DEWETTING BEHAVIOR OF HYDROGEN BONDED POLYMER COMPLEX FILM UNDER BASIC VAPOR CONDITION

[1]KIRANREHAN, [2]CHAO SU, [3]ALI A. ALTAM, [4]HAJO YAGOUB, [5]SHUGUANG YANG, [6]JIANXU

[1,2,3,4,5]State Key Laboratory for Modification of Chemical Fibers and Polymer Materials &College of Material Science and Engineering, Donghua University, Shanghai.
[2]Center for Advanced Low-dimension Materials, Donghua University, Shanghai
[6]Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing.
E-mail: shgyang@dhu.edu.cn

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(vinylpyrrolidone) (PVPON) and poly(acrylic acid) (PAA). The dewetting behavior of PVPON/PAA films under basic vapor 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. Optical microscope was combined with confocal laser scanning microscopy to find that after basic vapor the hydrogen-bonded PVPON/PAA films undergo morphological transition from micro pores to droplets which are throughout the whole surface of the film. Results obtained from FTIR spectroscopy further confirms that PAA is ionized in response to the basic vapor treatment as a function of exposure time. Reflective spectroscopy was applied to further characterize the morphology evolution on the film surface.

Key Words - Hydrogen-Bonding, Polymer Complex, Dewetting.

I. INTRODUCTION

Strategies for the utilization of dewetting phenomenon to fabricate ordered patterns are often studied. During last decade, dewetting phenomenon has received much recent attention both experimentally and theoretically [1]. 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. On the other hand, the mechanism and dynamics investigation of the dewetting process itself have been studied extensively. Theoretically, for the non-wetting liquid, if the film thickness is less than critical thickness, capillary force dominates and dewetting phenomenon occurs[2]. In 1960s simple liquid dewetting was investigated [3], and the dewetting phenomena of complex fluid have drawn considerable interest since 1990s [4]. Reiter studied the dewetting behavior of thin polystyrene film (thickness < 100nm) on silicon wafer above the glass transition temperature (Tg)[5], and stated that dewetting can be used as a probe to investigate the polymer chain mobility in the thin film[6]. The dewetting behavior at the solid-air (vacuum) have also been explained[4], while those at solid-liquid interface are rarely explored[7].

II. RESULTS AND DISCUSSIONS

The films were assembled via hydrogen bonds between PVPON as hydrogen acceptor and PAA as hydrogen donor. The PVPON/PAA)20 films were fabricated at pH=2 and after one day annealing in acidic solution (pH=2) at room temperature, the film will become smooth and get to the high level of miscibility [8]. These films exhibited Fabry-Perot fringes by which their thickness can be calculated. Generally, in LbL film or interpolymer complex PVPON and PAA can reach to high level of miscibility.The FAM labeled PAA (PAA-FAM) was LbL assembled with PVPON to prepare the film. Both films exhibited Fabry-Perot fringes which can be used to estimate the film thickness and refractive index [9]. However in the vicinity of 440nm, the absorbance of the PVPON/PAA-FAM film is extra increased, indicating the film was dyed with FAM. Themorphological evolution PVPON/PAA-FAM film also studied under basic vapor condition by using Confocal laser scanning microscopy (CLSM). The morphological evolution of the PVPON/PAA LbL film in the basic vapor annealing was explored by using an optical microscope. The OM images of the PVPON/PAA films after immersion in basic vapor environment at 25◦C for different period of time was shown in Figure 1. The images feature a series of morphologies, first small micropores; several hundred nanometers in diameter grow after 2hr immersion. Increase in the immersion time, these small micropores turns into worm like holes, further increase in time results in combination of holes to form ribbons. Finally, ribbons decay and small droplet appear on the film surface leads to dewetting. Morphology of the film varies with time, yet PAA is ionized as it has confirmed from FT-IR results, hydrogen bonds would break and polymer chains

would rearrange to meet the environment change thus inducing different morphologies.

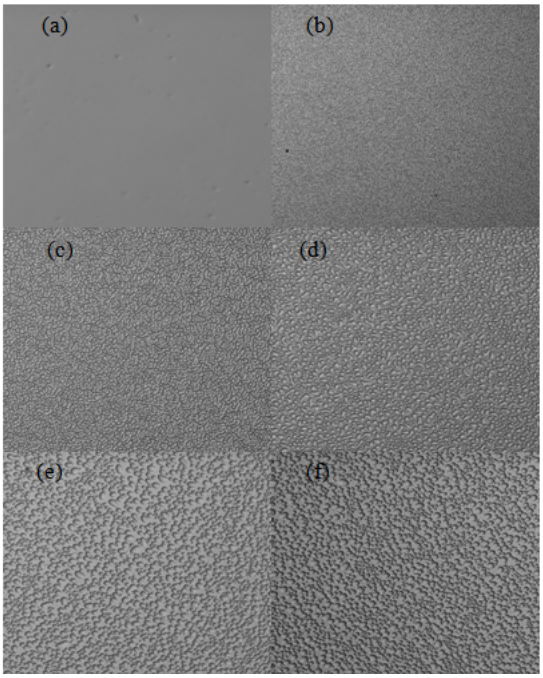


Figure 1. Optical micrographs of the $(PVPON/PAA\text{-}FAM)_{20}$ film after basic vapor incubation for different time (a) 0 hr, (b) 2 hr, (c) 4 hr, (d) 6 hr, (e) 8 hr, (f) 10 hr.

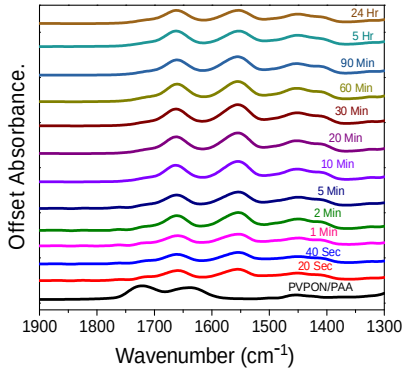


Figure 2. FT-IR spectra in the region from 1900 to 1350 cm^{-1} of $(PVPON/PAA)_{20}$ films before and after immersion in basic vapor at 25 °C for different time.

FT-IR spectroscopy was further utilized to characterize the PVPON/PAA films after basic vapor incubation. The IR absorbance peaks of free PAA and PVPON are located at 1706 cm^{-1} and 1680 cm^{-1}, respectively [10]. However, in PAA there are several hydrogen bonding modes among COOH groups, which results in a C=O stretching vibration located at 1709 cm^{-1}. In LBL assembled PVPON/PAA film, PAA's peak shifts to higher frequencies (1721 cm^{-1}), while PVPON's peak shift to lower frequencies (1640 cm^{-1}) due to hydrogen bonding between PVPON and PAA [11]. However, after incubation in basic vapor the peaks at 1719 cm^{-1} and 1639 cm^{-1} are completely displaced by the peaks at 1660 cm^{-1} and 1556 cm^{-1}. The peak at 1660 cm^{-1} is contributed from PVPON which has hydrogen bonding with water [11]. The characteristic PAA carbonyl vibration band around 1721 cm^{-1} in the FT-IR spectra disappeared after the film was immersed in basic vapor for 20 s, indicating that the PAA in the film was ionized as shown in Figure 2.

CONCLUSION

Based on LBL assembly, PVPON and PAA can construct a hydrogenbondedthin film. In basic vapor environment, the PAA will ionize, hydrogen bonds in the film will detach, and hereby the different morphologyevolution leading to dewetting will form. And ionization degree of PAA can influence the morphology and morphology development of thehydrogen-bonded PVPON/PAA film.

REFERENCES

[1] Thiele,U. Open questions and promising new fields in dewetting.Eur. Phys. J. E.2003, 12(3), 409-416.
[2] Brochard-Wyart,F.,"Droplet: capillarity and wetting".Soft Matter Phys., Spinger-Verlag Berlin Heidelberg, 1999, p. 29
[3] Vrij,A.Possible mechanism for the spontaneous rupture of thin, free liquid films.Discuss. Faraday Soc.1966, 42,23-33.
[4] Redon,C.;Brochardwyart,F.;Rondelez, F. Dynamics of dewetting.Phys. Rev. Lett.1991, 66(66),715-718.
[5] Reiter,G.Dewetting of thin polymer-films.Phys. Rev. Lett.1992, 68(1),75-78.
[6] Reiter,G.Dewetting as a probe of polymer mobility in thin films.Macromolecules1994, 27(11),3046-3052.
[7] Péron,N.;Brochard-Wyart,F.;Duval, H. Dewetting of low-viscosity films at solid/liquid interfaces. Langmuir2012, 28(45),15844-15852.
[8] Yang, S., et al., From Cloudy to Transparent: Chain Rearrangement in Hydrogen-Bonded Layer-by-Layer Assembled Films. ChemPhysChem, 2007. 8(3): p. 418-424.
[9] Diehl, H. and R. Markuszewski, Studies on fluorescein—VII. Talanta, 1989. 36(3): p. 416-418.
[10] S.A. Sukhishvili, S. Granick, J. Am. Chem. Soc. 122 (2000) 9550.
[11] S. Yang, Y. Zhang, Y. Guan, S. Tan, J. Xu, S. Cheng, X. Zhang, Soft Matter 2 (2006) 699

★★★