

Surface Morphology of Langmuir–Blodgett Blend Films of Poly(vinyl acetate)–Poly(methyl acrylate)

Masami Kawaguchi,* Shinsuke Suzuki, Toyoko Imae,† and Tadayo Kato

Department of Chemistry for Materials, Faculty of Engineering, Mie University,
1515 Kamihama, Tsu, Mie 514, Japan

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Films of poly(vinyl acetate) (PVAc), poly(methyl acrylate) (PMA), and their blended mixtures were prepared on a mica substrate by the Langmuir–Blodgett method, and they were studied using an atomic force microscope (AFM). AFM images showed that PVAc was spread more uniformly than PMA. Since PVAc–PMA mixtures were immiscible, PMA components were squeezed out and their AFM images strongly depended on the mixed ratio of PVAc–PMA.

Introduction

Polymer blends in the thin film states are of special interest for both practical applications and fundamental studies.^{1–5} The technological interest is focused on the production of polymer blends with specific interfacial properties and surface structures by controlling the composition. Such an interest motivates a lot of fundamental investigations of surface morphological control.

The thin films of polymer blends can be prepared by various methods, such as spin coating, the Langmuir–Blodgett (LB) film method, casting, epitaxy, and the adsorption method. Such thin films have been characterized by optical, X-ray, and neutron reflection methods, or by optical, electron, and scanning probe microscopes.^{6,7} The reflection techniques have proved the composition profile of the films in a direction normal to the film plane, whereas the latter methods are useful for investigating the lateral surface morphology of thin films. Among the scanning probe microscopes, atomic force microscopy (AFM) is one of the most successful of these new devices to image lateral surfaces of organic materials, provided that the forces involved are small enough not to disrupt the sample.

We have previously reported that binary blends of poly(vinyl acetate) (PVAc) and poly(methyl acrylate) (PMA) spread at the air–water interface were immiscible from the surface pressure and ellipsometric measurements though both polymers have very similar chemical structures.^{8,9} Furthermore, it was found that any PMA chains cannot contact with the water surface when PVAc is spread to fully cover the water surface, irrespective of the

spreading order. This means that PVAc chains preferentially adsorb at the air–water interface over PMA chains, indicating that PMA is squeezed out and lies on PVAc films at the air–water interface. In this study, in order to confirm such a vertical separation between PVAc and PMA, we have explored lateral surface morphologies of the LB films of the pure PVAc and PMA, and the binary mixtures of PVAc and PMA deposited on a mica surface using the AFM method. Furthermore, the resulting images will be discussed by a combination of the previous studies^{8,9} on surface pressure and ellipsometric measurements.

Experimental Section

Materials. PVAc and PMA were synthesized by radical polymerization of freshly distilled monomers with azobis(isobutyronitrile) as an initiator in benzene at 60 °C. The resulting polymers were poured into a large amount of methanol, and the precipitated PVAc was dried in a vacuum. The respective polymers were dissolved in acetone and fractionated into several fractions using *n*-hexane at 25 °C as a precipitant. We chose one fraction for PVAc and PMA; the molecular weights of the fractionated PVAc and PMA were determined to be 594 and 460 × 10³ from the intrinsic viscosity measurement in benzene at 25 °C, respectively.^{8,9}

The spreading solvent used to deposit PVAc, PMA, and their mixed films at the air–water interface was spectrograde benzene, and we used it without further purification.

A freshly cleaved brown mica surface was used as a substrate for LB films of PVAc, PMA, and PVAc–PMA mixtures.

Surface Pressure Measurements. The surface pressure measurement apparatus was the same as described in detail before.¹⁰ A Teflon trough (10 × 100 × 290 mm³) was filled with deionized water and the temperature was controlled at 25 ± 0.2 °C by circulating thermostated water. Films of PVAc and PMA were spread on the water surface in the trough by applying the method of “successive additions” of the benzene solutions of the corresponding polymers with a Hamilton microsyringe to adjust the surface concentration. The successive addition method is beneficial to avoid effects from impurities concomitantly compressed. On the other hand, PVAc–PMA binary mixtures with 1:4, 1:2, 1:1, 2:1, and 4:1 expressed in weight fraction PMA were added successively for the respective mixed films and changes in the surface pressure were monitored as a function of surface concentration of PVAc.

The droplets were delivered to touch the surface of the water; i.e., the distance between the drops and the surface was as small as possible. They were distributed randomly over the entire trough surface, and the solvent was allowed to evaporate for at least 30 min before starting the experiment. Unless the surface pressure did not remain constant over 10 min, we regarded it as

† Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya, Aichi 464-01, Japan.

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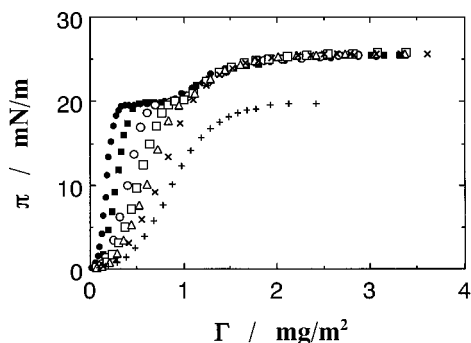


Figure 1. Surface pressures of PVAc (\times), PMA ($+$), and PVAc–PMA mixtures with various PVAc/PMA ratios as a function of surface concentration of PVAc: (\bullet) PVAc/PMA = 1/4; (\blacksquare) PVAc/PMA = 1/2; (\circ) PVAc/PMA = 1/1; (\square) PVAc/PMA = 2/1; (\triangle) PVAc/PMA = 4/1.

an equilibrium surface pressure. The equilibrium value was not changed if longer time periods than 30 min were passed. The experimental errors in the surface pressure were less than 0.1 mN/m.

Langmuir–Blodgett Film Preparation. PVAc, PMA, and PVAc–PMA mixed films were spread at the air–water interface from the benzene solutions of PVAc, PMA, and PVAc–PMA binary mixtures with 1:4, 1:1, 1:1, 2:1, and 4:1 expressed in weight fraction for desired surface polymer concentrations, respectively.

They were transferred onto a mica surface by the LB vertical dipping technique using an NL-LB140S-MWC trough (Nippon Laser & Electronics Lab, Nagoya, Japan).¹¹ A deposition speed of 1.0 cm/min resulted in transfer ratios of ca. unity. All specimens were placed in a desiccator immediately after the manufacture and could be stored under controlled temperature and humidity.

AFM Observation. AFM experiments have been performed using a Nanoscope III equipped with microfabricated silicon cantilevers (Digital Instruments, Santa Barbara, CA), and AFM images of the deposited films were taken under tapping mode at ambient temperature (ca. 25 °C) in air.¹¹ Images were recorded in several areas on all samples. At least three films were prepared at the same surface concentration, and their images were observed.

Results and Discussion

Figure 1 shows the surface pressures for individual PVAc and PMA films as a function of concentration of the corresponding polymer and the surface pressures of the five PVAc and PMA mixtures as a function of PVAc surface concentration. Both PVAc and PMA showed typical expanded type isotherms. The collapse surface pressures are 25.7 and 19.3 mN/m, and the limiting areas are 1.75 and 1.5 m²/mg for PVAc and PMA, respectively. The differences in the collapse surface pressure and those in the limiting area between PVAc and PMA should be attributed to the chain mobility and the segment–segment

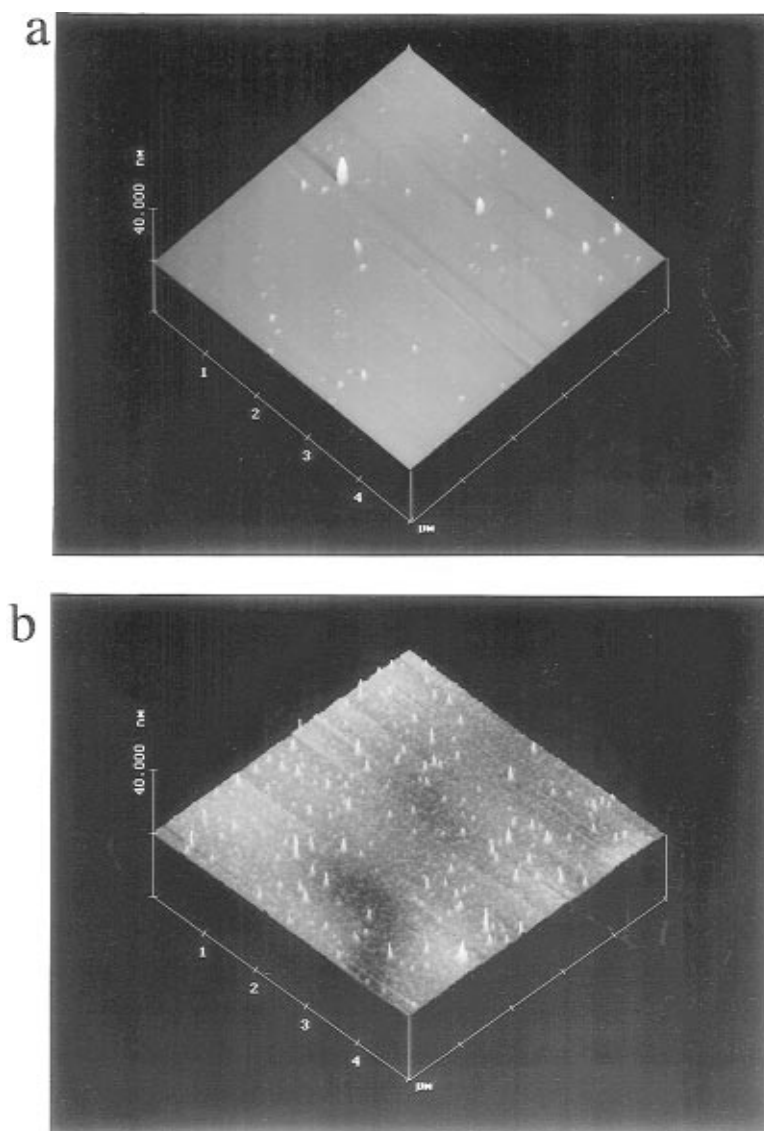


Figure 2. AFM images of the LB films of PVAc at 1.0 (a) and 2.0 (b) mg/m².

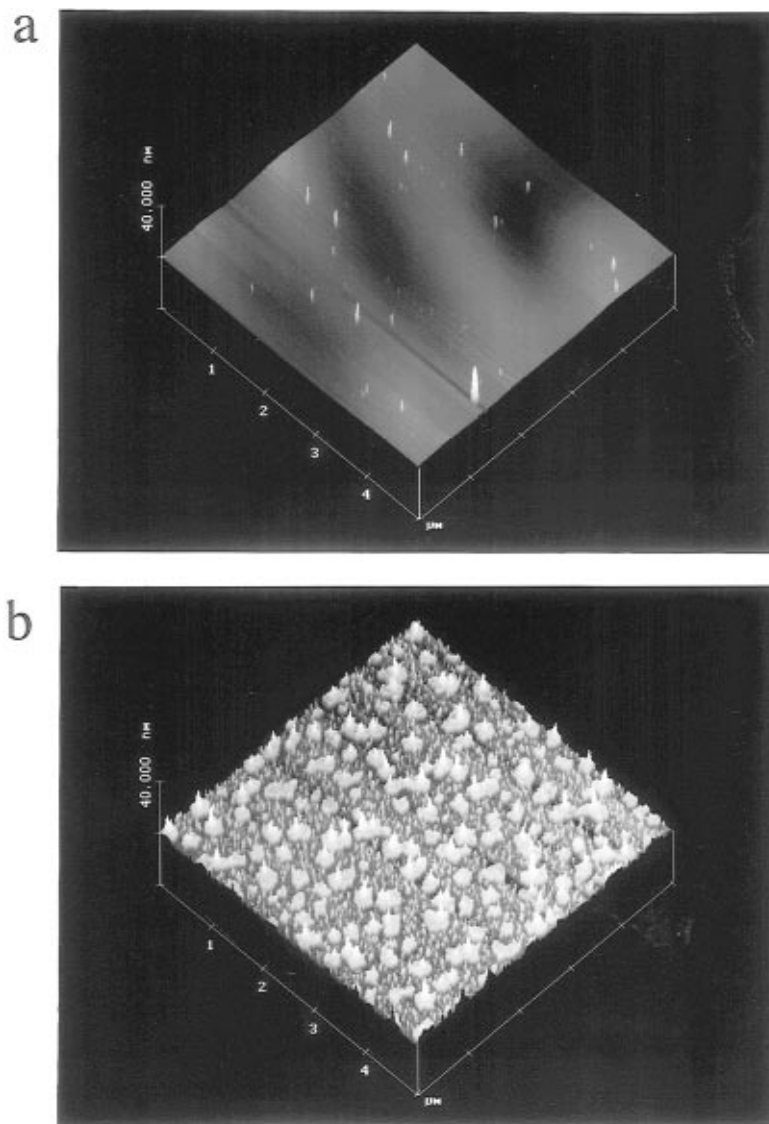


Figure 3. AFM images of the LB films of PMA at 1.0 (a) and 2.0 (b) mg/m^2 .

interaction, respectively. Since the glass transition temperature of PVAc is higher than that of PMA,¹² PMA chains are more flexible and show the less cohesive interaction than PVAc ones.

The surface pressure–surface concentration isotherms of the respective mixtures have an apparent plateau region around 20 mN/m , which is consistent with the plateau surface pressure of pure PMA, and a final plateau region around 26 mN/m . The observation of two plateau regions is one evidence for the immiscibility of PVAc and PMA at the air–water interface and for PMA appearing to be squeezed out at the air–water interface.

Typical AFM images of monolayers of pure polymers and mixed polymers are shown in Figures 2–5. In most images the islands like granules are observed. The granules displayed in the AFM images are not spiky because the vertical scale of the images is expanded by 2 orders of magnitude (the lateral scale in the figures is 5 μm with 1 $\mu\text{m}/\text{division}$ and the vertical scale is 40 nm with 20 $\text{nm}/\text{division}$). Thus, the real dimensions of the granules are several nanometers to a few tens of nanometers in height and several tens nanometers to a few hundred

nanometers in lateral size. So, the 3D granules are rather flat. The vertical scale is selected by taking into account twice the radius of gyration of an unperturbed chain and the layer thickness spread at the air–water interface.⁹

Figures 2 and 3 show 3D AFM images of pure PVAc and PMA films deposited on a mica surface at two surface concentrations of 1.0 and 2.0 mg/m^2 , respectively. The respective surface concentrations are well in the corresponding plateau surface pressures, and the water surface should be well covered by the polymer. At the surface concentration of 1.0 mg/m^2 , except for a few larger granules, PVAc has a surface with a height difference of less than 3 nm, whereas PMA has a height difference of 4–7 nm, and thus, PVAc forms a more uniform film than PMA. The resulting granules should be attributed to the formation of loops, since the surface concentration of 1.0 mg/m^2 is well beyond the reciprocal of the limiting area for the respective polymers.

At the PVAc surface concentration of 2.0 mg/m^2 , the number of the granules increases and the size of these granules is almost the same as that at 1.0 mg/m^2 , indicating that PVAc forms a film with many loops. Since the average layer thickness of the PVAc film spread at the air–water interface was determined to be 3–4 nm from ellipsometry,⁹ the LB film transferred on the mica

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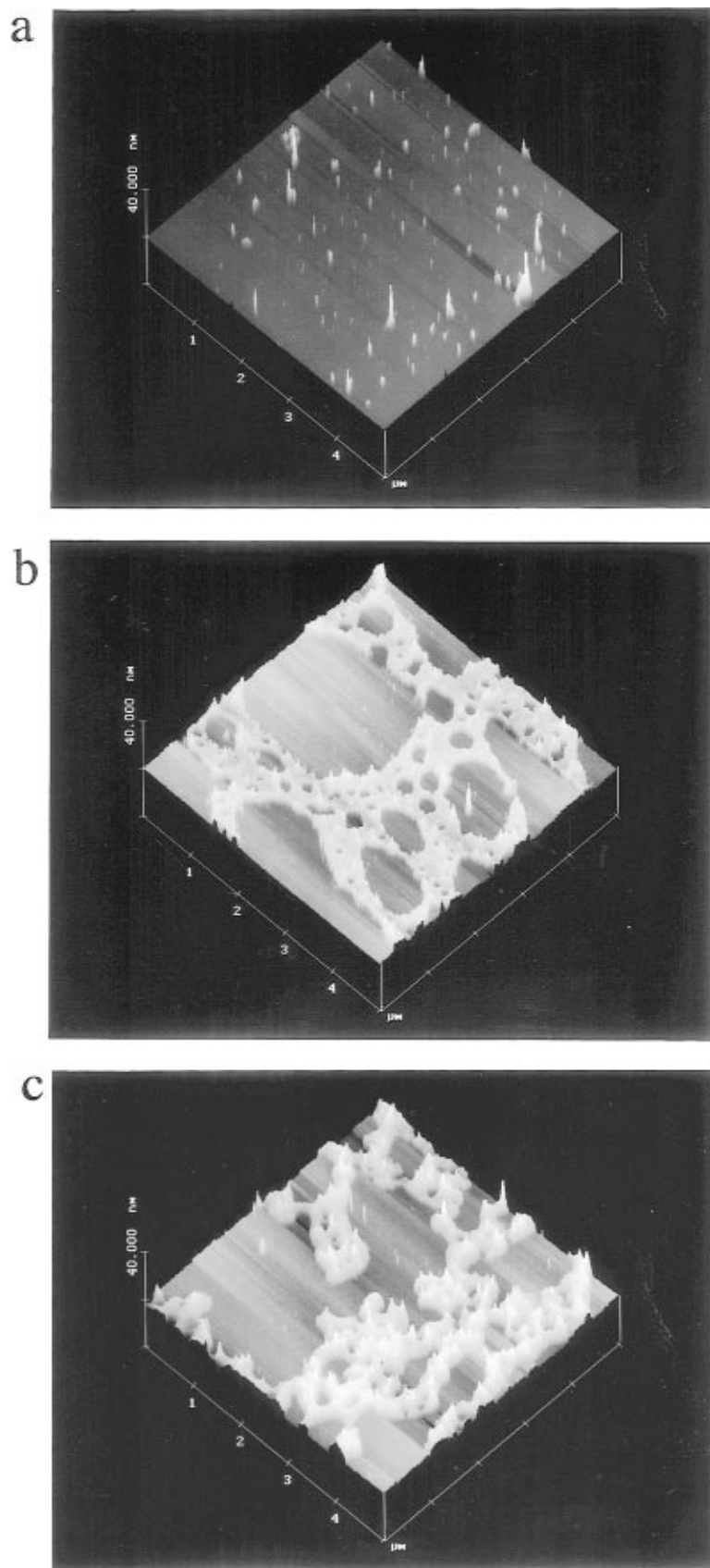


Figure 4. AFM images of the LB films of PVAc–PMA mixtures at a fixed PVAc concentration of 0.5 g/m^2 for various PMA surface concentrations of 0.5 (a), 1.0 (b), and 2.0 (c) mg/m^2 .

substrate seems not to be far from the real image of the PVAc film spread at the air–water interface.

On the other hand, at the PMA surface concentration of 2.0 mg/m^2 , many large size granules appeared randomly; the vertical distance from the top of the cup to the bottom

surface ranged from 5 to 10 nm . This indicates that some parts of the spread PMA chains seem to form many large loops at the air–water interface due to the higher chain flexibility. This may be one evidence that the spread PMA film is much more heterogeneous than PVAc at the air–

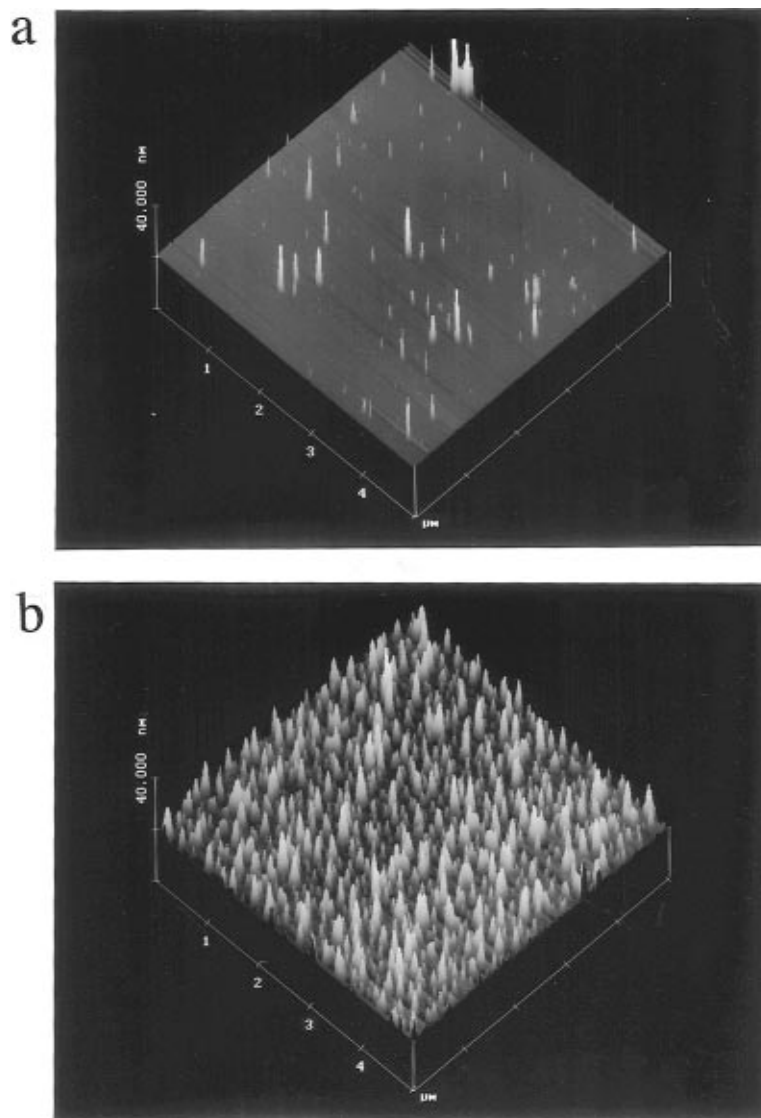


Figure 5. AFM images of the LB films of PVAc-PMA mixtures at a fixed PMA concentration of 0.5 g/m^2 for two PVAc surface concentrations of 1.0 (a) and 2.0 (b) mg/m^2 .

water interface and that the limiting area of PMA is smaller than that of PVAc. The vertical distance determined by AFM is larger than the ellipsometric layer with a thickness of $3\text{--}4 \text{ nm}$ spread at the air-water interface.⁹

Figure 4 shows AFM images of the PVAc-PMA blends prepared from their binary mixture solutions, where a PVAc surface concentration is fixed at 0.5 mg/m^2 and a PMA surface concentration is varied. An increase in PMA surface concentration changes the surface morphology of the mixed film: (1) at a PMA concentration of 0.5 mg/m^2 , there are some differences in the surface morphology features when compared with those for the pure PVAc and PMA films at 1.0 mg/m^2 , the granule population is higher, and some granules have more than 10 nm height, leading to a much rougher surface; (2) at a PMA concentration of 1.0 mg/m^2 , the surface morphology is a Swiss cheese pattern containing many holes with different sizes of $150\text{--}1500 \text{ nm}$ diameter, and the vertical distance from the film surface to the hole top can be estimated to be $2\text{--}3 \text{ nm}$, irrespective of hole size; and (3) at a PMA concentration of 2.0 mg/m^2 , the hole size becomes smaller and more irregular than that at 1.0 mg/m^2 PMA concentration, leading to a higher vertical distance of $5\text{--}10 \text{ nm}$, and such a higher vertical distance is similar to the pure PMA film at 2.0 mg/m^2 surface concentration. We believe that squeezing out PMA should cause changes in the

topography by taking into account that PVAc-PMA mixtures are immiscible and PMA first spread at the air-water interface is easily displaced by PVAc added late.^{8,9} Thus, the Swiss cheese pattern formation is induced by aggregation of the granules of PMA. The surface fraction of overlayer (bright parts) formed by the squeezed PMA chains can be determined manually. The calculated surface fraction was referred to as the relative surface coverage by PMA, and it was almost the same at PMA concentrations of 1.0 and 2.0 mg/m^2 , indicating that PMA dewetted PVAc and forms the higher overlayer.

Figure 5 shows AFM images of the PVAc-PMA blends prepared by their binary mixture solutions, where the surface concentration of PMA is fixed at 0.5 mg/m^2 and the surface concentration of PVAc is changed. At a PVAc surface concentration of 1.0 mg/m^2 , the surface with a height difference of $4\text{--}15 \text{ nm}$ is rougher than that at 0.5 mg/m^2 (Figure 4a), although the granule population is almost the same. This means that PMA chains gather together to form large granules due to the immiscibility of PVAc and PMA. At a PVAc surface concentration of 2.0 mg/m^2 , the number of the granules increases without changes in their size, as compared with that at 1.0 mg/m^2 PVAc. Formation of the granules is dominantly attributed to the PMA squeezed out; however, PVAc can also take part in the granule formation. Furthermore, it is im-

portant to note that there is no observation of Swiss cheese-like form. This suggests that the PMA surface concentration of 0.5 mg/m^2 , which is less than the reciprocal of the limiting area of PMA, may not be sufficient to form the Swiss cheese pattern. Thus, in the PVAc–PMA blends PMA mainly caused an increase in both the number and the size of granules.

Conclusions

The AFM images have shown the differences in the surface morphology between PVAc and PMA LB films and the changes in surface morphology of PVAc–PMA blended LB films with the various components. PVAc

formed a more smooth film than PMA. For the binary mixtures of PVAc–PMA, at a fixed surface concentration of PVAc the surface images changed from granule islands to a Swiss cheese-like pattern with an increase in PMA, whereas at a fixed surface concentration of PMA the height and population of granules increased with increasing PVAc component. These changes in the PVAc–PMA blends are mainly attributed to the fact that PMA is squeezed out of the film. Furthermore, a Swiss cheese-like morphology is possible above the PMA surface concentration, i.e., the reciprocal of the limiting area of PMA.

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