Regular patterns generated by self-organization of ammonium-modified polymer nanospheres

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Abstract

Macroscopic regular stripe-crack patterns have been observed in the course of drying the aqueous suspensions of ammonium-modified polymer nanospheres. These forms emerged because the evaporation of dispersed water and self-assembly of nanospheres originates shrinkage during drying the aqueous suspensions. The drying condition plays an important role as well as the nature of the ammonium-modified polymer nanospheres for the stripe-crack pattern formation. By means of the vertical deposition method, directional stripe-crack patterns have been achieved in the macroscopic scale. Surprisingly, we have still noted an interesting secondary stripe pattern occurred spontaneously on the stripes.

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1. Introduction

Microscopic and macroscopic self-organization patterns have been attracting considerable attentions for their potential applications in modern science and technology [1–5]. As often encountered in the case of self-organization in the thermodynamic equilibrium [6] and the fracture of solids in nature [7], crack patterns and evolution has been an important topic of broad interest for the theoretical and practical meanings of the surprising process [8–12]. For example, Hull and co-workers simulated prismatic cracking of cooling basalt lava flows through studying the cracking patterns during the drying of sol–gel [13,14]. Among these patterns, stripes have also been of interesting and importance in the area of ecology or geology [15–17] and manmade system [18,19]. Recently, the unique aspects and niche applications of colloids or latexes are focusing on investigating the self-assembled colloidal crystals and understanding the pattern-formation models and mechanisms in various systems [20–22]. Okubo et al. [6] investigated the dissipative structural pattern in the course of drying of colloidal suspensions. Leung et al. [7] observed and examined spiral cracks by drying a fine aqueous suspension such as nickel phosphate (Ni₃(PO₄)₂) and ferric hydroxide (Fe(OH)₃). Shorlin and co-workers [21] studied the isotropic and directional shrinkage-crack patterns by dyeing alumina (Al₂O₃) particles in water. Although colloidal or latex particles have produced self-organization or crack patterns as mentioned above, we are not aware of latex systems that spontaneously form macroscopic stripe-crack and secondary patterns as Hull and Pauchard respectively observed in drying silica sols and protein solutions [13,14,23–25].

In this paper we have described the observation via a surfactant-free emulsion copolymerization of (ar-vinybenzyl) trimethylammonium chloride or 2-aminoethyl methacrylate hydrochloride and styrene in the presence of cross-linker. All poly-
merizations were carried out in an atmosphere of nitrogen for 24 h in a 500-ml four-necked flask fitted with a reflux condenser and a stirrer. Details on preparation were given in previous work [27]. The polymer nanospheres with various components were synthesized according to the similar procedure. Stripe-crack patterns spontaneously generate by drying an aqueous suspension of ammonium-modified polymer nanospheres placed on the substrate (typically involving silica, silicon, and mica plates) surface. In order to be convenient for detecting and recording in the optical microscope, typical samples are prepared by carefully dropping 2 to 100 µl of the aqueous suspensions containing nanospheres onto the substrates. The silica or silicon substrates were soaked in a 7:3 volumetric mixture of 98% H₂SO₄ and 30% H₂O₂ overnight (caution: strong oxide), rinsed with deionized water, and then dried in a stream of nitrogen prior to use, and mica plates were used as received. This procedure was chosen to improve adhesion or interaction between hydrophilic nanospheres and substrates [13,14]. The suspensions were dried on the substrates in the ambient atmosphere at room temperature. Directional stripe patterns were obtained by the vertical deposition procedure as follows: clean silica or silicon slides were vertically placed in 5 ml of aqueous suspension of nanospheres in a clean vial, and the entire apparatus was placed in a dish at room temperature or higher. Directional stripe-crack patterns appeared as the dispersing water evaporated. The stripe-crack patterns were detected by optical microscopy after evaporation of the dispersing water.

3. Results and discussion

Figure 1a suggests that the typical spokewise stripe patterns show up as well as cracking pathways when the result-

![Fig. 1](image_url)

**Fig. 1.** (a) A portion image of the spokewise stripe-crack patterns formed by drying ammonium-modified polymer nanosphere suspensions at room temperature in optical microscopy. The insert is a TEM image of polymer nanospheres. (b) AFM image in a tapping mode and section analysis of the stripe-crack patterns. (c) The surface plot of the AFM image in a tapping mode; the insert is an AFM image of the stripe pattern in the area of 1.0 × 1.0 µm. (d) AFM image of the patterns of carboxyl-modified polymer nanosphere with low polydispersity; the insert is optical micrographs.
ing polymer nanosphere suspensions are dried on a substrate at room temperature. We have noted no cracks and fragments further occur in the course of the formation of spokewise stripe-crack patterns. Crack tips in Fig. 1a distribute hierarchically in the radical direction; that is, the number of crack paths \( N \) varies with the radical distance \( R \) (the center of the patterns as the reference center). For instance, when \( R \) is 100 µm, \( N \) is 35, while 200 µm for 72 and 500 µm for 180. At the same time, it is not difficult to find that the radical distance-crack number ratio remains approximatively constant (about 2.7 to 2.9) in this case. This result means that the spacing between two close cracks is approximate. AFM image in Fig. 1b shows regular stripe-crack patterns in the area of 100 × 100 µm. The section analysis of Fig. 1b further reveals that the mean widths of the stripes and the cracks are 13.5 and 3.8 µm, respectively. In addition, the typical ratio of the length and width of the stripes is larger than 10, and even the length of the stripes reaches more than 1.0 cm, though the stripes sometimes fold up and detach from the substrate to form sharp needles [28]. The typical thickness of drying film ranges from 30 to 200 µm with varying solid content of polymer nanosphere suspensions in our experiments.

We have also noted that the formation of stripe-crack patterns depends on the nanosphere component. In other words, ammonium-modified polymer nanospheres play an important role in producing irregular or regular patterns, as Hull and Okubo described in other proposed systems [6,13,14,23–25]. Examination of the TEM of the insert in Fig. 1a implies that nanospheres, the building blocks of stripe-crack patterns, are 125.0 nm in average diameter with polydispersity index 10.5%. The size of ammonium-modified nanospheres is not important for the pattern formation. The comparison of Figs. 1c and 1d, however, reveals that different polymer nanospheres may produce various patterns at the macroscopic and the microscopic scale. Figure 1c shows that ammonium-modified polymer nanospheres form stripe-crack patterns on the macroscale but disordered close packing in the insert of Fig. 1c on the microscale. In contrast, Fig. 1d indicates the fine hexagonal close packing from carboxyl-modified polymer nanospheres in AFM image but no stripe patterns display in the optical microscope image (the insert). We have not observed the stripe-crack patterns during the drying of those sulfonate or hydroxyl-modified nanosphere suspensions. It is well known that electrostatic interaction and hydrophilic or hydrophobic interaction have been demonstrated to be important for the self-assembly and drying process [6,13,14,20]. We infer, therefore, that the nature of ammonium-modified nanospheres with positive charges was possibly different from that of those polymer microspheres such as carboxyl-modified microspheres with negative charges, which may have led various phenomena and outcomes to occur. Further works about these would be ongoing solved because of their complexity [6,13].

Figure 2 shows the different patterns occurred in a drying suspension at polymer nanosphere concentrations varying from 3.0 to 0.4 wt% in solid content. At higher concentration of 3.0 wt%, regular spokewise stripe-crack patterns in Fig. 2a formed from the outside edge toward the center and crack tips distribute hierarchically in the radical direction. When the concentration of polymer nanospheres decreased down to 1.0 wt%, the stripe-crack patterns were still obvious but the regularity became unclear (Fig. 2b). Stripe-crack patterns and/or cycles produced only around the boundaries at the outer regions at lower concentration, but could not propagate into the center, as shown in Fig. 2c. An important cause is that polymer nanospheres tend to move from the center area to the boundary region through the convection flow of the dispersed water and nanospheres during dried at ambient
temperature [6,29]. When nanospheres moved to the boundaries at the outer regions, most of them may stop at boundary region due to the evaporation of water. This result has been demonstrated from low density of nanospheres in the center of the drying films formed at low concentration. Patterns in Fig. 2c finally formed from the stress generated by drying of the suspensions.

Figure 3 shows an in situ observation of the formation of spokewise stripe-crack patterns as the dispersing water evaporated. This observation indicates that the stripe-crack pattern is a slow physical variation or combination process [10, 11,21]. Ammonium-modified polymer nanosphere suspensions were initially fluid, and polymer nanospheres then began to self-assemble as the dispersing water evaporated. As mentioned above, the flow of polymer nanospheres from the center areas to the boundary regions is enhanced by the convection–evaporation process and then nanospheres preferentially self-assemble into close packing at the boundaries due to the disappearance of dispersing water [6,29]. Subsequently, evaporation of dispersed water leads to large shrinkage strains that can result in primary cracks; that is, the evaporation of the suspensions generates stress to induce cracks to nucleate. We found that cracks nucleated after about 60 s while the drying front line (marked by arrows) appeared and began to contract, as shown in Fig. 3. We conceived that the contraction of the drying front line, coupled with evaporation of water and adhesion to the substrate, led cracks to nucleate due to the horizontal constriction stress at the earliest stage in the formation process of the stripe-crack patterns (Fig. 3a). The horizontal constriction stress concentration was low and did not infiltrate into the cracks between stripes, which relieved the stress locally along the sides of cracks, but concentrated stress at the crack tips [30]. The crack tips then extended from boundary to center and formed the spokewise stripe-crack patterns, while no further cracks occurred. Initially, cracks nucleated and the drying front line moved toward the center at a relatively slow rate, and the primary stripe patterns formed in the outer regions after 120 s, as shown in Fig. 3b. Following this, cracks propagated rapidly and linearly but no further fragments were produced as the drying front line moved toward the center as shown in Figs. 3c and 3d. During the propagation of crack tips, the velocity of the crack tips and the drying velocity are approximate, though both of them increased from 2.7 and 2.6 µm/s to 6.6 and 6.8 µm/s, respectively. Finally, the propagation of cracks and the removal of water in the dryness resulted in the spokewise stripe-crack patterns in Fig. 3e.

Among many effect factors, evaporation and convection should be very important for the pattern formation. Using the vertical disposition, a simple and flexible method that controls the movement of drying front and the convection flow of water, we have achieved directional stripe-crack patterns. Figure 4a shows the directional stripe-crack patterns formed by the vertical disposition. The SEM image (the insert in Fig. 4a) and the optical microscopy image shows that these stripes and cracks are directional and parallel each other, and the width of stripes is about 18.0 µm with 2.0 mm in length. In this case, the drying front line may be parallel to and moving toward the surface of drying liquid and induce the directional stripe-crack patterns accompanying with the gradient distribution of crack patterns formed by drying the suspensions of polymer nanospheres of 50.0 nm in average size. More surprisingly, interesting secondary hierarchical patterns in Fig. 4b formed spontaneously but the AFM image of Fig. 4c indicates that they were not cracks but grooves on the surface of each stripe in some stripe-crack patterns. The reason for this observation is not clear, as we prematurely
thought; it should be similar to the observation in Hull’s reports [13,14].

4. Summary

The unique and fascinating spokewise and directional stripe-crack patterns have been observed by drying ammonium-modified polymer nanosphere suspensions in this work. Directional stripe-crack patterns depend on the condition and method in the experiment; that is, they control the movement of the drying frontier. We thought the patterns might originate from integrated effects such as self-organization, thermodynamics, and stress [6,13,14,21–25,31,32]. The causes and implications of the resulting stripe-crack patterns not only continue to generate developments of the crack evolution and patterns, but also are of theoretical and practical importance in possible understanding the stripe-crack patterns such as drying mud in nature.

Acknowledgments

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References