Film Splitting Flows of Dilute Polymer Solutions

G. A. Zevallos[(1)], M. Pasquali[(2)] and M. S. Carvalho[(1)]

[(1)] Department of Mechanical Engineering
Pontificia Universidade Catolica do Rio de Janeiro
Rio de Janeiro, RJ, 22453-900, Brazil

[(2)] Department of Chemical Engineering
Rice University
Houston, TX, , USA

Presented at the 12th International Coating Science and Technology Symposium
September 23-25, 2004 • Rochester, New York
Unpublished

Roll coating is widely used to apply a thin liquid layer to a continuous flexible substrate. At low speeds the flow is two-dimensional and steady; as the roll speed is raised, the two-dimensional flow becomes unstable and is replaced by a steady three-dimensional flow which results in more or less regular stripes in the machine direction, as illustrated in Fig.1. This type of instability or rather the three-dimensional flow to which it may lead, is commonly called *ribbing*; it can limit the speed of the process if a smooth film is required as a final product.

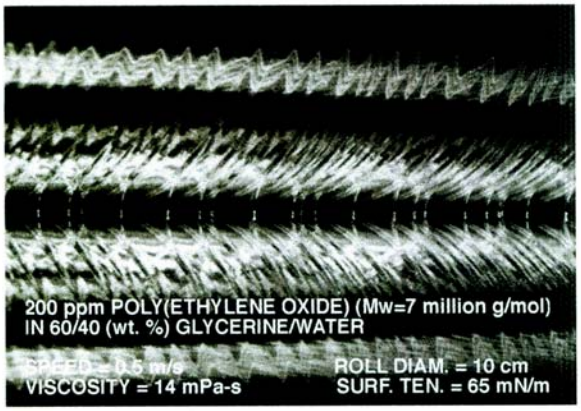

Fig. 1: Three-dimensional periodic flow in forward roll coating film splitting (from Carvalho et al., 1994).

The film-splitting flow of a Newtonian liquid exiting from two rotating rolls and the associated instability have been studied extensively. Pearson (1960) was the first to analyze why a flow that otherwise leads to a uniform meniscus can turn unstable. He showed that the adverse pressure gradient near the film-split meniscus necessary to decelerate the flowing liquid destabilizes the free surface, whereas surface tension has a stabilizing effect. A critical value of the ratio between these two forces, i.e., the capillary number $Ca \equiv \mu V / \sigma$, marks the onset of the free surface nonuniformity. Here, μ is the liquid viscosity, σ its surface tension, and V is the mean roll speed. Further experiments and theoretical models to describe the film-splitting

instability of Newtonian liquids between rigid rolls have been developed by Pitts and Greiller (1961), Mill and South (1967), Greener et al. (1980), Savage (1984), Benkreira et al. (1982), and Coyle et al. (1990).

In practice, coating liquids often contain polymers. Non-Newtonian behavior can drastically change the nature of the flow near the free surface and consequently alter the performance of a coater. The first analyses of non-Newtonian effects in roll coating flows were restricted to shear-thinning behavior and simple power-law models. By solving the two-dimensional conservation equations of a shear-sensitive liquid, Coyle et al. (1987) showed the effect of shear-thinning on the film thickness and pressure distribution along the coating bead. Bauman et al. (1982) experimentally tested the effect of certain polymer additives on the ribbing instability. They observed that the critical speed at which ribbing first appeared was lower than in the case of a Newtonian liquid. They advanced simple arguments about the effect of liquid elasticity on the stability of the flow. They concluded that the elastic stresses that appears in the extensional flow near the free surface destabilizes the flow. The formation of small liquid drops at the film split meniscus, a phenomenon known as spatter and misting, was studied by Glass (Glass 1978a-d). He observed roll spatter in coating of aqueous dispersions of colloidal polymer plus other ingredients in `latex' paints by evaluating several trade paints and comparing their propensity to spatter. Their main conclusion was that paints with high apparent extensional viscosity produced large and stable filaments. Soules et al. (1988) and Fernando and Glass (1988) addressed spattering in commercial paints. They found that the instability occurred at lower capillary number in liquids with higher apparent extensional viscosity (measured by fiber-suction technique). Moreover, the length of filaments and the intensity of misting increased with the apparent extensional viscosity. Carvalho et al. (1994), and later Dontula (1999), with more details, analyzed experimentally the film splitting flow of aqueous solutions of PEG and PEO. They concluded that minute amounts of flexible polymer lowered drastically the critical speed at which the three-dimensional instability occurs. Grillet et al. (1999) and recently Lopez et al. (2002) studied experimentally the instability of non-Newtonian flow between two non-concentric cylinders. The latter used two aqueous polymer solutions with similar shear-thinning behavior but different elastic characteristics, i.e., Xanthan (inelastic) and Polyacrylamide (elastic). With the elastic (Polyacrylamide) solution, the critical capillary number for the instability dropped with growing polymer concentration by up to one order of magnitude compared to the Newtonian case. With the Xanthan solution, the critical capillary number decreased only slightly. The resulting three-dimensional pattern of the free surface is also a strong function of the liquid properties, which suggests that the instability mechanism may be different in the case of viscoelastic liquids.

Accurate theoretical predictions of the onset of ribbing when viscoelastic liquids are used is still not available. The mechanisms by which the liquid elasticity makes the flow unstable at Capillary numbers much lower than in the Newtonian case is not completely understood.

The stability problem can be approached in two ways: (1) by analyzing the two-dimensional flow kinematics at the free surface and extracting simple criteria to estimate the critical capillary number; (2) by computing the two-dimensional flow by solving the mass and momentum balance equations together with a suitable constitutive equation for the stress, and then assessing the stability of this flow to infinitesimal three-dimensional perturbations.

Simple criteria to estimate the stability of film splitting flows have been proposed for Newtonian liquids by Pitts and Greiller (1961) and for viscoelastic liquids by Graham (2003).

The stability criterion proposed by Pitts and Greiller (1961) is based on a spanwise momentum balance along the perturbed free surface. In their analysis, the viscous (and viscoelastic) stresses are neglected and only the pressure is considered as the driving force for the instability. The flow is considered unstable if the transverse normal tensile stress under the perturbed free surface at the midpoint between the crest and the throat of the developing wave is smaller than the transverse normal stress at the same streamwise location beneath the crest of the wave (or, conversely, if the pressure beneath the crest of the wave is higher than that at the midpoint between the crest and the throat). In this case, the gradient of spanwise stress will drive flow from the throat into the crest of the wave and thus the instability will grow. The flow is stable if

$$\frac{dp}{dx} < \sigma\left(-\frac{dH}{dx} + N^2 \right)$$

where H is the curvature of the film splitting meniscus and N is the wavenumber of the perturbation. Of course, this simple criterion does not predict correctly the wavenumber of the instability, but it identifies correctly the competition of the relevant forces. Based on this analysis, Pitts and Greiller (1961) estimated that the critical capillary number at the onset of ribbing is a function of the gap between the rolls $2H_0$ and ought to be

$$Ca^* = 28\frac{H_0}{R}.$$

Recently, Graham (2003) proposed a different simplified criterion to asses the stability of a flow under a curved free surface. The key, novel component of the analysis is the introduction of a local cylindrical coordinate system at the free surface which allows the incorporation of the normal stress difference at the free surface on the radial component of the momentum balance equation. According to Graham's criterion, the flow is stable when

$$\frac{dT_{rr}}{dr} - \rho g_r = \frac{\sigma_{\theta\theta} - \sigma_{rr}}{R} - \rho g_r < \varsigma N^2.$$

However, this analysis neglects an important term present in the earlier work of Pitts and Greiller (1961), namely the stabilizing effect of meniscus curvature variation due to free surface position variation, e.g. $\varsigma dH/dx$, this term was present in an earlier analysis by Graham (2002). Whereas this term is irrelevant in flows where the free surface develops between nearly parallel plates (such as planar Hele-Shaw flow, for example), it is important in flows between diverging surfaces, such as roll coating flows, because it accounts for the effect of an outward motion of the free surface which stabilizes the flow because it reduces the capillary pressure drop across the free surface and thus diminishes the pressure gradient beneath the free surface.

Scriven and co-workers analyzed the stability problem more rigorously in the case of various Newtonian coating flows by evaluating the response of the two-dimensional, steady-state flow to infinitesimal periodic disturbances. Such linear stability analysis was used successfully to determine critical capillary numbers at

different gap to roll ratio at the onset of ribbing for both rigid and deformable forward roll coating flows of Newtonian liquids (Christodoulou and Scriven 1988; Coyle et al. 1990; Carvalho and Scriven 1999).

Modelling of viscoelastic coating flows must rely on theories that can capture sufficiently well the interplay of flow and liquid microstructure. Moreover, coating flows always involve free surfaces; the domain where the differential equations are posed is unknown *a priori* and it is part of the solution, and the shape of the free surfaces must be captured well because capillarity is one of the key forces that control the flow. These two characteristics make the problem extremely complex, and prototypical steady viscoelastic free surface coating flows have been studied only recently (Pasquali 2000; Pasquali and Scriven 2002; Lee et al. 2002). Likewise, the stability analysis of viscoelastic flows is fraught with difficulties. Simple non-viscometric flows have been tacked successfully recently (Sadanandan and Sureshkumar 2002; Smith et al. 2003), and methods for linear stability analysis of viscoelastic free surface flows are still under investigation.

In this work, the two-dimensional, viscoelastic, free surface roll coating flow is analyzed with two differential constitutive models: the Oldroyld-B and the FENE-P equations. The free boundary problem is transformed into a fixed boundary problem by mapping the unknown domain into a reference one (Christodoulou 1990; de Santos 1991; Sackinger et al. 1996; Carvalho and Scriven 1997) and the continuity, momentum, conformation, and mesh mapping equations are solved with the DEVSS-TG/SUPG method with finite element basis functions (Pasquali and Scriven 2002).

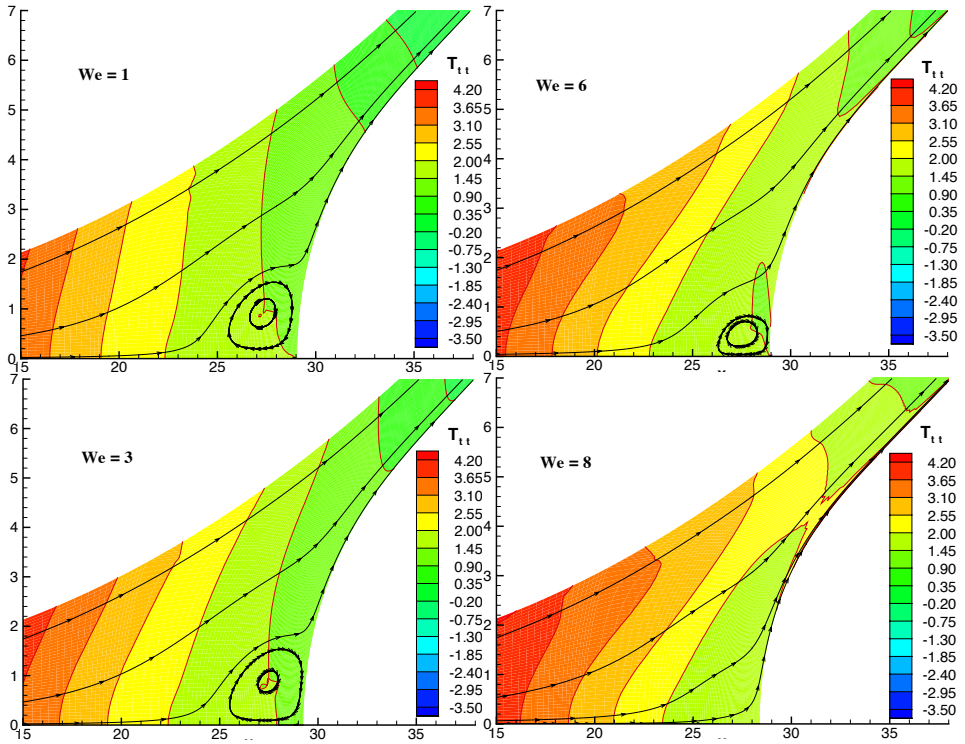

Figure 2: Evolution of the streamlines and normal stress component along the streamlines as Weissenberg number grows at *Ca = 0.2*.

The main difference between extensional and shear flows is that in extension polymer molecules are being extended along the preferred direction of stretch and orientation, and are being contracted along the

direction where they are already contracted and least likely to be oriented, whereas in a shear flow the principal directions of stretching do not coincide with the principal directions of molecular orientation. The flow near the free surface has a strong extensional character which leads to important changes in the stress field when large polymer molecules are diluted in a Newtonian solvent. The evolution of the streamlines and of the normal stress component along the streamlines T_{tt} as a function of Weissenberg number at $Ca = 0.2$ is presented in Fig.2. Predictions were obtained with the Oldroyd-B model. At low Weissenberg number, the flow is close to that of a Newtonian liquid and there is a large recirculation attached to the free surface. As the Weissenberg number rises, the polymer molecules become more and more stretched, the constant stress bands are distorted in the direction of the main flow and a region of high stress appears attached to the free surface, downstream of the stagnation point. This region of high extension pulls liquid away from the recirculation and its size decreases as the Weissenberg number of the flow rises. At $We = 6$ the recirculation is much smaller than the one observed in Newtonian flow, and at $We = 8$, it has vanished. The elastic forces that come from the extended polymer molecules completely changes the nature of the flow near the free surface. The flow at the film splitting stagnation point becomes much stronger as the elastic forces rise at a fixed capillary number.

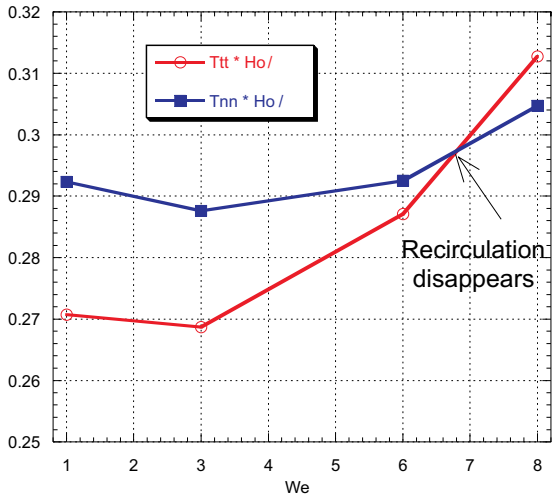

Figure 3: Normal stress along and perpendicular to the free surface at the film splitting stagnation point as a function of Weissenberg number at Ca = 0.2.

Figure 3 shows the evolution of the normal stresses along and perpendicular to the free surface, T_{tt} and T_{nn}, at the stagnation point as the Weissenberg number rises at $Ca = 0.2$. The Newtonian flow is stable with respect to three-dimensional perturbation, i.e. the stress difference $T_{tt} - T_{nn}$ is not strong enough to overcome the stabilizing action of surface tension. The normal stress along the streamlines T_{tt} grows as the liquid becomes more elastic. This effect is even stronger beyond the capillary number at which the recirculation attached to the free surface disappears. It is clear from the graph, that the stress difference $T_{tt} - T_{nn}$ that destabilizes the flow grows as the liquid becomes more elastic. Therefore, at a given capillary number, there is

a critical value of the Weissenberg number above which the normal stress difference along and perpendicular to the free surface becomes stronger than the stabilizing surface tension force and the flow becomes unstable with respect to cross-web disturbances.

References

Bauman, T., Sullivan, T. and Middleman, S., "Ribbing instability in coating flows: effect of polymer additives." *Chem. Eng. Commun*., vol.14, pp.35-46, 1982.

Benkreira, H., Edwards, M.F. and Wilkinson, W.L., "Ribbing instability in the roll coating of Newtonian fluids". *Plastic and Rubber Proc. Appl*., vol. 2, pp.137, 1982.

Carvalho, M. S., Dontula, P. and Scriven, L. E., "Non-Newtonian effects on the Ribbing instabilities". *TAPPI Coating Conference*, Dallas, USA, 1995.

Carvalho, M. S. and Scriven, L. E., "Three-dimensional stability analysis of free surface flows: Application to forward deformable roll coating". *J. Comput. Phys*., vol. 151, pp.534, 1999.

Christodoulou, C. N. and Scriven, L. E., "Finding leading modes of a viscous free surface flow: An asymmetric generalized eigenproblem". *J. Sci. Comp*., vol. 3, pp. 355, 1988.

Coyle, D.J., Macosko, C.W. and Scriven, L.E., "Film-Splitting flows of shear thinning liquids in forward roll coating". *AICHE Journal*, vol. 33, pp. 741, 1987.

Coyle, D.J., Macosko, C.W. and Scriven, L.E., "Stability of symmetric film-splitting between counter-rotating cylinders". *J. Fluid Mech*., vol. 216, pp. 437, 1990.

De Santos, J. M., "Two-phase cocurrent downflow through constricted passages". *Ph.D. Thesis, University of Minnesota*, MN. Available from UMI, Ann Arbor, order number 9119386, 1991.

Dontula, P., "Polymer Solutions in Coating Flows", *Ph.D. Thesis, University of Minnesota*, MN. Available from UMI, Ann Arbor, order number 9119386, 1999.

Fernando, R.H. and Glass, J.E., "Dynamic uniaxial extensional viscosity (DUEV) effects in roll applications II: Polymer blend studies". *J. Rheol*., vol. 32, pp.199, 1988.

Glass, J.E., "Dynamics of roll spatter and tracking 2: Formulation effects in experimental paints". *J. Coating Technol*., vol. 50, pp. 61, 1978.

Glass, J.E., "Dynamics of roll spatter and tracking 3: Importance of extensional viscosities". *J. Coating Technol*., vol. 50, pp. 71, 1978.

Graham, M. D., "Theory of viscoelastic free surface instability", *74th Annual Meeting of the Society of Rheology*, Minneapolis, MN, USA, 2002.

Graham, M. D., "Interfacial hoop stress and instability of viscoelastic free surface flows". *Phys. Fluids*, vol.15, pp. 1702, 2003.

Greener, J., Sullivan, T., Turner, B. \& Middleman, S., "Ribbing instability of a two-roller coater: Newtonian fluids", *Chem. Eng. Commun*., vol. 5, pp. 73, 1980.

Grillet, A.M., Lee, A.G. and Shaqfeh, E. S. G., "Observations of ribbing instabilities in elastic fluid flows with gravity stabilization". *J. Fluid Mech*., vol. 399, pp.49, 1999.

Lee, A. G., Shaqfeh, E. and Khomami, B., "A study of viscoelastic free surface flows by the finite element method: Hele-Shaw and slot coating flows". *J. Non-Newtonian Fluid Mech*., vol.108, pp. 327, 2002.

Lopez, F. V., Pauchard, L., Rosen, M. and Rabaud, M., "Non-Newtonian effects on ribbing instability threshold". J. *Non-Newtonian Fluid Mech*., vol. 103, pp. 123, 2002.

Mill,C.C. and South,G.R., "Formation of ribs on rotating rollers". *J. Fluid Mech*., vol. 28, pp. 523, 1967.

Pasquali, M. and Scriven, L. E., "Free surface flows of polymer solutions with models based on the conformation tensor". *J. Non-Newtonian Fluid Mech*., vol.108, pp. 363, 2002.

Pearson,J.R.A., "The stability of uniform viscous flow under rollers and spreaders". *J. Fluid Mech*., vol. 7, pp. 481, 1960.

Pitts, E. and Greiller,J., "The flow of thin liquid films between rollers", *J. Fluid Mech*., vol. 11, pp. 33, 1960.

Sadanandan, B. and Sureshkumar, R., "Numerical eigenspectrum of non-viscometric viscoelastic flows: results for the periodic channel flow. *J. Non-Newtonian Fluid Mech*., vol.108, pp. 143, 2002.

Smith, M. D., Joo, Y. L., Armstrong, R. C. and Brown, R., "Linear stabiity analysis of flow of an Oldroyd-B fluid through a linear array of cylinders", *J. Non-Newtonian Fluid Mech*., vol.109, pp. 13, 2003.