

Dewetting Behavior of Hydrogen Bonded Polymer Complex Film under Hydrothermal Condition

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Electronic Supplementary Information

Abstract Hydrogen-bonded polymer complex films with the thickness ranging from 50 nm to 2400 nm were prepared by layer-by-layer (LbL) assembly of poly(2-ethyl-2-oxazoline) (PEOX) and poly(acrylic acid) (PAA). The dewetting behavior of PEOX/PAA films under hydrothermal condition was investigated. It was found that the dewetting occurred at solid-liquid interface, and the typical morphologies such as holes, irregular cellular structure, and droplets were observed. Atomic force microscopy (AFM) revealed the initial rupture of the film. Microscopic Raman and infrared (IR) imaging demonstrated that the PEOX and PAA chains remained association during the dewetting process.

Keywords Hydrogen-bonding; Polymer complex; Dewetting

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INTRODUCTION

Dewetting is a reverse process of wetting or spreading. Such a phenomenon is encountered frequently in our daily life, such as oil layer breaks on the non-adhesive pan or water film ruptures on our skin. It has attracted considerable attention in both fundamental research and important technological application issues^[1–12].

Theoretically, for the non-wetting liquid, if the film thickness is less than critical thickness, capillary force dominates and dewetting phenomenon occurs^[13]. Simple liquid dewetting was investigated in 1960s^[14], and the dewetting behaviors of complex fluid have drawn considerable interest since 1990s^[15–38]. Brochard-Wyart *et al.* studied the dewetting dynamics of thick film (20–50 μm) of silicon oil on low-energy surface^[15]. They deliberately created a hole on the film and monitored the hole growth. As a result, they found that the hole growth was relevant to the film viscosity and the contact angle between film and substrate^[15]. Reiter studied the dewetting behavior of thin polystyrene film (thickness < 100 nm) on silicon wafer above the glass transition temperature (T_g)^[16], and also commented that dewetting could be used as a probe to investigate the polymer chain mobility in the thin film^[17]. Up to now, the dewetting behaviors of different films have been

investigated, such as homopolymer^[18], protein^[32], block copolymer^[33], polymer blend or mixture^[34, 35], liquid crystal^[36] and even metal^[37, 38] *etc.* The dewetting behaviors at the solid-air (vacuum) have also been widely studied^[15–38], while those at solid-liquid interface are rarely explored^[39–41].

In this work, we studied the dewetting process of a hydrogen-bonded polymer complex film under hydrothermal condition. Hydrothermal environment means that the dewetting process occurs at solid-liquid interface. The hydrogen-bonded polymer complex films are fabricated by layer-by-layer (LbL) assembly that is considered to be a simple but effective method to prepare thin films^[42–44]. Dewetting has been applied to construct nano-structure of LbL assembled film, but the whole dewetting process of LbL assembly has not been investigated so far^[45–48]. Herein, the whole dewetting process of LbL assembled PEOX/PAA film has been revealed, which is helpful for us to understand the rupture of hydrogen-bonded polymer complex thin films.

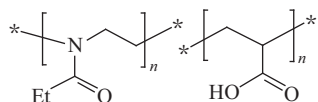
EXPERIMENTAL

Materials

Poly(2-ethyl-2-oxazoline) (PEOX, $M_w = 5.0 \times 10^5$) was obtained from Alfa Aesar. Poly(acrylic acid) (PAA, $M_w = 4.5 \times 10^5$) was purchased from Sigma-Aldrich. Both PEOX and PAA were used as received without further purification. The chemical structures of PEOX and PAA are shown in Scheme 1.

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Scheme 1 Chemical structures of PEOX and PAA molecules

Film Fabrication

The LbL assembly of PEOX and PAA was conducted on a silicon or a quartz substrate with an automatic machine (Kejing Auto-Instrument Co. Ltd., Shenyang, China). The surface of the substrate was cleaned by the following procedure: (a) immersing the substrate in a boiling $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ (7/3, V/V) solution for 30 min (“piranha”: this solution is extremely corrosive); (b) washing the substrate with deionized (DI) water for 5 times; (c) drying it with a nitrogen flow. Then, the substrates were alternately dipped into PEOX solution and PAA solution for 4 min with interval of three rinses (1 min each). The pH values of assembling solutions and rinsing solutions were adjusted to pH = 2.0 with HCl solution under monitoring of a pH meter (Delta 320, Mettler Toledo). After assembling, the wet film was blown dry with nitrogen flow, and then stored in a desiccator. The film is marked as $(\text{PEOX}/\text{PAA})_n$, where n indicates that the film is fabricated by n assembly cycles. A series of films, $(\text{PEOX}/\text{PAA})_n$ ($n = 5, 10, 15, 20, 25, 30, 40$) were prepared.

Hydrothermal Treatment

Hydrothermal treatment of $(\text{PEOX}/\text{PAA})_n$ films was carried out in a 40 mL PTFE sleeve. The film on the substrate and 28 mL aqueous solution (pH = 2.0, 70% of the total volume) were sealed in the PTFE sleeve that was then packed in the stainless-iron autoclave. The temperature increased to the set value at a rate of 2 °C/min, and was held on the set temperature for different periods. The holding time at the set temperature was defined as hydrothermal treatment time. After hydrothermal treatment, the cell was quickly cooled down in an ice-water bath and then the film was taken out and carefully blown to dry with nitrogen flow.

Characterization

The glass transition temperatures (T_g s) of PEOX, PAA and PEOX/PAA complexes (prepared by mixing PEOX solution and PAA solution^[49]) were measured with a Netzsch 204F1 differential scanning calorimeter. The heating and cooling rates were 10 °C/min. UV-Vis spectra of the thin films before and after hydrothermal treatment were recorded with a Shimadzu UV-2550 spectrophotometer. The morphology characterization of the thin films after hydrothermal treatment was conducted on an optical microscope (CDM-960) and an atomic force microscope (Agilent 5500). The AFM measurement was performed under the tapping mode in air at room temperature. A commercial silicon probe (model TESP-100) with a resonant frequency (≈ 170 kHz) was used to scan the film. Raman spectra were obtained by a Renishawin Via Reflex laser Raman spectrometer (the laser wavelength is 532 nm). The micro-infrared images were obtained with a Thermo Fisher Nicolet iN 10 MX Fourier transform infrared imaging microscope (FTIR-IM). An optical interferometer, NanoCalc-XR (Ocean Optics, Germany), was used to measure the film thickness. The

instrument recorded near-normal reflection spectrum of the thin film deposited on silicon wafer, and the film thickness was extracted by the analysis of interference data on spectrum.

RESULTS AND DISCUSSION

LbL assembly has been proven to be an effective approach to fabricate model thin film systems for both fundamental research and practical application^[42–44] since Decher *et al.* reported this method in the early 1990s^[50]. In addition, hydrogen-bonding LbL assembly, demonstrated by Rubner and Zhang^[51, 52], can be used to finely adjust film thickness ranging from several nanometers to several micrometers^[53–57]. We previously studied the hydrothermal treatment of hydrogen-bonded PVPON/PAA film lower than 100 °C^[57]. The results showed that the film shrunk as the hydrothermal treatment temperature increased, and there were shallow pits on film surface but no dewetting at 90 °C. The occurrence of dewetting on the experimental time related to the viscosity and chain mobility that strongly depended on temperature^[16, 17]. The glass transition temperature (T_g) of hydrogen-bonded PVPON/PAA complex is 190–200 °C^[49]. Although T_g or melting temperature decreased in the hydrothermal system^[58, 59], it still required high hydrothermal temperature to ensure the polymer chain mobility for the PVPON/PAA system. In this study, we selected another hydrogen-bonded polymer complex system PEOX/PAA^[55] with T_g about 70 °C (Fig. S1, in electronic supplementary information, ESI). The hydrothermal treatment was conducted in the temperature region from 120 °C to 160 °C.

The $(\text{PEOX}/\text{PAA})_{20}$ film, about 1.0 μm thick, was sealed in hydrothermal environment. After hydrothermal treatment for a certain period, the system was quenched down, and optical microscopy was used to observe the morphology of the film. Fig. 1 shows the optical microscopic images of the films after hydrothermal treatment at 140 °C for different time. After 0.5 h hydrothermal treatment, the film surface exhibited some microholes (Fig. 1a). Due to the resolution of

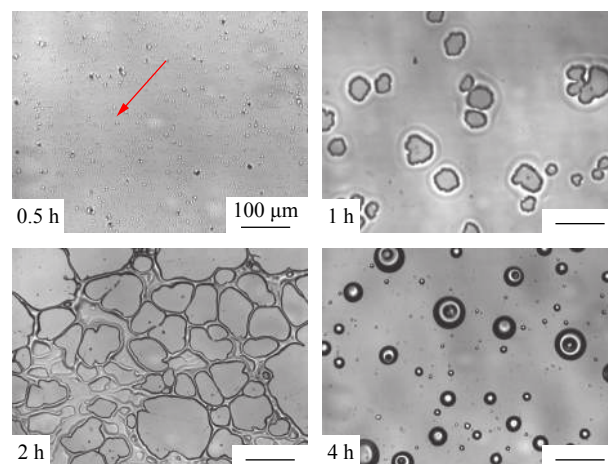


Fig. 1 Optical microscopy images of $(\text{PEOX}/\text{PAA})_{20}$ after hydrothermal treatment at 140 °C for different periods: 0.5, 1.0, 2.0 and 4.0 h (All the images share the same scale.)

optical microscopy, the micropores on the optical microscopic images were not obvious; however, the holes on the film were very clear in the AFM images (Fig. 2a). The cross-section analysis indicated that the average diameter and depth were 2 μm and 250 nm, respectively. After 1 h hydrothermal treatment, the holes grew bigger and the average diameter increased to about 30 μm . The holes became deep to expose the substrate. After 2 h hydrothermal treatment, the holes continued to expand, and the rims coalesced to form “ridges”. After 4 h hydrothermal treatment, the droplets were formed. The dewetting behaviors of (PEOX/PAA)₂₀ under hydrothermal condition at 120 and 160 $^{\circ}\text{C}$ were also investigated. At 120 $^{\circ}\text{C}$, we only observed the hole formation after 4 h hydrothermal treatment, while at 160 $^{\circ}\text{C}$, the droplets were formed after 1 h hydrothermal treatment. For comparison, the AFM image of original film before hydrothermal treatment is also given in Fig. S2 (in ESI). As a summary, optical and AFM images showed that the dewetting was observed for the hydrogen-bonded PEOX/PAA film at the solid-liquid interface under the hydrothermal condition.

UV-Vis spectroscopy was applied to characterize the (PEOX/PAA)₂₀ film before and after hydrothermal treatment. (Fig. 3) Before hydrothermal process, the hydrogen-bonded PEOX/PAA film exhibited oscillation peaks on UV-Vis spectra. These oscillation peaks, so-called Fabry-Pérot fringes, are caused by light interference. As a smooth film, the thickness is close to the wavelength of visible-light, and the refractive index has the contrast to substrate, there will be optical interference of light beam from spectrometer and hence Fabry-Pérot fringes present on

the spectrum^[56]. Fabry-Pérot fringes can be used as an indicator to reflect the film morphology change^[57]. In our case, we observed that the number of oscillation peaks decreased and the amplitude of oscillation became weak after 0.5 h hydrothermal treatment, while the film still showed strong absorbance at UV region but Fabry-Pérot fringes disappeared after 1.0 h hydrothermal treatment. However, when the hydrothermal treatment time was over 2 h, not only Fabry-Pérot fringes disappeared but also the absorbance at UV region decreased. When hydrothermal treatment time was further prolonged to 8 h, no specific absorbance was found.

The results from UV-Vis spectra are corresponding to the morphology observation from optical microscopy. After 0.5 h hydrothermal treatment, there are many small holes in the film, which involve air into the film, leading to the decrease of effective refractive index of the film^[60, 61]. The refractive index of air is close to 1.0, while the refractive index of PEOX/PAA is around 1.5. The decrease of effective refractive index made the amplitude of Fabry-Pérot fringes weakened^[56, 57, 61]. After hydrothermal treatment for 1 h, many large pores appeared in the film, which made the film heterogeneous, resulting in the light scatter away and no Fabry-Pérot fringes. After 2 h or longer hydrothermal treatment, the absorbance of the film at the UV region decreased, indicating that some materials transformed into the aqueous phase. When the hydrothermal treatment time was 8 h, we could not observe the droplets by optical microscopy. These droplets slid away and transformed into aqueous solution. Carefully checking the hydrothermal solution, we found PEOX/PAA complex in the hydrothermal solvent. The result is interesting and implies that it is possible to remove the solid film from the substrate by dewetting under the hydrothermal condition.

After 2 h hydrothermal treatment, irregular cellular pattern was observed. The microscopic Raman was used to detect different positions of the film (Fig. 4) with the original PEOX/PAA film as a reference. The hydrogen-bonded PEOX/PAA film exhibited main Raman peaks at 1724 and 1617 cm^{-1} , which were attributed to C=O vibrations of PAA and PEOX, respectively^[55].

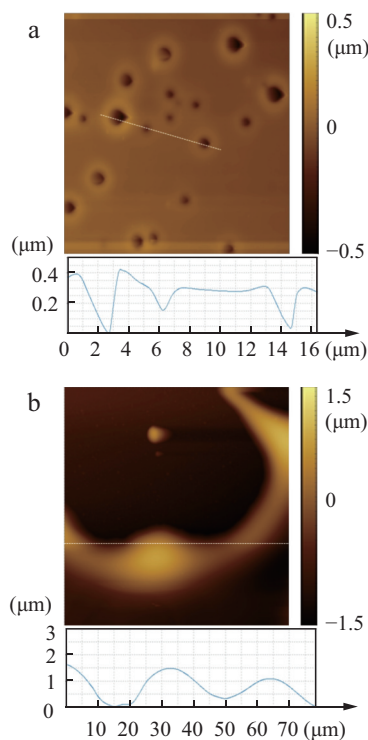


Fig. 2 AFM images of the films' surface treated with different hydrothermal time under 140 $^{\circ}\text{C}$, conditions: (a) 0.5 h (30 μm $\times$ 30 μm); (b) 1 h (70 μm $\times$ 70 μm)

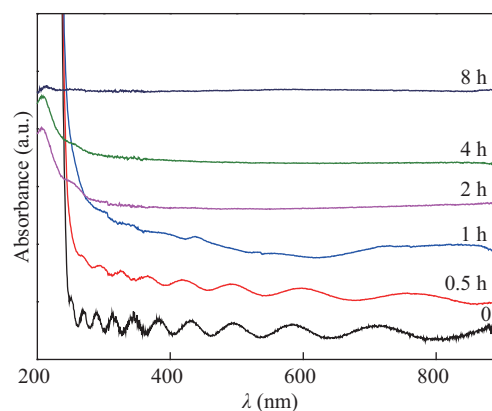


Fig. 3 The UV-Vis spectra of films treated with different hydrothermal time under 140 $^{\circ}\text{C}$ (The spectra were overlaid for clearance.)

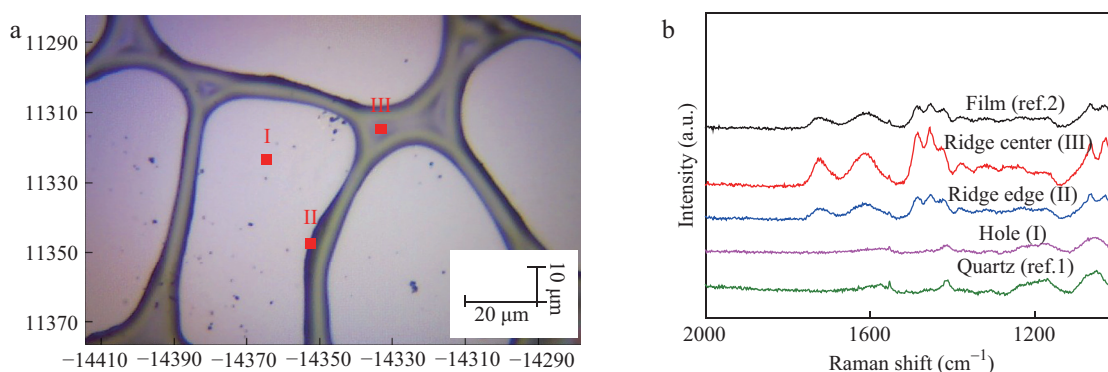


Fig. 4 The (a) microscopic pictures and (b) Raman spectra of the films at different positions after hydrothermal treatment of 2 h (with original PEOX/PAA film and bare quartz substrate as the references)

When the holes expand, their rims coalesce to form ridges. The ridges link together to present irregular cellular structure (Fig. 4a). It can be seen that the spectrum of hole (position I) is almost the same to that of the bare quartz substrate, indicating that the substrate is completely exposed in the hole growth. The spectra of the ridge edge (position II) and the central part of the ridges (position III) show the same Raman peak to that of the original PEOX/PAA film, but the intensities are stronger. The stronger intensity is due to the fact that the ridges are thicker than the original film because the ridges are formed by coalescence of the holes' rims. The Raman data reveal that PEOX and PAA are associated together to move during dewetting, otherwise the Raman peak position would shift.

The microscopic FTIR was also used to characterize the dewetting of (PEOX/PAA)₂₀ deposited on the silicon wafer. Silicon wafer does not have specific IR absorbance, and is fit for IR spectroscopy and IR imaging. The dewetting behavior of PEOX/PAA film on silicon substrate is similar to that on the quartz substrate (Fig. S3, in ESI), while dewetting of PEOX/PAA film on silicon is relatively quicker than that on quartz. On the silicon wafer, the droplets were formed after 2 h hydrothermal treatment, while on quartz substrate, the droplets were observed after 4 h hydrothermal treatment.

After 2 h hydrothermal treatment, the film deposited on silicon wafer was characterized with microscopic FTIR (Fig. 5). The micro-infrared spectroscope can provide the image of film by using visible light illumination (Fig. 5a), which may guide the IR spectrum and imaging. Fig. 5(a) clearly shows the droplet on the substrate after 2 h hydrothermal treatment. The spectrum of designed area (red square frame in Fig. 5a) is shown in Fig. 5(b), which exhibits two strong vibration bands. One is attributed to the C=O stretching of PAA carboxylic acid group at 1724 cm⁻¹, the other is at 1617 cm⁻¹ from the C=O stretching of PEOX, which are consistent with the original PEOX/PAA film^[55]. The designed area in Fig. 5(a) was scanned using IR intensity signal at 1724 and 1617 cm⁻¹ separately. The images of intensities at 1724 and 1617 cm⁻¹ are presented in Figs. 5(c) and 5(d), respectively. The pictures are almost the same, which indicates that the droplets formed by dewetting are composed of PEOX and PAA. IR imaging further demonstrates that during the dewetting process, PEOX and

PAA chains are associated and move together.

Two basic dewetting mechanisms have been provided. One is spinodal decomposition and the other is nucleation and growth^[13, 23]. The unstable film takes the mechanism of spinodal decomposition while the meta-stable film adopts the mechanism of nucleation and growth. The spinodal decomposition is caused by the amplification of capillary wave, and the holes form spontaneously^[14, 21]. The meta-stable film needs to cross the energy barrier for forming holes, and hence there is a nucleation process^[14].

The stability of the film is dependent on the film thickness that affects the dewetting mechanism^[23]. A series of PEOX/PAA films with different thickness were prepared. In the previous work, we investigated the LbL assembly of PEOX and PAA^[55] and found that the film exhibited exponential growth in the first 10 assembly cycles, while transferred to linear growth after 10 cycles^[55]. The thicknesses of (PEOX/PAA)₅, 10, 15, 20, 25, 30, 40 films were measured to be 50, 300, 650, 1000, 1350, 1700 and 2400 nm, respectively. These films were treated in hydrothermal environment at 140 °C. As the film's thickness increases, the dewetting rate becomes slow. We compare their morphologies after 2 h hydrothermal treatment and show the optical images in Fig. 6. For 50, 300 or 650 nm films, droplets were mainly observed, and the irregular cellular patterns were identified for 1350 and 1700 nm films, while holes were observed for 2400 nm film.

Among these films, the dewetting morphology of (PEOX/PAA)₅ film (50 nm) is interesting. The morphologies of the (PEOX/PAA)₅ film after different periods of hydrothermal treatment are shown in Fig. S4 (in ESI). The morphologies are different as compared with the other thicker films. After 2 h hydrothermal treatment, the droplets formed. However, the droplet size is much smaller and density is much higher, which makes the droplets link together.

A lot of papers have reported the dewetting behavior of a thin film (< 100 nm) annealing upon its *T_g*, and claimed the spinodal decomposition mechanism^[16–29]. For the thick film (> 1.0 μm), the dewetting mechanism is mainly nucleation and growth^[15, 20]. There are defect-induced and thermal-induced hole formation, which are considered as heterogeneous and homogeneous nucleation, respectively^[23]. For the spinodal decomposition mechanism, a continuous arrangement of pores is observed. For the heterogeneous

nucleation, the initial hole size and distribution are strongly dependent on the defect size and distribution. For the thermal nucleation dewetting, the holes are formed by thermal agitation, and hence the holes randomly distribute on the film with non-uniform size. In our system, the hydrogen bonded film under hydrothermal condition can be considered as a viscous liquid which is resulted from the synergistic

effect of temperature and water. Above T_g , the film relaxes, water can penetrate into film easily under hydrothermal environment, and the whole film becomes liquid-like and dewetting process occurs. According to morphology analysis, the (PEOX/PAA)₅ film is spinodal decomposition dewetting, while the other films with the thickness more than 100 nm are nucleation dewetting.

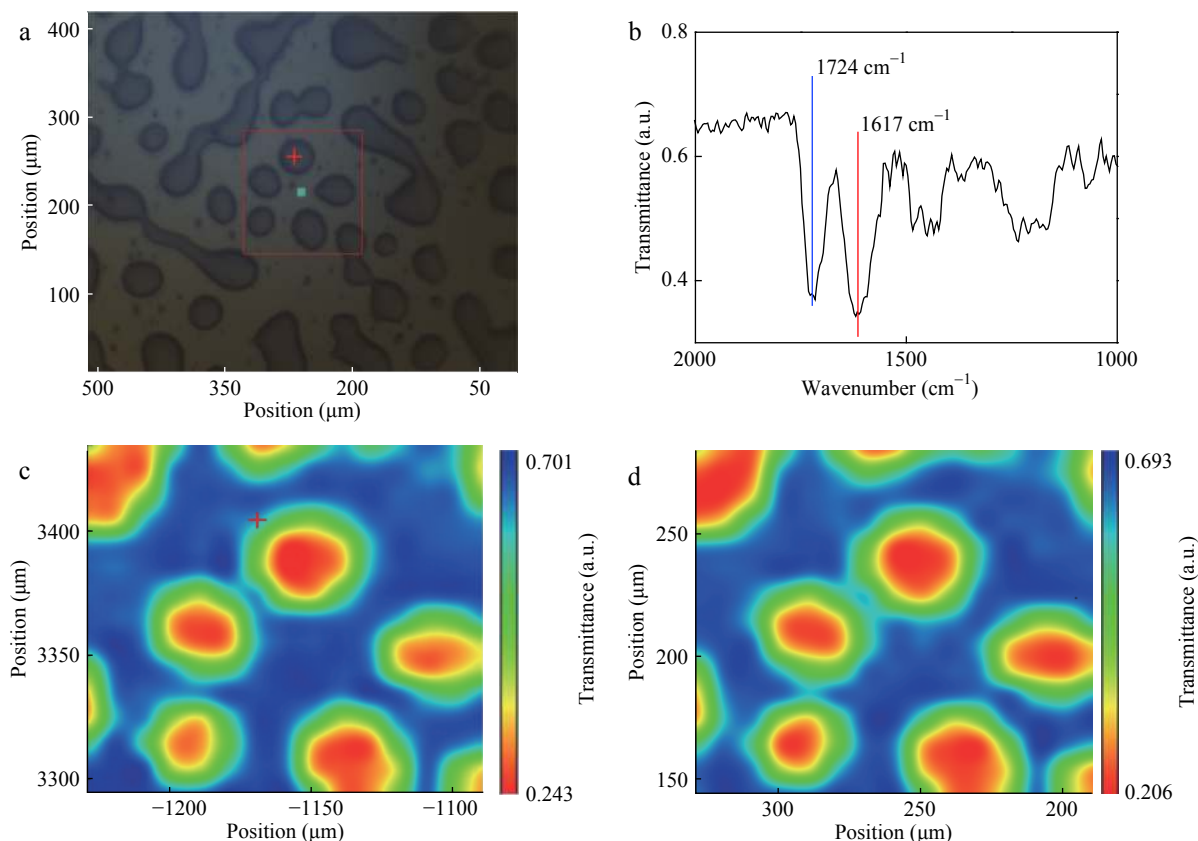


Fig. 5 Hydrothermal treatment (time: 2 h; temperature: 140 °C) of (PEOX/PAA)₂₀ deposited on silicon wafer; (a) Image formed with normal visible illumination; (b) IR spectrum of the red square designed area in (a); (c) and (d) are the infrared images based on the intensity of peaks at 1724 and 1617 cm^{-1} , respectively.

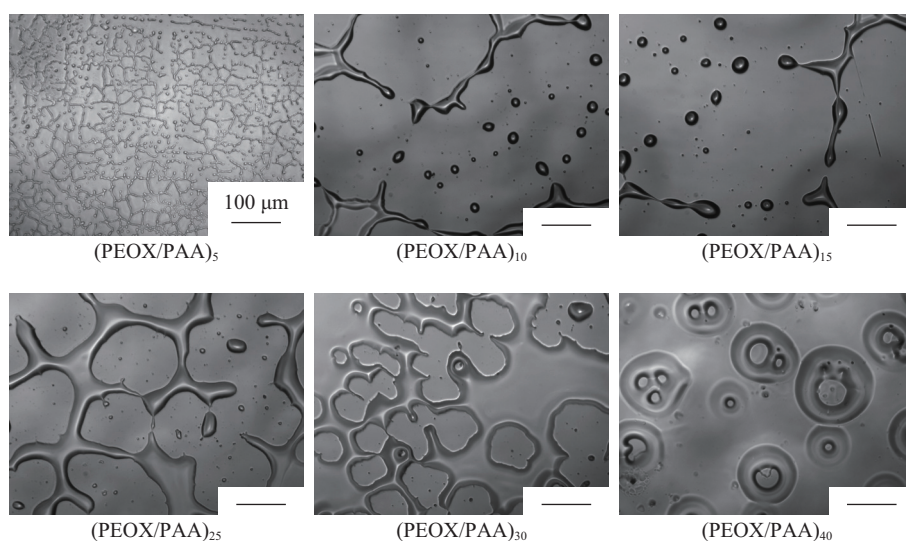


Fig. 6 Images of films with different thickness under the same hydrothermal treatment condition (time: 2 h, temperature: 140 °C) (All the images share the same scale.)

CONCLUSIONS

The hydrogen-bonded polymer PEOX/PAA complex films show dewetting behavior under hydrothermal condition. Four different typical stages of dewetting can be distinguished: (a) film rupture and hole formation; (b) growth of the hole; (c) holes expansion to form irregular cellular structure; (d) droplet formation. During the dewetting process, PEOX and PAA chains are associated and move together. The dewetting mechanism is related to film thickness. As the film thickness increases, the dewetting becomes slow and the mechanism transfers from spinodal to nucleation.

Electronic Supplementary Information

Electronic supplementary information (ESI), which includes DSC curves of PAA, PEOX and PEOX/PAA complexes; the images of the films with different hydrothermal time under (a) 120 °C and (b) 160 °C; optical images of the film surface on Si substrate under hydrothermal treatment; optical images of (PEOX/PAA)₅ (50 nm) after hydrothermal treatment of different periods of time, is available free of charge in the online version of this article at <https://dx.doi.org/10.1007/s10118-018-2109-8>.

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