# Mechanical Instability of Swollen PVC Films

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**SYNOPSIS**

The swelling of soft coatings on a tough substrate immersed in solvent is investigated. Equilibrium aspects of the coating deformation due to swelling as well as its kinetics have been explored; in particular, the appearance of patterns on the originally smooth surface of the swollen film is described and modeled. The patterns are the result of a mechanical instability such as buckling or wrinkling. The time dependence of the wrinkles height is measured and, by using the energy dissipation criterion for wrinkle spread, the ratio of the adhesion energy by the bulk modulus is determined as a function of swelling time. © 1995 John Wiley & Sons, Inc.

Soft coatings on tough substrates represent a special kind of composite structure. They are stressed by environmental agents such as temperature, solvents, and humidity which provoke differential responses of the components: substrate, coating film, and interfacial (e.g., adhesive) layer. The results may be peeling, wrinkling, cracking, and various types of fracturing, typically confined to the soft layer and the interface. Cracks show little penetration into the tough substrate, but large numbers of cracks and deformations may form on coatings.

Buckling under compressive stress is described by Pompe[1] for thin layers deposited on substrates. Matuda et al.[2] measured the height and the width of wrinkles of carbon layers on glass and silicon substrates by different methods.

It is very important albeit difficult to obtain a measure of the adhesion energy in many systems. There is an excellent possibility of estimating the bonding energy by using naturally created instability phenomena. For instance, the ratio between the aluminum oxide–aluminum work of adhesion per unit length and the bulk modulus $E$ of the film-forming aluminum (hydrous) oxide was determined for coatings formed by anodic films on aluminum[3,4] in a previous publication from this laboratory. In this study, we report on the formation of striae and wrinkles generated by the mechanical instability of swollen poly(vinyl chloride) (PVC) films attached to stainless steel rod surfaces. The kinetics and equilibrium aspects of the patterns formed by swelling have been studied.

## MODEL

The PVC film has a perfectly smooth surface before swelling, but a pattern appears on the surface as the PVC is immersed in the solvent. The pattern is formed either by a regular arrangement of straight lines parallel or normal to the axis of the rod or by wrinkles. As time progresses the height of wrinkles or striae becomes larger. The pattern formation may be qualitatively explained in the following way. The kinetic process of the swelling of a plastic film is governed by the diffusion of the solvent into the film. This layer is under a mechanical constraint, namely, the outer surface of the layer is free to expand, whereas the inner surface is fixed to the metallic cylinder and the width expansion of film is constrained by the two polytetrafluoroethylene (PTFE) rings. Small expansions are accommodated by stretching the PVC film, while for large expansions the film is forced to wrinkle as shown in Figure 1 where we observe wavy, regular wrinkles with well-defined width and amplitude. This wavy shape with am-

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Journal of Applied Polymer Science, Vol. 57, 1567–1573 (1995)
 CCC 0021-8995/95/131567-07

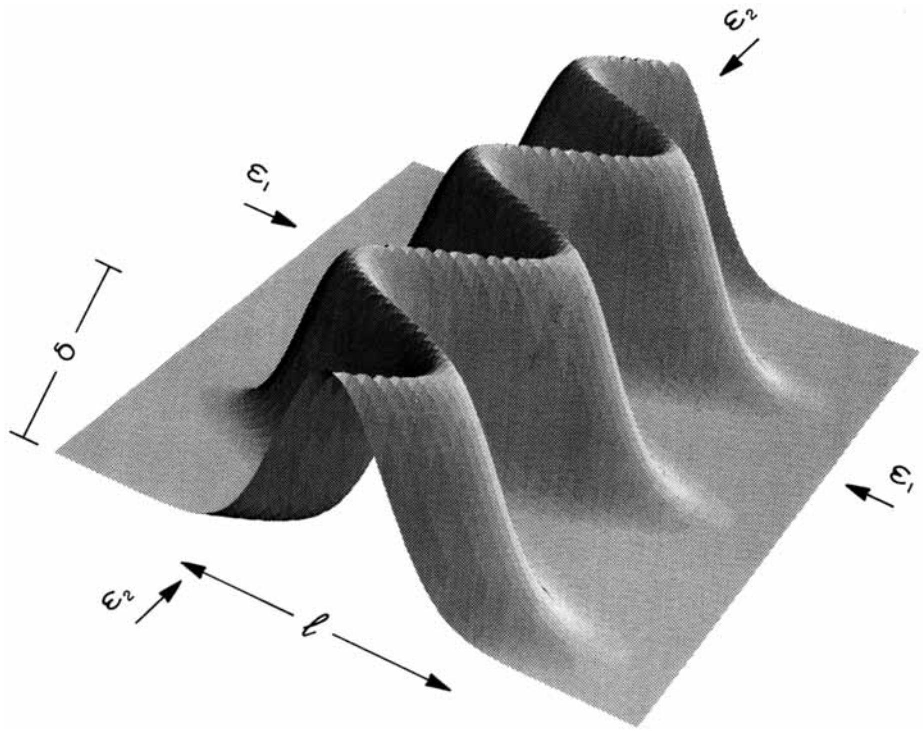


**Figure 1** Schematic representation of a wrinkled film corresponding to a tangential compressive strain $\varepsilon_1$ and axial compressive strain $\varepsilon_2$.

plitude $\delta$ and width $l$ along the wrinkle corresponds to tangential compressive strains $\epsilon_1$ and axial compressive strain $\varepsilon_2$.

The stresses may be relieved by buckling of the PVC film. The initial stage of bulge formation is shown by (1) in Figure 2; latter stages of bulge development are indicated by (2), (3), and (4). At stage (2), striae are seen in the outer periphery of the PVC film.

## EXPERIMENTAL

Axially symmetric test pieces were made. These were mounted in the test cell shown schematically in Figure 3. The cell walls are Pyrex glass and the cover is made of PTFE. All the substrate specimens were prepared from the same stainless steel (AISI 304). The samples were 4 cm long and 0.46 cm diameter stainless steel tubes. The length of the surface exposed to the solution is adjustable. The substrate structure was abraded with emery paper (grade 600). The surface then was washed using a soap solution in a ultrasonic bath for 15 min. The tube was rinsed with distilled water, acetone, ethanol, and finally with distilled water. The sample was dried in air. The PVC samples were commercial autoadhesive films $\sim$ 0.08 mm thick (VULCAN, under a license of Rubbermaid Inc, USA) made of plasticized PVC, coated on one side with adhesive. The solvents were chloroform and acetone (Merck, analytical grade). The swelling rate is very large for these films; in the first 60 s it is nearly linear, and proceeds at a rate of 30% (w/w) $\min^{-1}$. During PVC swelling *in situ* observations were made using an Olympus Model 52-TR-BR stereoscope and a Zeiss Axioplan optical microscope. Wrinkle heights were measured from photographs taken at various times after the buckling process started.

## RESULTS

PVC films are made by lamination and hence are bidimensionally anisotropic. Polymer chains are preferentially aligned along the length of the film roll.[5,6] We carried out several preliminary experiments. In order to check the anisotropic swelling on PVC films in solvents, 10- $\times$ 30-mm films were cut along and normal to the lamination direction and

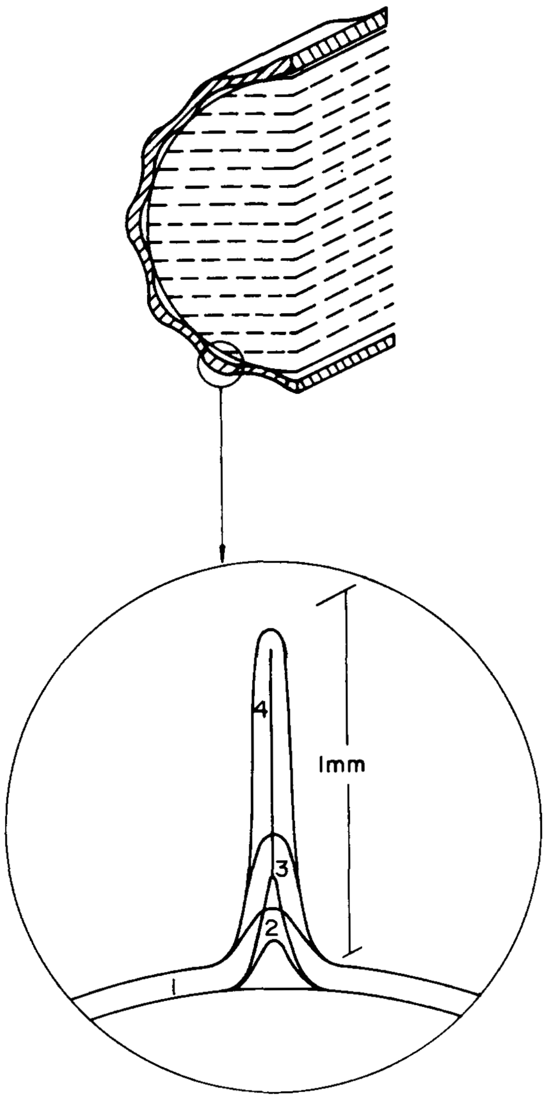


**Figure 2** Schematic diagram showing the time evolution of the striae heights. (1), (2), (3), and (4) indicate patterns formed for successively increasing times.

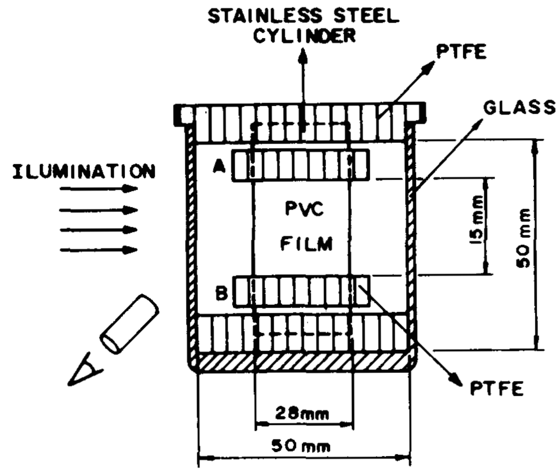


**Figure 3** Schematic diagram of the test cell. *A* and *B* indicate the removable PTFE clamps which cover the PVC film top and bottom edges.

immersed in a 500-mL beaker with solvent. After 10 s of immersion time the film expansion was measured to be predominantely normal to the lamination direction (measured strain ~ 0.1). This is expected since swelling should take place preferentially in the dimension normal to the oriented polymer chains.

Careful observation of the samples shows that PVC films on stainless steel rods have a smooth surface before swelling (see Fig. 4), and as the film swells a pattern is observed. Small wrinkles may be observed at the middle of the PVC layer or at the edges in contact with the PTFE rings. They may arise from poorly bonded areas or heterogeneities in the PVC layer. The pattern consists of numerous line segments of cusps into the PVC film. The patterns are only formed after extensive swelling. Pictures of the patterned films are shown in Figure 5(a)–(f). Axial [Fig. 5(b) and (d)] and radial [Fig. 5(a), (c), (e), and (f)] striae were observed in our experiments depending on the lamination direction of the film. The top and bottom edges of the film were clamped by two PTFE rings as shown in Figure 3.

The measured height of the wrinkles is plotted as a function of time in Figure 6. The patterns shown

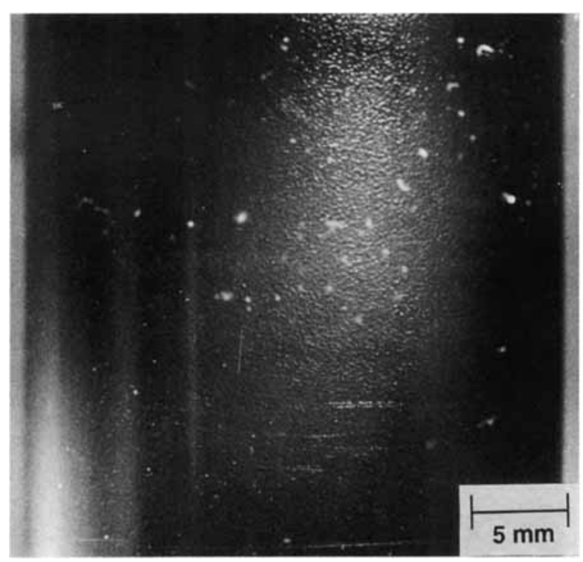


**Figure 4** Optical micrograph showing a PVC film on a stainless steel cylindrical substrate. No pattern is observed, other than normal rugosity.

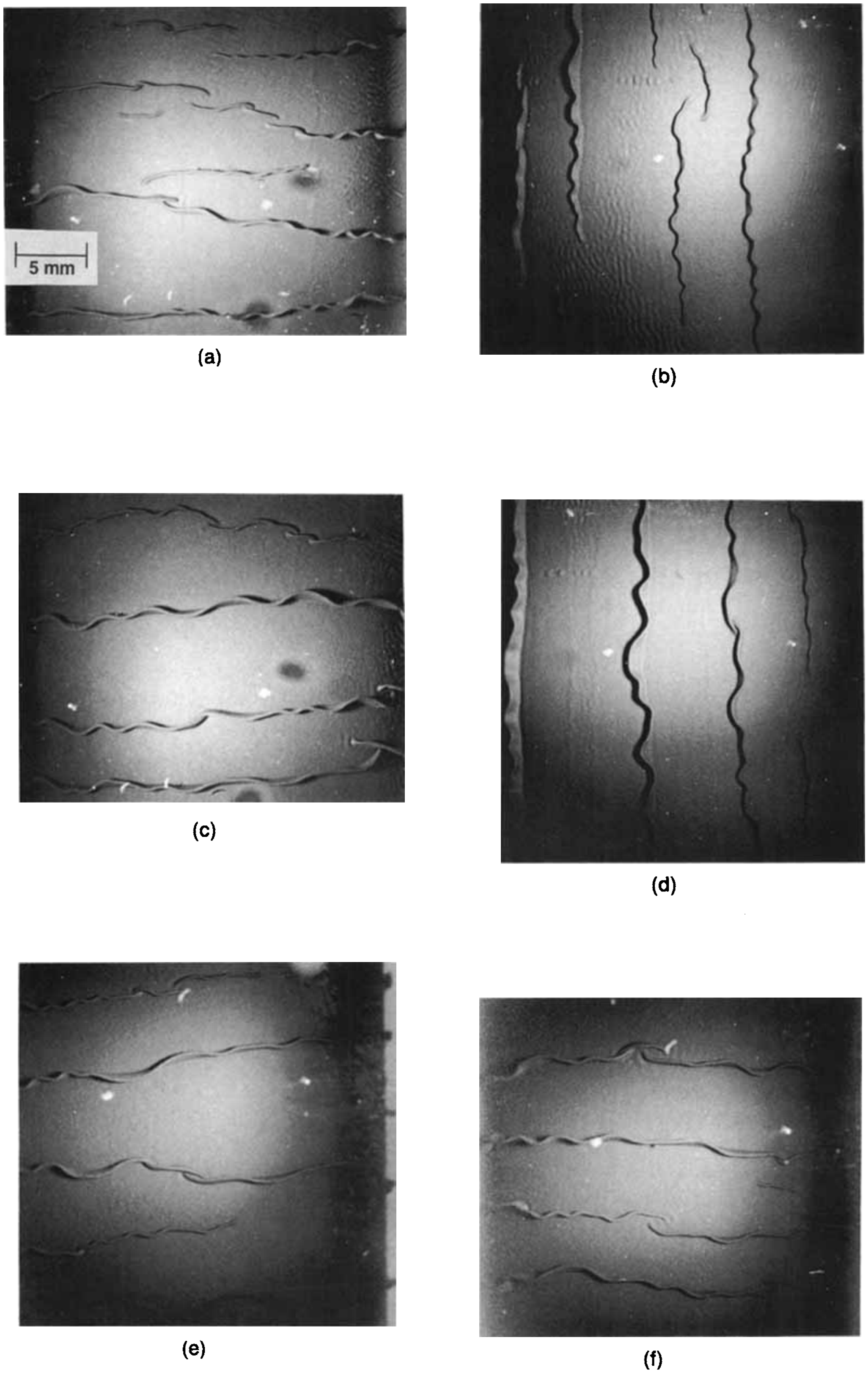


**Figure 5** Optical micrographs showing cylindrical strained PVC layers that developed striae. Radial striae are shown in (a), (c), (e), and (f) and axial striae are shown in (b) and (d).

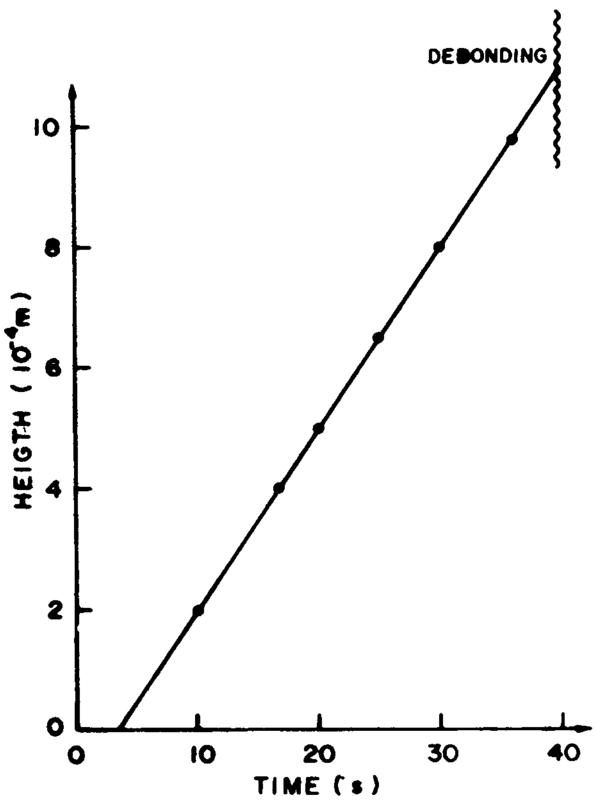


**Figure 6** Striae heights as a function of swelling time.

in Figure 5 were all obtained while the top and bottom edges of the PVC film were clamped by the PTFE rings indicated by $A$ and $B$ in Figure 3. If the clamps are now removed, the solvent also penetrates through the film–cylinder interface, while for the patterns shown in Figure 5 the solvent interacts with the PVC film only through diffusion across the film exposed area. Typical patterns obtained in this case are shown in Figure 7(a) and (b). After 10 s of immersion, the pattern was photographed.

Radial and axial striae, shown in Figure 5(a)–(f), respectively, correspond to the maxima of outward radial displacements of the swollen PVC film. Our results do not show cracks formed as the result of bending of the PVC layer at its cusps. Wrinkles of anodic films on aluminum are reported to rupture.[3] This was seldom observed in our experiments: only a few rupture sites were observed. This is assigned to the larger elasticity (or plasticity) of the swollen PVC films, which allows for deformation even at large angles. When the films are dried in air, they return to their original shape except for marks at the positions corresponding to the striae or wrinkles.

## DISCUSSION

### Energetics of Coating Instabilities

#### *Kinetics of Wrinkle Formation*

The very well defined width of the wrinkles in Figure 5 shows that the wrinkle width may be constant for immersion periods of up to 15 s. The width and the pattern of the striae in this case practically did not change in time. However, at film debonding sites there is a substantial change in width and shape as shown in Figure 7(b), which depicts the debonding process. At the line indicated by $B$ in the figure, the sinusoidal shape is transformed into irregular-shaped wrinkles.

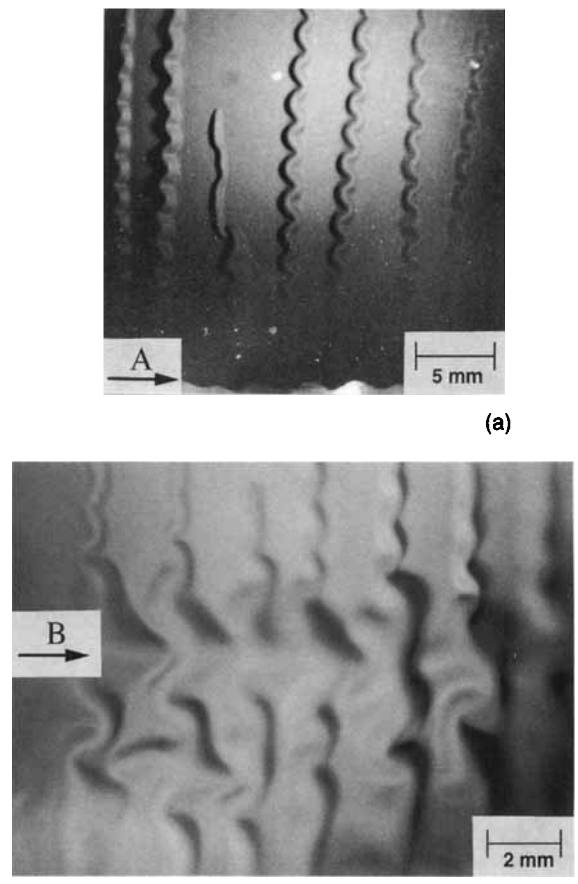


**Figure 7** (a) Optical micrographs showing a PVC film on stainless steel, unclamped at the bottom and top edges. The bottom edge of the PVC film is indicated by $A$ and shows a wavy pattern. (b) Same film as shown in (a) for 15-s immersion time. A compressive stress orthogonal to the wrinkle direction is now observed (indicated by $B$). At film debonding sites there is a substantial change in wrinkle width and shape.

Wrinkle width variation by any other factors than those caused by buckling should show a wide range of wrinkle widths, due to the statistics of the defects. The existence of well-defined widths of wrinkles can therefore be used to estimate $\gamma/E$.[1]

$$\frac{\gamma}{E} = \left(\frac{6}{5}\right)^2\left(\frac{d}{1-\upsilon^2}\right)\left(\frac{\delta}{l}\right)^4 \times \left\{1 + \left(\frac{5}{3}\right)^2\left(\frac{d}{l}\right)^2\left[1 - \frac{25}{12}\left(\frac{d}{l}\right)^2\right]\right\} \quad (1)$$

which used the energy dissipation criterion for wrinkle spread where a small curvature of the wrinkle is assumed. $\delta$, $l$ are defined in Figure 1, $\upsilon$ is Poisson's ratio, $d$ is the film thickness, $\gamma$ is the bonding surface energy, $E$ is the bulk modulus of the film, and $\varepsilon$ is the strain. Thus from the experimental values obtained from Figure 5, i.e., $\delta = 500 \pm 50$ μm, $d = 80 \pm 10$ μm, $l = 500$ μm, we obtain for $\gamma/E = (2.0 \pm 0.8)\ 10^{-5}$ m.

### *Bonding Surface Energy and Bulk Modulus Ratio Variation with Time*

The wrinkle heights were measured for various time intervals after the onset of failure by buckling. The results are shown in Figure 6, where after a formation period the measured wrinkle height increases almost linearly with swelling time. We evaluated $\gamma/E$ values in PVC films by using the wrinkle heights at various times in Eq. (1). The results are shown in Figure 8. The calculated values of $\gamma/E$ vary by almost 3 orders of magnitude. This may be associated with possible variations of $E$ values by 2 orders of magnitude since during swelling the PVC film becomes softer than it was before immersion in the solvent. There is also an increase in $\gamma$ values when the solvent modifies the film–substrate interface. Since there is an uncertainty in the measured value of striae width, we plotted $\gamma/E$ for three values of the film thickness.

There may be a restriction in using Eq. (1) for large values of $\delta/l$, which implies in a large curvature of the wrinkles. An expression for $\gamma/E$ may be calculated for large curvatures of the wrinkles, which is not the purpose of this study. However, our results clearly indicated that our method is suitable for determining $\gamma/E$ values and also their time dependence for swollen PVC films.

## CONCLUSION

The formation of striae and wrinkles generated by the mechanical instability of swollen PVC films adherent to stainless steel surfaces was investigated. The equilibrium aspects of the swelling were studied, as well as its kinetics, in particular the appearance of patterns on the originally smooth surface of the film during swelling. *In situ* observation by optical microscopy of the swollen surface allows us to determine $\gamma/E$ values and their time dependence. A

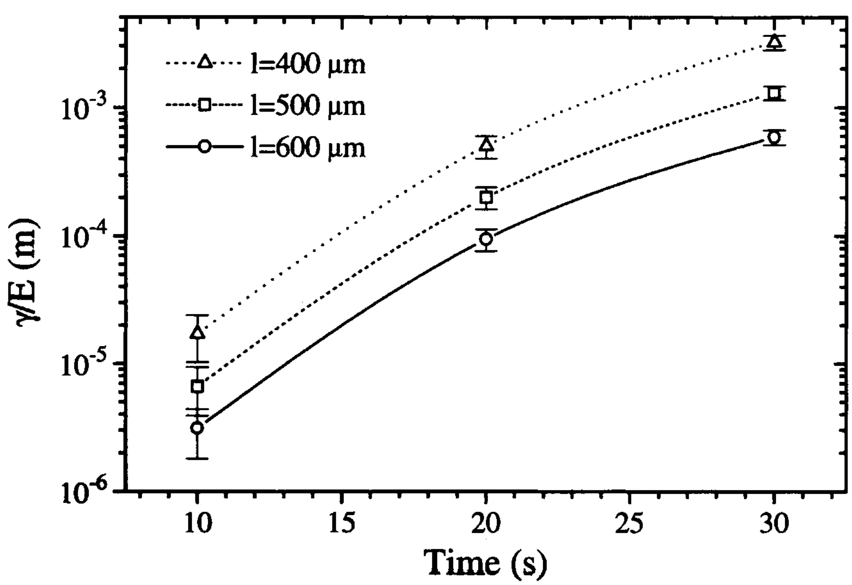


**Figure 8** $\gamma/E$ dependence on the swelling time.

variation of almost 3 orders of magnitude of the $\gamma/E$ values was measured, during swelling.

The authors are grateful to CNPq (520060/93-8) and FAPESP (93/0961-5) for financial support and L. O. Bonugli for technical assistance.

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*Received January 19, 1995*
*Accepted April 11, 1995*