Water-enhanced Adhesion at Interface in Immiscible Bilayer Film of Polystyrene and Poly(methyl methacrylate)

M Harada¹, T Koga¹, K Fukumori¹, J Sugiyama¹ and T Geue²
¹ Toyota Central R&D Labs., Inc., 41-1 Yokomichi, Nagakute, Aichi 480-1192, Japan
² Laboratory for Neutron Scattering, ETHZ & PSI, CH-5232 Villigen PSI, Switzerland
E-mail: harada@mosk.tytlabs.co.jp

Abstract. From nano-scratch tests, strong interfacial adhesion has been found for polystyrene (PS) and poly(methyl methacrylate) (PMMA) bilayer films prepared by a water floating (WF) method, while a PS layer on a PMMA film produced by a spin coating (SC) method peels off easily at the interface. Neutron reflectivity measurements demonstrated a clear difference in the interfacial width (\(\sigma\)) between the two bilayers; \(\sigma = 9\) nm for the film obtained by the WF method, whereas \(\sigma = 5\) nm for that by the SC method. Plasticization of the films by water would be responsible for broadening of the interface to enhance adhesion strength.

1. Introduction
Control of interfacial toughness between two kinds of polymers is one of the most important targets in research and development of coatings and blends. To understand the mechanical properties of the interfaces between polymers, the interfacial structure was investigated and the correlation between the width of the interfaces and the energy of adhesion was clarified for polymer bilayers [1, 2]. The origin of the interfacial strength was interpreted with an entanglement model of polymer chains that the interface energy is governed by the number density of the entanglement points per the interface area [3]. Therefore, the adhesion strength between polymer films increases by thickening of the mixed layer at the interface, and above a critical thickness cohesive failure could occur in the films.

The interfacial thickness of immiscible polymers for annealed bilayers are dominated by the Flory-Huggins interaction parameter and the Kuhn segment length. However, most of interfaces between polymers in practice are far from equilibrium. Here, we focus on the effect of coating process, where some small molecules mediate the formation of the interface. Bilayer films consisting of polystyrene (PS) and poly(methyl methacrylate) (PMMA) are employed, since the interface between PS and PMMA is well understood system in equilibrium [4].

For investigation of the interfacial width between immisible polymers, neutron reflectivity (NR) measurements have been a powerful tool. However, the samples must be thin films on very flat substrates. Although the energy of adhesion has been studied macroscopically by various experimental techniques, the mechanical properties for thin films can be analyzed by nano-scratch (NS) tests. By combining the NR measurements and the NS tests, structure and strength of interfaces are evaluated for the same bilayer films.
2. Experiments

Monodisperse polystyrene (PS) and poly(methyl methacrylate) (PMMA) with a number-average molecular weight of 115,000 and 105,000 were purchased from Polymer Source Inc. Note that a perdeuterated polymer is actually employed for PS to give enough contrast against PMMA when the polymer reflect neutrons. Silicon wafers with a 3-inch diameter were used as substrates for bilayer films.

Bilayer films were prepared by two kinds of processes. In each process, the bottom layers were commonly spin-casted from a 2 wt% toluene solution of PMMA onto a silicon wafer at 2000 rpm for 30 seconds and dried under vacuum at 120 °C for 24 hours. The thickness of the bottom films was evaluated to be around 60 nm from X-ray reflectivity measurements. The top layers were formed by a spin coating (SC) method or a water floating (WF) method, respectively. In the SC method, a PS film was spin-coated on the PMMA bottom layer from 2 wt% solution of a selective solvent for PS. We employed 1-chloropentane as a selective solvent, which is reported to dissolve PS but not to dissolve PMMA [5]. PS/PMMA bilayers with a clear interference color were obtained and dried under vacuum at room temperature for 24 hours. On the other hand, in the WF method, a floating PS film on a water surface was skinned off by the PMMA-coated silicon wafer from the water side. Here, the PMMA film was once dipped in water and swollen by uptaking water molecules [6]. The floating PS film was provided by peeling off a spin-cast PS film from a Si wafer on a water surface. After water at the PS/PMMA interface was evaporated, the bilayers were kept in a vacuum chamber at room temperature overnight. Since room temperature is far below glass transition temperature of PS (100 °C) and PMMA (110 °C), we expect that the interface of the bilayers does not reach to its equilibrium structure. In each coating process, two bilayer samples were prepared to estimate errors.

Nanoscratch tests were performed by TI 900 TriboIndenter™ (Hysitron Inc.). We used a cono-spherical diamond probe with an included angle of 60° and a radius of 1 µm. The bilayer samples were scratched in a constant slope and a speed with the probe held perpendicular to the samples. The probe was typically moved 100 nm vertically and 10,000 nm horizontally in 30 seconds (333 nm/s in speed). Normal force working on the probe was measured, while monitoring the probe position controlled by a feed-back circuit. The measurements were carried out twice for one sample at different positions.

Neutron reflectivity measurements were performed on AMOR reflectometer at SINQ facility of Paul Scherrer Institut in Switzerland [7]. Pulsed neutrons reflected specularly by the bilayer samples were counted in a time-of-flight mode. Neutron reflectivity spectra were analyzed by Motofit package to obtain cross-section profiles of scattering length density ($\rho_{SL}$) [8]. A bilayer model on a silicon substrate was employed for the fitting of the spectra. In the fitting, the parameters, such as $\rho_{SL}$ and thickness ($t$) of the two layers and the roughness ($\sigma$) of the three interfaces, were optimized to minimize the chi squared, while the $\rho_{SL}$ values of the air and the substrate were fixed.

3. Results and discussion

3.1. Nanoscratch tests

The results of the nanoscratch tests for the bilayers prepared by the SC method and the WF method are shown in figure 1. The top view of the AFM image presents a groove on the bilayers generated by the nanoscratch probe. The width of the groove has increased as the probe penetrates into the bilayer. The two normal force curves measured at different points are almost identical for each samples. The strength of the normal force has risen, as the probe goes down from the surface and the contact area between the probe and the bilayers expands.

The increase of the normal forces for the bilayer prepared by the SC method is smooth until the probe reaches to 50 nm and the normal force drops at 60 and 70 nm, as shown in figure 1(a). Since the decrease of the normal force could happen when the contact area shrinks, the...
drops should be attributed to the fracture of the film. On the other hand, as shown in figure 1(b), the normal force curve of the WF method presents a stick-slip motion from 50 nm to 90 nm. The stick-slip motion could be induced by inhomogeneity in the film on a nanoscale, which may be generated in the preparing process of the bilayer by the WF method.

Since the fracture of the film should be followed by the peel-off at the interface, the adhesion energy of the bilayer by the SC method is low. Meanwhile, the interface layer of the bilayer by the WF method could be thick enough to have a similar mechanical property as the bulk of the polymer.

3.2. Neutron reflectivity measurements
Neutron reflectivity spectra and scattering length density profiles of the bilayers prepared by the two kinds of procedures are shown in figure 2. The spectra are displayed using the scattering vector \( q = (4\pi/\lambda) \sin \theta \), where \( \lambda \) and \( \theta \) are the wavelength and the incident angle of the neutrons. The profiles inserted on the upper right of the spectra are the cross-section profiles of \( \rho_{SL} \) from the surface to the substrate of the bilayers. Figure 2(a) and figure 2(b) represent the results of the SC method and the WF method, respectively. The results obtained for separately prepared bilayers with the same method are overlaid in the neutron reflectivity spectra. Since no distinct differences are observed for the spectra, the cross-section profiles showed little change as well.

The both spectra show interference fringes, whose amplitude damps down with an increase of \( q \). The number of fringes in figure 2(b) is smaller than that in figure 2(a), corresponding to a broader interface in the bilayer of the WF method. From the cross-section profiles, the thickness of the each layer and the position of the interface have been clarified. The thickness of the bottom PMMA layer was consistent with the evaluation by the X-ray reflectivity measurements.

The difference in the interfacial structures of the bilayer films are presented in the cross-section profiles of figure 2. The top layer with a high \( \rho_{SL} \) value and the bottom layer with a low \( \rho_{SL} \) value are observed between the air (\( \rho_{SL} = 0 \)) and the substrate (\( \rho_{SL} = 2.07 \)). The observed two \( \rho_{SL} \) values are identical with the calculated values of PS and PMMA. The transition region between the two layers is the interface layer, which should not be ideally sharp but has a width including roughness and mixing. After fitting with a hyperbolic tangent function, the thickness of the interface \( \sigma \) was evaluated as \( \sigma = 5 \) nm for the bilayer obtained by the SC method, whereas \( \sigma = 9 \) nm for that by the WF method.

![AFM images after nanoscratch test and normal force curves for nanoscratch test of bilayers prepared by (a) spin coating method and (b) water floating method.](image)

**Figure 1.** AFM images after nanoscratch test and normal force curves for nanoscratch test of bilayers prepared by (a) spin coating method and (b) water floating method.
3.3. Strength and thickness of interfaces

The interfacial width $\sigma$ between a strong segregation pair of PS and PMMA is around 5 nm in equilibrium. Since the interface of the bilayer prepared by the SC method is same in thickness, the peel-off behavior observed for the PS film on the PMMA is reasonable. When a bilayer is prepared by the WF method, a thicker interface, generated by increase in the roughness and the mixing, has enhanced the strength of adhesion. Thus, the normal force curve indicates that the mechanical property of the bilayer could be similar to that of a PS film. A comprehensive understanding has not given for the factors to determine the interfacial thickness in various kinds of selective solvents or coating processes. However, we believe that water uptake in the bottom PMMA layer would be responsible for the broadening on the interface.

4. Conclusion

Two kinds of polymer bilayers of PS and PMMA were prepared by the spin coating method and the water floating method. The strength of the interface was enhanced by the water floating method, while the spin-coated PS layer is not adhesive to the PMMA layer. Although the interfacial structure of the spin-coating bilayer was similar to that of the bilayers in equilibrium, the broadening at the interface was observed for the PS/PMMA bilayer produced by the water floating method. Water should have worked as a plasticizer in the coating process, which may be associated with stickers.

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