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Dynamic delamination of drying colloidal films: Warping and creep behavior

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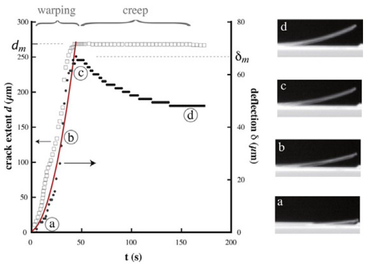
HIGHLIGHTS

- We examine out-of-plane displacement of thin colloidal films during the drying process.
- Different behaviors can be distinguished from elastic to plastic then creep.
- Direct characterization of the mechanical properties is supported by measurements using indentation testing.

GRAPHICAL ABSTRACT



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ABSTRACT

During the consolidation of thin films, mechanical instabilities usually result from large mechanical stresses development. In particular morphologies of fractures and debonding reveal different behaviors of the materials. We report dynamic debonding induced by drying process of colloidal systems by direct measurements in a one-dimensional geometry. From the measurements of the film out-of-plane displacement, different behaviors can be distinguished from elastic to plastic then creep. The time evolution of the mechanical properties of colloidal films is in accordance with measurements using indentation testing as a response to an external force.

1. Introduction

Many industrial processes dedicated to material elaboration or to coating achievements, are based on the solidification of complex systems. In most common technological operations, the solidification is obtained through drying process of particulate materials. When the drying rate is high, large stresses appear and can lead to the formation of mechanical instabilities such as cracks providing a large variety of morphologies. These crack patterns can be commonly observed in nature, for soils in hot regions. Due to evaporation of water, the drying stress causes the clay to fracture into polygonal cells [1] (Fig. 1a). In practice, the control of these phenomena is crucial for all the coating technologies since they significantly alter the final film quality, and usually need to be avoided. There are two main kinds of drying cracks: the shrinkage cracks which propagate perpendicular to the film surface, and the peeling cracks which propagate parallel to the surface. The first type of cracks have been widely studied [2,3]. In the case of peeling cracks,

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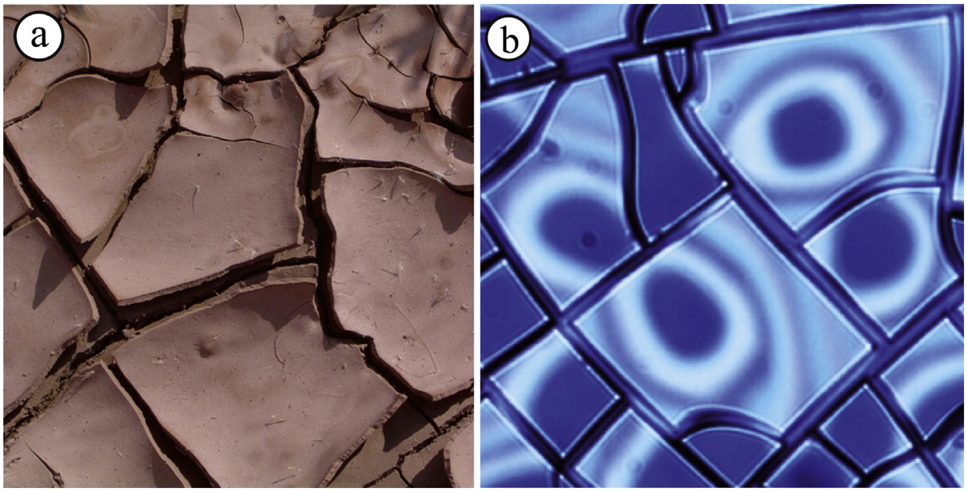

Fig. 1. (a) Warped mud, and desiccation polygons formed by the drying of clay. The largest polygons are approximately 30 cm in length (photograph courtesy of J.C. Géminard). (b) Colloidal film on a substrate. The channel cracks divide the transparent layer into polygons. The interference fringes indicate that the film also partially debonds from the substrate (image width =200 μm).

a model predicts a relationship between the thickness of the mud peel and the radius of curvature of the fragment [4,5]; this model is based on the differential contraction of layers. For practical reasons, only few works deal with the dynamics of the delamination crack front since it is not an easy task to follow the crack propagation. Moreover, the dynamics of the delamination of a film is a complex process since it is related to the evolution of the mechanical properties induced by the drying stress development. The drying film combines elastic, viscous and plastic behaviors. The final state of the dried film depends on these evolving properties. Indeed, channeling cracks, curl, warp, all induce deformations strongly related to the mechanical properties of the materials; also the resulting morphologies are characteristic processes of the time evolution of the material. This can be evidenced during the drying of paint layers or mud. Usually, peeling cracks start propagating from the corner and the borders of a fragment: the delamination is partial, e.g. the delamination process stops, fragments adhere to the underlayer only by a single region exhibiting a well defined surface area [6]. Then, the fragments become convex toward the drying side, lifting the corners off of the underlying layers (Fig. 1b). This evidences a plastic behavior of the system at the end of the evaporation process. Indeed, if it were purely elastic, the warped film should instantaneously relax back, and recover its initial flat state at the final stage.

In the following, we study the delamination process resulting from the drying of colloidal films in a well-controlled experiment, that exhibits no boundary conditions and presents a one-dimensional geometry. This is achieved by considering the drying of a thin film coating on a horizontal fiber. This particular geometry allows us a precise visualization of bending deformations of delaminated fragments. We deduce from these time deformations, a characteristic relaxation time which is recovered with indentation testing measurements. This duration stands for the relaxation time for the stress. In addition, different behaviors are evidenced during the delamination process: the system is elastic when delamination starts, then becomes plastic and viscoplastic. The experiments have been reproduced using four systems exhibiting different mechanical properties.

Table 1
Main characteristics for the samples considered in the experiments. Particle diameter: $2a$, solid weight fraction ϕ_m (data given by the manufacturer Grace Davison).

	$2a$ (nm)	ϕ_m
Ludox SM-30	10	0.30
Ludox HS-40	16	0.40
Ludox TM-50	26	0.50
nanolatex PS	30	0.30

2. Experimental

2.1. Starting materials

Four different types of particulate materials were used: concentrated aqueous dispersions of silica particles (Ludox SM-30, HS-40, TM-50 purchased from Sigma–Aldrich) and nanolatex particles (provided by Rhodia Recherche, Aubervilliers, France); HS-40 was used in most experiments. Main properties of these dispersions are reported in Table 1. These dispersions are stable in the absence of evaporation. In the case of the silica sols, the stability of the dispersion is governed by the interparticle colloidal interaction, e.g., by the competition between van der Waals attraction and electrostatic repulsion (Derjaguin–Landau–Verwey–Overbeek[7,8]). In the case of the nanolatex, particles are made of polystyrene, stabilized by the presence of surfactants (SDS); since the glass transition temperature of the particles is around 100 *dgrC*, the particles are assumed to be rigid (not deformable) at room temperature. Values of the surface tension $\gamma_{w,a}$ of the dispersions were measured by the Wilhelmy plate method and range in [57;67] mN m^{-1}. For each dispersion, the weak polydispersity of the particles prevents from crystallization (polydispersity ∼0.18).

2.2. Methods

The dynamics of delamination is investigated by observation of a strip of gel in side view. A sketch of the experimental set-up is shown in Fig. 2a. Experiments are performed by drawing a horizontal Nylon fiber, radius 200 μm, out of a fluid reservoir at a constant velocity. The reservoir contains the aqueous colloidal dispersion, and as the wire is pulling, a uniform film of constant thickness coats all around the fiber. Note that the characteristic time for the hydrodynamic instability, e.g. Rayleigh-Plateau instability growth rate, is larger than the characteristic time for drying [9]; it implies that no variations of the film thickness are detected before the material starts to consolidate. After the motor is stopped the film is let to dry at an ambient relative humidity RH ∼50%: particles concentrate and a gel of typical thickness 10 μm is formed. During the solidification