# Fracture and Fingering Patterns in Entangled Moving Rims

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The stability of polymer thin films on top of a solid surface is of importance for numerous applications ranging from the lubrication to microlithographic resist films. When forced to cover a non-wettable substrate, thin liquid film will be unstable and dewet. Dewetting refers to the process of fluid retraction from a substrate it was forced "against his will" to cover (via a spin-coating process for instance). The origin of this behavior is found in the capillary driving force acting at the three phase contact line, resulting from an imbalance between the three interfacial tensions of the liquid-air, liquid-substrate and substrate-air interfaces [1].

The film rupture is induced by the growth of numerous holes surrounding by a rim which could exhibit a variety of artistic morphologies of instability. The first case of rim instability appears at the early stage of dewetting in the elastic regime and is related to stress dissipation by fracture propagation (Fig. 1).

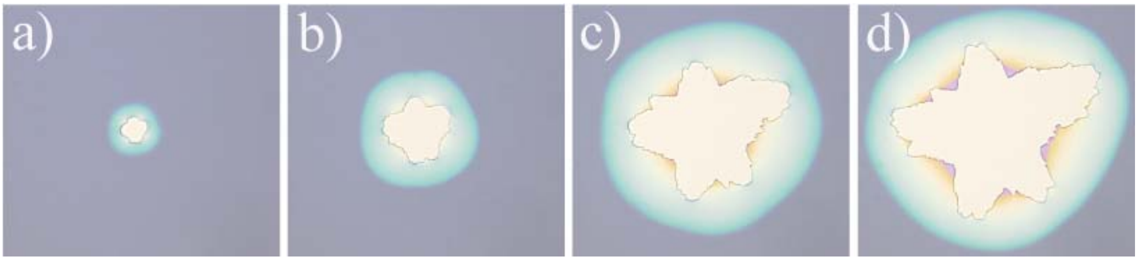


FIG. 1 – Rim fracture propagation in a supported film of polystyrene ($M_w$ = 950 kDa, $h$ = 140 nm) heated at 160°C. Acquisition times : (a) 330, (b) 998, (c) 1268 and (d) 1538 s. Scale bar corresponds to 50 $\mu$m.

At longest experimental times, rims show fluctuations in width appearing as an undulation and finally yield to a 'finger-like' pattern by viscous fingers formation (Fig. 2). The transition between the two main dewetting regimes (elastic and viscous) is associated by a modification of the shape of the rim and a transition in the time dependence of the dewetting velocity.

Our results indicate that rim instabilities can be consider as an attractive experimental tool (i) for studying the role of the film/substrate interaction (slippage and friction) and (ii) for determining relaxation times of polymer chains confined in nanometric thin films.

We will report new experimental observations which show that wall slip, resulting from polymer chain entanglement within the film, is a key ingredient for both instabilities and we will

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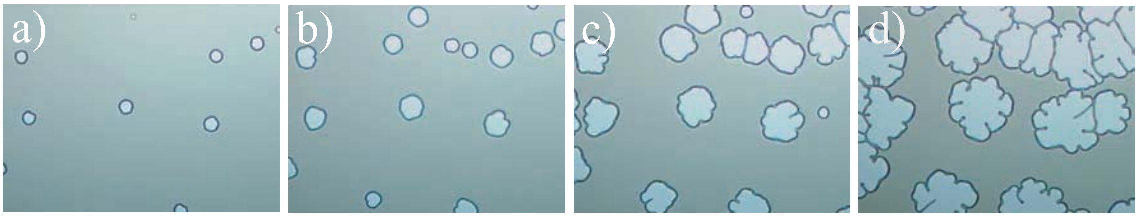


FIG. 2 – Rim fingering instability in a supported film of polystyrene ($M_w$ = 600 kDa, $h$ = 45 nm) heated at 140°C. Acquisition times : (a) 1200 s, (b) 12600 s, (c) 16920 s and (d) 17760 s. Scale bar corresponds to 200 × 175 $\mu$m$^2$.

clearly demonstrate that these instabilities are related to the relaxation modes of a polymer melt [2].

The formation of cracks into the circular asymmetric rim can be interpreted as the instantaneous response of a dynamic elastic ring to an applied tangential stress. As a result, the fractures propagation forms a complex structure in a starry shape which provides a faster way to release the accumulated stress and thus to dewet [2]. The energy dissipation process is strongly affected by geometry, which is not the case for viscous liquids. In this viscous dissipation mode, the Laplace pressure increases rapidly and tends to weaken elastic deformations. The result is a modification of the shape of rims which evolves toward a symmetric equilibrium shape. Undulations of the rim in the viscous regime show an analogy with the Plateau-Rayleigh instability, constructed for a ridge geometry, and characterized by the deformation of two coupled contact lines. Our experimental observations indicate that the wavelength characterizing the undulation of the deformed contact line (before droplets formation) continuously increases in time but always remains proportional to the rim width. The onset of the rim undulations, and consequently the selection of experimental wavelength, can therefore be accounted for a process similar to the Plateau-Rayleigh instability related to the minimization of the surface free energy [3].

We argue that determining the onset of this rim instability represents a reliableway for measuring the disentanglement time of polymer which corresponds to the characteristic transition time. We will report a novel concept which allows to extract reptation times from the rim instability of polymer thin films dewetting close to the glass transition temperature [4]. We will experimentally demonstrate that the onset of the viscous rim instability, occurring at the transition between two dewetting regimes, is related to the longest relaxation time (*i.e.* the disentanglement time) of the dewetting polymer.

Bibliography

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