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Hexagonal patterns in thin films: Experiments and modeling

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ABSTRACT

Perfect periodic hexagonal patterns were obtained in our lab in μm-thick drying polymer/metal oxide composite films. The appearance of the pattern depends mainly on the polymer and metal oxide ratio, while the size of the features depends on the temperature of deposition. To understand the generation of the hexagonal pattern we filmed the hexagons' nucleation and development in real-time, and suggest a corresponding model. The model shows that the hexagonal pattern initiates at a single point, advances through plastic deformation, and continuously and rapidly propagates to cover the entire surface. We show that this highly symmetrical pattern reduces most efficiently the strain energy in the material. The model correlates the pattern generation conclusively with uniformly- and rapidly-generated local plastic deformation, and not brittle fracture.

1. Introduction

Periodic damage patterns such as those shown in Fig. 1(a)–(d), have captured human imagination for centuries [1,2]. Such patterns are found in naturally abundant materials such as dried mud (Fig. 1(a)); man-made materials such as asphalt (Fig. 1(b)) and, on smaller scale, coatings (Fig. 1(c)) and ceramic glazes. Recently, similar patterns have also been observed on a giant scale across crater basins on Mars (Fig. 1(d)) [3]. The similarity in these patterns indicates that the same mechanisms are responsible for their formation, despite the variety in material density, composition, and length scale. It has been well established that the generation of such patterns occurs in non-uniform and inhomogeneous materials and is associated with shrinkage during drying or cooling. Cracks initiate at existing defect sites and progress in time to form a crack network [4–6]. The cracks open vertically from top (free surface) to bottom through the thickness of the film with gradually increasing openings. Further shrinkage and increased local stresses induce secondary crack nucleation, exhibiting reduced crack spacing with time. The secondary cracks intersect the former primary cracks at nearly right angles in a geometric constraint denoted T-shaped cracks ($\sim$90° intersection) [7].

In contrast to the mud, asphalt, paint and Mars cracks with distinct length scales, damage patterns of highly ordered polygons with mainly Y-shape intersections and seldom perfectly ordered hexagonal tiling are also naturally found, as shown in Fig. 1(e)–(g). Although the damage mechanisms in both conventional cracks (Fig. 1(a)–(d)) and hexagonal patterns (Fig. 1(e)–(g)) are intended to reduce the high strain energy generated in the layers during cooling or drying, we point out that their pattern might follow a distinctly different evolution processes. Experimental model systems with damage processes similar to those generating the patterns are studied in mono-dispersed Latex or silica colloidal suspensions commonly used for the fabrication of photonic crystals and opals [8–10], aqueous slurries of coffee grains [11], corn starch [12,13], and other substances suspensions. Although polygonal patterns have been produced in the drying process of corn starch [12–15], highly ordered and true hexagonal patterns, similar to those demonstrated in cooled basalt lava,

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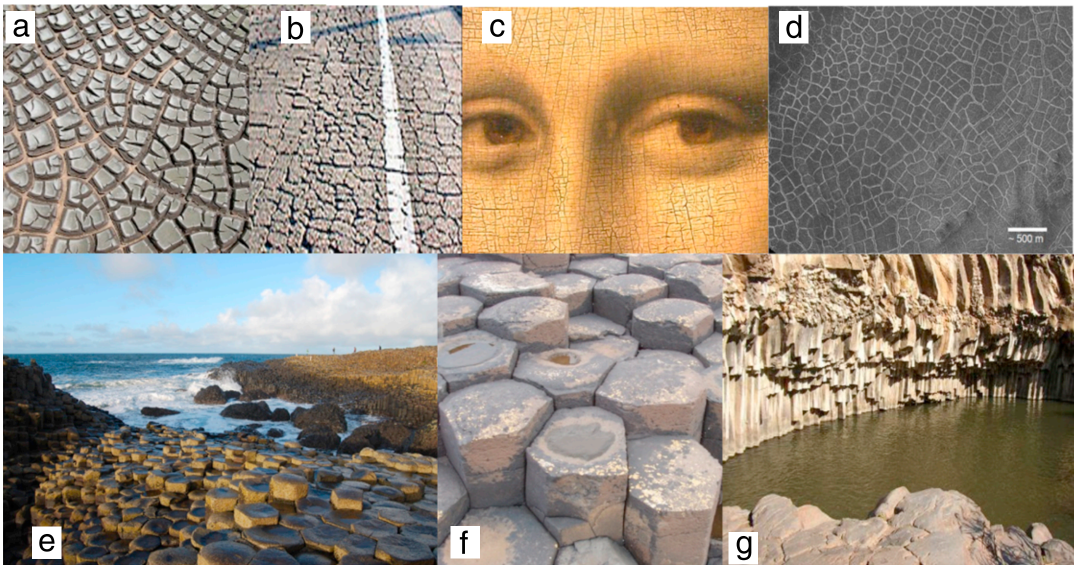

Fig. 1. Commonly observed damage patterns in: (a) mud, (b) asphalt, (c) paint (Mona Lisa), (d) crater basins on Mars (scale bar is 500 m); (e)–(f) ~1 m wide hexagonal basalt lava in The Giants Causeway, Ireland, and (g) basalt lava in The Hexagons pool, Golan Heights, Israel. (For image copyrights see Supplementary information.)

have not been obtained or reported so far despite the experimental efforts.

Interestingly, in 1999, Hull and Caddock suggested the comparison between the evolution of stress-induced patterns in drying sol–gel films and cooling basalt lava [16]. They found that the cracking patterns strongly depend on the drying profile and the bonding of the drying sol–gel and the surrounding material. They, however, could not experimentally generate hexagon patterns. In parallel, it was shown that the addition of an organic polymer to a sol–gel precursor solution results in the formation of a composite film with improved mechanical properties [17,18]. Namely, when an organic polymer, poly-ethylene-glycol, was added to a titania sol, it induced a gradual suppression of cracking to the extent that no cracks were observed in dried composite titania/polymer films processed with high polymer concentrations [19].

Therefore, to study stress relaxation and hexagonal pattern formation in thin films we examined the drying patterns of sol–gel slurries including a controllable amount of an organic polymer. For example, homogeneous ethanol solutions of a tungsten oxide precursor, WCl_6, and controlled amounts of an amphiphilic commercially available PluronicTM triblock copolymer, P123, were prepared. When a glass substrate is withdrawn from the solution, the sol–gel precursor undergoes rapid hydrolysis and condensation to form a composite WO_3/P123 thin film. The resulting films are grainy, but homogeneous in the fact that they do not show organic/inorganic phase separation. We found that by varying material composition and lab conditions, highly symmetric hexagonal patterns could be generated, for the first time, in manmade systems. Furthermore, by filming the initiation and evolution of the hexagons in real time (video included), we were able to gain unprecedented insight and formulate a new mechanism that is distinctly different from the common crack initiation and propagation concepts.

2. Experimental

Homogeneous ethanol solutions of a tungsten oxide precursor, WCl_6 (Sigma-Aldrich, stored under nitrogen and used as received), and controlled amounts of an amphiphilic commercially available Pluronic^{TM} triblock copolymer, P123 (Mw = 5750 g/mol, BASF, used as received), were prepared by dissolving 1.5 g WCl_6 and P123 (0.375, 0.5, 0.75, or 1 g) in 12 ml absolute ethanol under vigorous stirring. The P123 polymer is composed of relatively hydrophobic propylene-oxide (PO) center block, 70 monomer units, and two hydrophilic ethylene-oxide (EO) blocks, with 20 monomer units each. The alcoholysis reaction was exothermic and after stirring for 2 h a blue clear solution was obtained. The films were prepared by dip coating on glass substrates at withdraw speed of 10 mm/s in an environmental chamber maintained at high, >95%, relative humidity. When the glass substrate was withdrawn from the solution, the sol–gel precursor underwent rapid hydrolysis and condensation to form a composite WO_3/P123 thin film. The resulting films were grainy, but homogeneous in the fact that they do not show organic/inorganic phase separation.

3. Results

Drying patterns in thin films were generated by dip coating glass substrates from WO_3 precursor and P123 sol–gel slurries. The ratio between the inorganic precursor and organic polymer in the solution has a dramatic effect on the brittle-to-ductile transition of the layer property and the stress-induced drying patterns, as shown in Fig. 2. The tile-like cracking patterns observed in the film with the lowest polymer loadings (Fig. 2(a)) are similar to those obtained in conventional drying processes (Fig. 1(a)–(d)), and are associated with a brittle film, i.e. an inorganic metal oxide film. Increasing the polymer content in the film shows