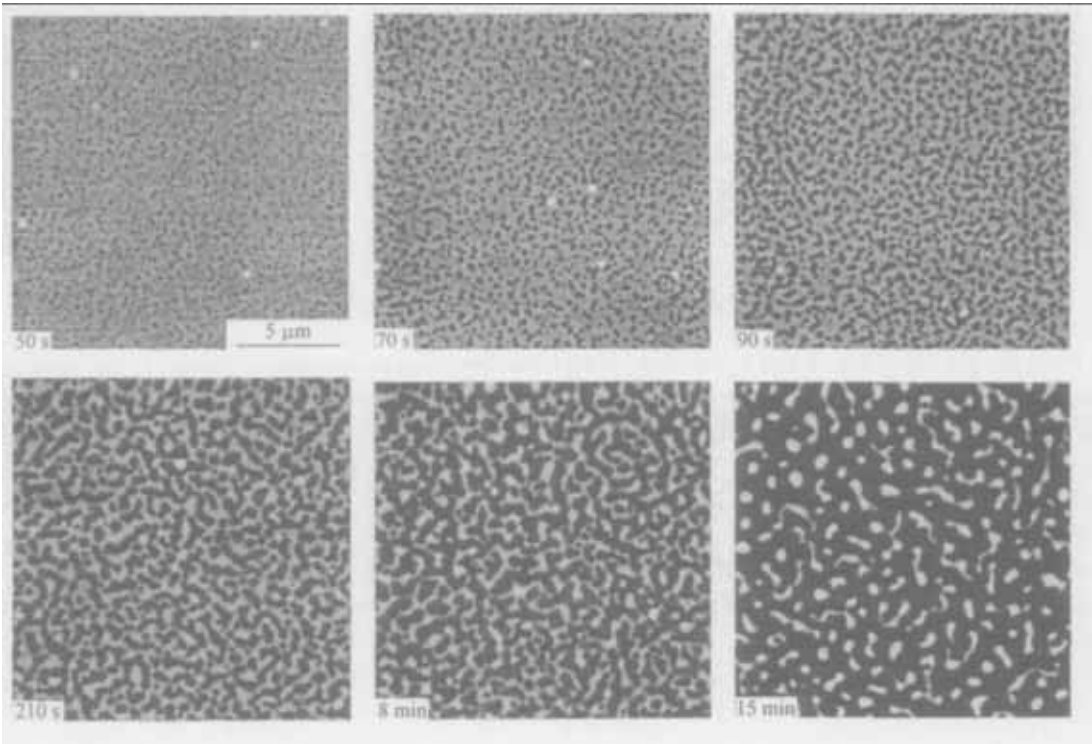


Fig. 3 AFM topographical images of a 3.2 nm thick PS film dewetting at 180°C in nitrogen gas

below 13.3 nm are essentially independent of N whereas q^* of the thicker samples increases with increasing N . These data provide unequivocal evidence of the dominance of spinodal dewetting in samples with $h < 13.3$ nm but heterogeneous nucleation in samples with $h > 13.3$ nm.

To clarify the issue of the sample morphology obtainable from spinodal dewetting, we examine the evolution of dewetting in unrubbed films with thickness below 13.3 nm. Figure 3 shows AFM topographical images obtained from a 3.2 nm thick PS film taken at different annealing times from 50 s to 15 min at 180°C. As seen, regions of regular ridges and valleys already appeared in 50 s. By 90 s, the morphology had developed into a bicontinuous structure. In Fig. 4, we show the evolution of the rupturing morphology of a 5 nm thick film annealed at 180°C. As one can see, holes of uniform size already emerged by 10 s, and they scattered randomly across the sample surface. Gradually, they grew in size until, after 330 s, the holes filled up the whole area of the film whereupon the thin ribbons connecting the holes broke up into droplets.

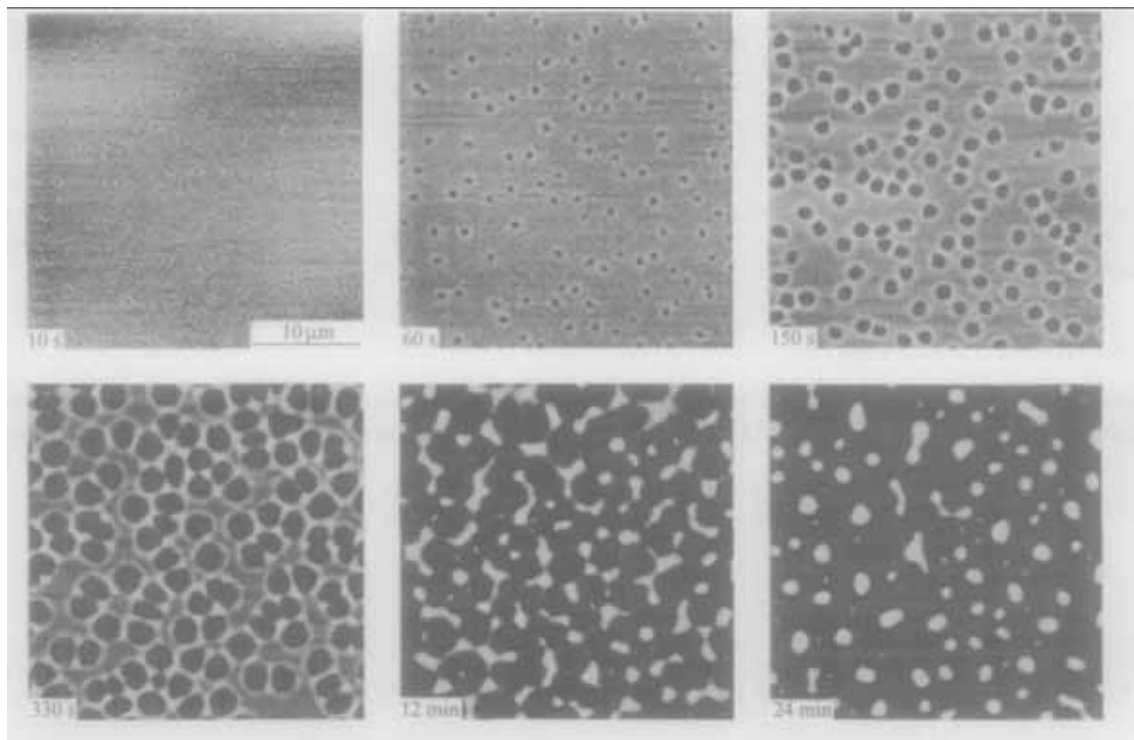


Fig. 4 AFM topographical images of an 5 nm thick PS film dewetting at 180°C in nitrogen gas

From the results of Fig. 3 and 4, one may deduce the dewetting morphologies formed in the early stage of spinodal dewetting. Basically, both the bicontinuous structure (Fig. 3) and holes (Fig. 4) may appear. The former forms in samples in the deep spinodal region whereas the latter appear in the thicker samples. This finding is reminiscent of the result from 3D nonlinear calculations by Sharma and Khanna^[7]. These authors found that the morphology from spinodal dewetting can have either the bicontinuous structure or holes, depending on the form of $G(h)$. If $G(h)$ is such that $G''(h) \approx 0$, holes are formed, otherwise, the classic bicontinuous structure is preserved. While at this point there are not enough data to verify the origin of the transition at $h = 13.3$ nm, a zero crossing of $G''(h)$ is certainly one possibility based on Sharma and Khanna's results. This is the question of our current study.

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