Splitting Fingers under Strain: Pattern Formation of a Dipolar Fluid in a Polymer Medium

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Received January 15, 1999. In Final Form: September 9, 1999

Westudy the formation and evolution of labyrinthine patterns for dipolar fluids inside a polymer medium under mechanical strain. A new general mechanism is proposed to describe the kinetics of the pattern formation that combines orientation ordering and subsequently breaking characteristics of dipolar fluids with branching characteristics of crack-propagation. This mechanism can lead to many of the patterns found in nature, including spots, stripes, labyrinthine, and starlike formations.

Introduction

Generic physical mechanisms acting on a flowable composite media, such as living tissue, can mediate the formation of macroscopic fingering patterns in natural systems. The kinetics for such pattern formation typically falls into two classes, those driven by the interplay of the surface tension and another force, such as the adhesion, density or temperature gradients, and electrostatics, and those driven by reaction–diffusion coupling, such as Turing's model and activator–inhibitor models. In this Letter, we show that for systems consisting of a dipolar fluid dispersed in a polymer matrix another class of fingering patterns occurs that is caused primarily by mechanical strain. The time evolution of the pattern is determined by the branching and eventual breaking of liquid crystalline fingers at areas of high elastic strain within the bulk of the finger. This mechanism can lead to the evolution of a wide range of patterns, from dipolar droplets that coalesce to form channels to fingers that eventually branch to form labyrinthine and triangular formations.

Experimental Section

A dipolar liquid, such as nematic liquid crystals, is known to undergo unusual phase separation dynamics when dispersed inside a reacting medium, such as a monomer under free-radical polymerization. In this experiment, liquid crystal and polymer composite films were made from chlorinated hydrocarbon nematic liquid crystals obtained commercially (Merck E7 and TL213) and a monomer consisting of a mixture of 2-ethylhexyl acrylate monomer and trimethylol propane triaacylate cross-linker that resulted in a weakly cross-linked microgel after polymerization. Concentrations between 60% and 80% liquid crystal by volume all resulted in finger formation. The monomer and liquid crystal solution were blended with a dichromatic dye, pyromethene 580 (Exxon), to obtain contrast, and the resulting isotropic mixture was placed by capillary forces into a glass cell with varying gap size 9.5–25 μm. The gap size affected only the diameter of the final channels and the periodicity of the undulations. The monomer was then photopolymerized under a UV lamp, 360 nm at 16 mW/cm² intensity, for 5 min so that the polymer was fully reacted. Initial morphologies consisted of small liquid crystal domains, 0.2–3 μm in diameter, dispersed in a continuous polymer matrix. The liquid crystal channels (or fingers) formed 5–30 min after UV exposure with the pattern progressing continuously over weeks as the liquid crystals continued to diffuse into the channels. Images were taken with a low-light high-resolution digital camera (Xillex Micromager-12) and a white light fluorescent confocal microscope (Nikon with Technical Instrument confocal attachment) with 10×, 40×, and 100× oil emersion lenses yielding a maximum resolution of 200 nm horizontal and 400 nm vertical.

Results and Discussion

When the polymer is the minority phase, polymer liquid crystal composite systems typically exhibit a reverse morphology to the standard oil-in-water experiment as the final morphology consists of the majority phase (the liquid crystal) forming discrete droplets while the minority phase (the polymer) forms a continuous porous matrix. Such a morphology is depicted in the background of Figure 1a. This optical image is taken in reflection mode so that the liquid crystal, normally transparent, appears dark, and the polymer matrix, normally opaque, appears light. This droplet pattern is usually considered to be stable; however, we observe that given sufficient strain and fluidity of the porous matrix that this phase is metastable and the liquid crystal domains will coalesce to form liquid crystal channels (or fingers) to reduce the interface surface energy. The finger formation is strain-induced and is caused by the roughly 10% volume contraction of the monomer upon polymerization within the confined geometry established by the fixed cell gap diameter of the Hele–Shaw cell. We observe very few fingers when the strain is relieved from the system by allowing the cell gap to freely decrease as the polymer contracts during po-

10.1021/la990045h CCC: $18.00 © 1999 American Chemical Society Published on Web 11/17/1999
lymerization, as shown in Figure 1b. Here the optical image is taken at lower magnification and in transmission mode so that the liquid crystal appears white and the polymer dark. The initial size of the channels is resolution limited (≈200 nm) and considerably smaller than the cell gap but the channels widen over time to a maximum width set by the cell gap. As is observed in panels c and d of Figure 1, the channels undulate with a wavelength that decreases with increasing strain because of a balance between the energy decrease due to the finger’s larger area and the elastic energy increase due to its local bending.

Similar liquid crystal undulating channels have been observed in cholesteric liquid crystalline mixtures under electric fields\(^\text{10}\); however, the progression of the fingering patterns observed here appears to be unique, to the best of our knowledge, to dipolar fluids in a polymer medium under mechanical strain. The time evolution of the pattern, shown in Figure 2, is determined by the growing fingers branching off at areas where the curvature of the undulation is maximized. This branching forces a labyrinthine pattern to form, Figure 2b, with all three-tiered branches having angles of either 90°, 120°, or 180°, and a subsequent flattening of the undulation. Over longer periods, the fingers physically break at the points of maximum curvature, with the porous media flowing in

\(\text{(10) Ribiere, P.; Oswald, P. J. Phys. (Paris) 1990, 51, 1703.}\)
around the breaks. This results in short branched fingers and finally the formation of three-pronged stars, Figure 1d. Due to the weakly elastic nature of the polymer and the evolution of the liquid crystal fingers, the strain is released over time and the patterns stop evolving.

In Figure 3, we show four frames of "movies" depicting the branching and breaking of the liquid crystal channels. On the left side, the formation of a third branch at the point of maximum elastic strain is observed where the branching provides a method to relieve the local stress, analogous to crack propagation. When the branch first forms, its diameter is considerably smaller than the cell gap. On the right side, a break in the finger is formed at a kink in the undulation, the porous fluid flows in around the break, and the resulting tip continues to grow lengthwise. The branching and breaks are due to the formation of point defects, a characteristic property of dipolar fluid channels. Polarization microscopy on the channels reveals that the liquid crystals are anchored mainly homeotropically (perpendicular) to the surface. The formation of point defects is due to a reversal of the overall orientation of liquid crystals in the finger. A representation of such a point defect is shown in the bottom of Figure 3. As a tip approaches a liquid crystal channel, the liquid crystals in the tip will always be oriented perpendicular to the liquid crystals anchored to the channel surface so that intersection does not occur, as seen clearly in Figure 1c; therefore, the fingers are self-avoiding and require breakage to achieve space-filling structures. We note that although the branching of the dipolar fluid occurs in a porous medium and that fractal-like behavior exists on short time scales, fractal formation is not observed over long time scales since a macroscopic length scale is set by the cell gap.

This system is different than other labyrinthine patterned dipolar fluids\textsuperscript{11-13} in that the labyrinthine structures are formed by elastic strain-induced branching rather than by the balancing of interfacial (Young) and electrostatic (Biot-Savart) forces\textsuperscript{4} or by the intersection of two progressing fingers.\textsuperscript{10} Here, no electromagnetic fields exist to drive the pattern formation nor do the fingers (channels) ever intersect. Also, while the domains are clearly diffusing under strain gradients, no reaction-based diffusion is occurring in this material and the resulting patterns are not consistent with binary fluid phase separation.\textsuperscript{14} As such, we have proposed a new general mechanism for labyrinth pattern formation that combines orientation ordering and subsequently breaking characteristics of dipolar fluids with branching characteristics of crack propagation. Such pattern formation should be generally applicable to naturally occurring systems consisting of dipolar fluids confined in a flowable amorphous solid subject to vertical strain, with the time scale for pattern evolution being set by the strain strength and the flowability of the solid medium.

**Acknowledgment.** We thank T. Nehei for helpful discussion. This work was supported by the Packard Foundation.

LA990045H


