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Surface Aggregation Structure and Surface Mechanical Properties of Binary Polymer Blend Thin Films

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SUMMARY: During preparation of very thin polymer belnd films from a solution of polymers, the phase-separated structures which are quite different from that observed for the bulk blend film was observed. From atomic force microscopic(AFM) observation, it is concluded that the surface undulation, which reflects the phase separated morphology of the blend system, is present. In the case of (polystyrene(PS)/poly(methyl methacrylate)(PMMA)) blend system, a large influence of end-group chemistry on the surface morphology was observed. The phase identification of the (rubbery polymer/glassy polymer) binary blend thin films was successfully achieved by scanning vioscoelasticity microsopy(SVM).

Introduction

Surface structure and properties of multiphase polymers have been paid a great attention these days because surface structure and properties are closely related to many technological applications[1,2]. As predicted by the mean-field theory, the polymer blend thick films showed the enrichment of lower surface free energy component at the air/solid interface[1,2]. In the case of polymer blend thin films, the molecular aggregation state can be expected to be different from that of the thick film due to the strong influence of the air and substrate interfaces. In this study, the surface structure and surface mechanical properties of various binary polymer blend systems have been studied on the basis of scanning force microscopy(SFM).

Experimental

Polymer blend thin films were prepared in order to image the surface structure and surface mechanical properties at the polymeric solid. Polymer blend systems used in this study were (polystyrene(PS)/poly(vinyl methyether) (PVME)), (PS/polyisoprene(PI)) and (PS/poly(methyl methacrylate)(PMMA)). The bulk (PS/PVME) blend is miscible state at room temperature, whereas the (PS/PI) and (PS/PMMA) blend systems are in an immiscible state at room temperature. Table 1 summarizes the physico-chemical properties of polymers used in this study for blends and the preparation methods. Unless specified the

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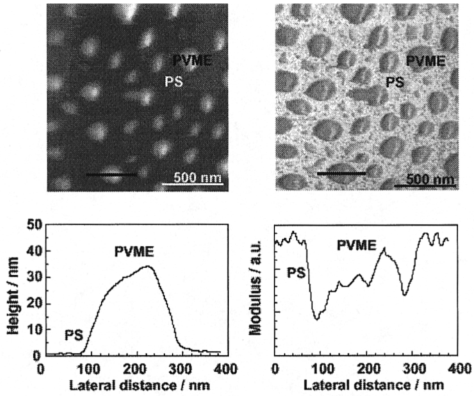
Table 1 Characterization of blend components

Blend	Blend Component	Mn	Mn/Mw	Tg/K	γ/mN m^{-1}	Preparation Method
(PS/PVME)	PS	26.6k	1.09	386	40.2	Dip-coating
	PVME	28.8k	1.98	249	36.0	
(PS/PI)	PS	55k	1.09	386	40.2	Spin-coating
	PI	52k	1.18	200	36.0	
(PS/PMMA)	PS	54.5	1.09	386	40.2	Spin-coating
	PMMA	46.3k	1.12	399	44.0	
(α,ω-$PS(NH_2)_2$/PMMA)						
	α,ω-$PS(NH_2)_2$	53.4	1.08	386	40.2	Spin-coating
	PMMA	46.3k	1.12	399	44.0	

chain end groups of PS and PMMA are composed of *sec*-butyl group and proton-terminated styrene unit, respectively. The diamino-terminated PS[α,ω-$PS(NH_2)_2$] was synthesized by a living anionic polymerization. The blend ratio of (Polymer A/Polymer B) was designated as (weight% /weight%). In order to avoid an influence of the surface segregation of low molecular weight component, the blends were prepared from monodisperse polymers except for (PS/PVME) blend.

AFM was used for the observation of the surface morphology of the blend films. The AFM images were obtained by an SPA 300 with SPI 3700 controller (Seiko Instruments Industry Co., Ltd.) at 293 K in air. The cantilever used for AFM observation was microfabricated from Si_3N_4 and its spring constant was 0.02 Nm^{-1}. The two-dimensional mapping of dynamic mechanical properties for the phase-separated surface of binary polymer blends were carried out by utilizing scanning viscoelasticity microscope (SVM)3). When the cantilever tip is positioned in a repulsive-force region of the force curve, the sample surface might be deformed by the indentation of the tip. The modulation of the indented tip leads to the modulation of the force between sample surface and tip. If the modulation is applied sinusoidally, the dynamic viscoelastic properties at the sample surface can be evaluated by measuring the amplitude of the modulated deformation of the sample and the phase lag, between modulation signal and modulated deformation of the sample. The SVM measurement and observation were performed at 293 K in air under a repulsive force region. The modulation frequency and the modulation amplitude were 4 or 5 kHz and 1.0 nm, respectively. The cantilever used was microfabricated from Si_3N_4 and its spring constant was 0.09 Nm^{-1}.



(a) Topography(AFM) (b) Modulus(SVM)

Fig.1: AFM and SVM images of (PS/PVME) (62/38 w/w) blend thin films with thickness of ca.25nm. Height profiles along a line are also shown.

Results and Discussion

(PS/PVME) Blend Ultrathin Films

[Polystyrene/poly(vinyl methyl ether)](PS/PVME) is a blend system with a lower critical solution temperature (LCST) type phase diagram. At room temperature, this blend system shows a phase mixing state in the bulk state. X-ray photoelectron spectroscopy (XPS) of the blend thick film showed the enrichment of lower surface free energy PVME at the surface. However, the surface enrichment of PVME became less prominent with a decrease in film thickness[4]. Infrared spectroscopic measurement revealed that the (PS/PVME) blend ultrathin film of ca.25 nm thick prepared from a (50/50 w/w) toluene solution by a dip-coating method has the blend ratio of (PS/PVME) (62/38 w/w) in a bulk region due to a selective adsorption of PS segments to the hydrophilic substrate. Fig.1 shows AFM and SVM images of (PS/PVME) (62/38) blend thin films with thickness of ca.25nm. Even if the observation temperature was below the bulk cloud point, AFM observation revealed that the (PS/PVME) ultrathin film with thickness of ca.25nm was in an apparent phase-separated state in which the droplet-like domains of 200-500 nm in diameter and 20-40 nm in height were formed. The characterization of the droplet-like domains was carried out using AFM observation of the (PS/PVME) ultrathin film with different (PS/PVME) blend ratios. The apparent surface area of the droplet-like domains on the AFM image decreased with a decrease in the PVME weight fraction. Then, it is apparent from the AFM observation that the droplet-like domains are composed of the PVME rich phase. Scanning viscoelasticity microscopic (SVM) observation was carried out in order to evaluate surface viscoelasticity of the as-cast (PS/PVME) (62/38) ultrathin film of ca.25 nm thick on the hydrophilic substrate[4]. Since the bulk T_g of PS is far above room temperature, whereas, that of PVME is below room temperature, it is expected that the glassy PS and the rubbery PVME phases can be distinguished apparently even at the surface on the basis of the SVM observation. Since droplet-like domain showed lower modulus than the matrix phase, it seems reasonable to conclude that the droplet-like domains are composed of the rubbery PVME rich phase and that, the matrix is composed of the glassy PS one. The contrast in the AFM image reflects the difference of the sample height, whereas, that in the SVM image comes from the difference of the modulus. Thus, the combination of AFM and SVM images can reveal the interfacial characteristics of the two-phase system even though the interfacial region between domain and matrix is not distinct.

(PS/PI) Blend Thin Films

The surface of the (PS/PI) film, which is a typical phase-separated blend system, was investigated by using AFM and SVM. In the case of the bulk blend film, a macroscopic phase separation was observed. Fig.2 shows the AFM and SVM images of the as-cast (PS/PI) (70/30 w/w) blend thin film of 100 nm thick prepared by spin-coating$^{5)}$. AFM image showed the well-defined phase-separated structure with the domains of ca. 2 μm in diameter and the apparent domain height was ca. 70 nm lower than matrix. On the other hand, in the case of the blend ratio of (30/70), it was observed in the AFM image that the domain was ca. 70 nm higher than matrix. Since the apparent area of the brighter part in the AFM image increased with the blend ratio of PS, it seems reasonable to conclude that the higher height region at the phase-separated surface is composed of the PS rich phase which has higher surface free energy component in this blend system. Also, when a surface etching treatment of the (PS/PI) (30/70) blend film was carried out using methylethylketone, which is a good solvent only for PS, the domains were disappeared from the surface. Therefore, this result indicates again that the domains and the matrix regions of (PS/PI)(30/70w/w) blend thin film are composed of the PS and PI, respectively. The formation of high PS-rich domain is closely related to the large surface tension of PS compared with that of PI. SVM observation was carried out at room temperature, which was far below and above Tgs of PS and PI, respectively. Since the lower modulus region in the SVM image corresponds to the lower height regions in AFM image, it is reasonable to conclude that the higher height region is composed of the glassy PS rich phase and also, the lower height region are composed of the rubbery PI one. The domain radius in the AFM image was almost the same as that observed

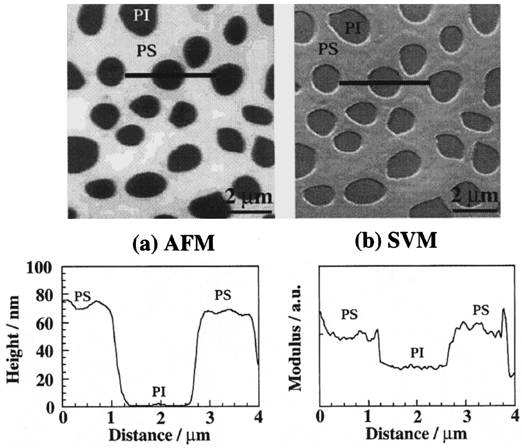


Fig.2: AFM and SVM images of (PS/I) (50/50) blend thin films with thickness of 100nm. Height profiles along a line are also shown.

by SVM. This would mean the fairly distinct interfacial boundary, in other words, a small interfacial thickness between the PS and PI phases. Since the (PS/PI) blend system has larger magnitude of interaction parameter, χ_{12} compared with that of (PS/PVME) system, the interfacial thickness must be much narrower than that of (PS/PVME) system.

(PS/PMMA) Blend Thin Films

It has been reported that the chain end groups which have a lower surface free energy than that of the main chain unit are enriched at the surface and that the thermal molecular motion at the surface is activated due to an increase in free volume fraction at the surface$^{6)}$. On the other hand, the chain end groups, which have a higher surface free energy than that of main chain unit, are depleted from the surface to minimize the interfacial free energy$^{7)}$. However, little study has been done on the control of phase separation based on the interaction between polymer chain end groups and substrate. The monodisperse proton-terminated PS(Mn=54.5k), diamino-terminated PS[α,ω-PS(NH_2)$_2$] (Mn=53.4k) and proton-terminated PMMA(Mn=46.3k) were used to prepare the polymer blend thin films. The (PS/PMMA) blend thin films were prepared onto a silicon wafer with native oxide layer by the spin-coating method from their toluene solution at several spin speeds. The change in spin speed corresponds to the change in the rate of solvent quench. The blend films were vacuum-dried for 24 h at room temperature. An apparent equilibrium aggregation structure at the blend thin film surface was obtained by annealing thin films at 423 K for 24 h and/or 48 h.

Phase-separated structure of the (PS/PMMA) blend thick film, whose thickness is 25 µm, was investigated to compare with that of the thin film. The AFM and the phase contrast

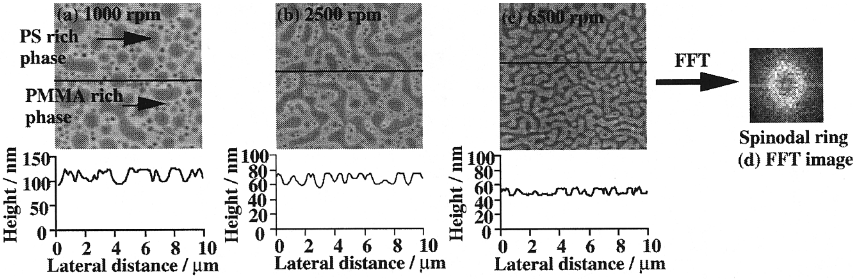


Fig.3: (a)-(c) AFM images and line profiles of the (PS/PMMA) (20/80) thin spin-coated at (a) 1000, (b) 2500 and (c) 6500 rpm and (d) FFT image.

microscopic (PCM) images of the (PS/PMMA) film of 25 μm thick revealed that although the surface was not in an apparent phase-separated state, a macroscopic phase-separated structure was formed in a bulk. XPS measurement revealed that the PS was enriched at the film surface due to its lower surface free energy compared with that of PMMA. In order to reveal the influence of film thickness on surface morphology, the surface structures of the (PS/PMMA) thin films with various blend ratios were observed with AFM. Figure 3(a) shows the AFM image of the (PS/PMMA) (20/80) thin films of ca.100 nm thickness spin-coated at 1000 rpm. It was confirmed by surface etching treatment with cyclohexane that the higher regions were the PMMA-rich phase in all the (PS/PMMA) thin films. Fig.3 (b)-(c) shows the AFM images for the (PS/PMMA) (20/80) blend thin films of ca.100nm thickness with several spin speeds. The thickness of the film decreased with an increase in spin speed. The bicontinuous-like phase-separated structures were observed in all the (PS/PMMA) (20/80) blend thin films. The size of the phase-separation decreased with an increase in spin rate. Fig.3(d) shows the fast Fourier transform (FFT) image for the (PS/PMMA) (20/80) thin film prepared at 6500 rpm. A spinodal ring due to the periodic structure was observed in the FFT image. The phase-separated structure for the (PS/PMMA) (10/90) and (70/30) blend thin films were the reverse sea-island-like and the sea-island-like phase-separated structures, respectively. The bright area in AFM image is smaller than that expected from the bulk composition. This behavior can be attributed to an increase in the apparent surface PS fraction due to a selective adsorption of PMMA to the silicon substrate. The AFM image of (PS/PMMA) blend system after extensive annealing revealed that the phase-separated structure is not stable because of the negative spreading coefficient of PS against PMMA.

The phase-separated structure for the (α,ω-PS(NH_2)$_2$/PMMA) thin films were investigated in order to reveal the influence of the chain end group chemistry on the surface morphology. AFM observation revealed that the bicontinuous-like phase-separated structure was observed

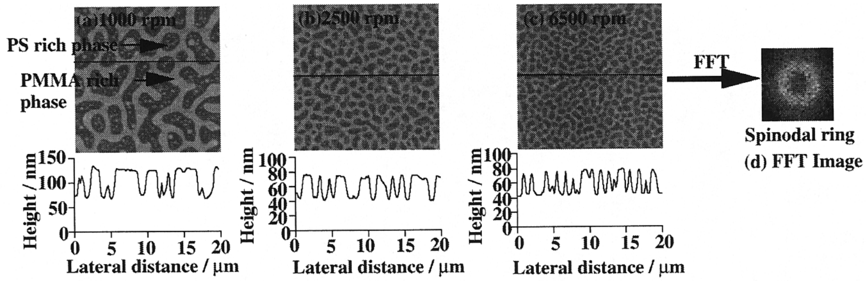


Fig.4: (a)-(c) AFM images and line profiles of the for (α,ω-PS$(NH_2)_2$/PMMA) (50/50)thin spin-coated at (a) 1000, (b) 2500 and (c) 6500 rpm and (d) FFT image.

at a PS fraction of 50wt%. The inverse sea-island-like and the sea-island-like phase-separated structures were formed in the case of the (α,ω-PS$(NH_2)_2$/PMMA) (30/70) and (70/30) thin films, respectively. Both AFM and XPS revealed that the surface PS composition increased with an increase in bulk PS composition. These results indicate that no preferential adsorption of the both components onto the hydrophilic silicon substrate occurred.

Fig. 4 (b)-(c) show the AFM images for the (α,ω-PS$(NH_2)_2$/PMMA) (50/50) thin films spin-coated at several spin speeds. The bicontinuous-like phase-separated structures were observed in all AFM images for the (α,ω-PS$(NH_2)_2$/PMMA) (50/50) thin films. The size of the phase separated domains decreased with an increase in spin rate. Fig. 4(d) shows the FFT image for the (α,ω-PS$(NH_2)_2$/PMMA) (50/50) thin film at 6500 rpm spin speed. A spinodal ring was observed in the FFT image. The presence of periodic structure suggests that the blend thin film was formed via spinodal decomposition during the solvent evaporation process. The phase-separated structure of the (α,ω-PS$(NH_2)_2$/PMMA) thin film was stable even after annealing above Tg for 25 hours. These results indicated that the phase separation of polymer blend thin film was greatly influenced by the preferential adsorption of one component to the substrate because the area ratio of air/polymer and polymer/substrate interfaces to the total volume of thin film is greater than that of the thick film.

The higher height regions for the (PS/PMMA) and (PS/PI) blend prepared by spin-coating methods are always higher surface energy component. Figure 5 schematically shows the formation mechanism of the height difference of binary immiscible polymer blend systems during the solvent evaporation process8). Polymer B with lower surface free energy tends to cover the air-polymer interfacial region in order to minimize the interfacial free energy. However, since the time required for the film formation is fairly short due to a very fast evaporation of the solvent and the limitation of the diffusion of the confined molecular chain,

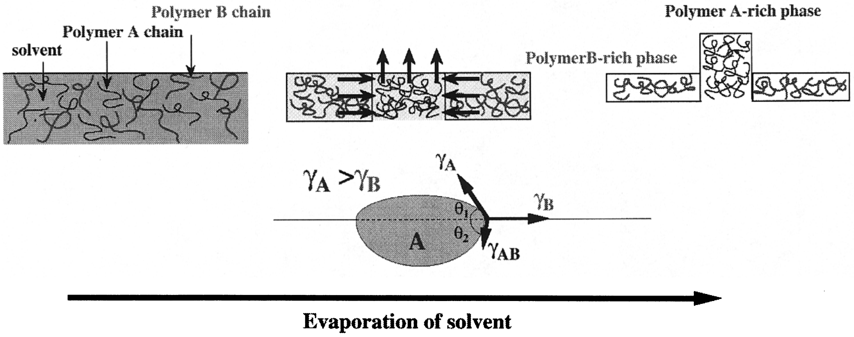


Fig.5: Schematic representation of the formation mechanism of the height difference of binary immiscible polymer blend systems.

the surface containing both polymer A and polymer B components with a little residual solvent was formed. After film was formed, a local rearrangement of the surface occurs due to the presence of the residual solvent. The higher height polymer A phase was formed owing to the large surface tension acting at the direction to the polymer A phase from the triphase boundary and the spreading of lower surface free energy polymer B component in order to minimize the interfacial free energy.

Conclusion

The phase-separated structures which are quite different from that for the bulk blend film was observed for the polymer blend thin films prepared from polymer solution. Atomic force microscopic(AFM) observation revealed the surface undulation which reflects the phase separated morphology of the blend system. In the case of (PS/PMMA) blend system, a large influence of end-group chemistry on the surface morphology was observed. The phase identification of the (rubbery/glassy) binary polymer blend thin films was successfully achieved by scanning vioscoelasticity microscopy(SVM).

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