Confinement-induced Miscibility of Different PS-PMMA with Phenoxy Resin at the Air/Water Interface

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Abstract: The miscibility of the mixed monolayer behavior of different polystyrene-poly(methyl methacrylate) (PS-b-PMMA; PS-co-PMMA; PS-r-PMMA) with phenoxy resin(Phr) was studied from the measurements of surface pressure-area per molecule (π-A) isotherms using the Wilhelmy plate method with a KSV model mini-trough at three different temperatures (10℃, 25℃ and 40℃). The miscibility and non-ideality of the mixed monolayers were examined by calculating the excess surface area as a function of composition. The analysis of surface pressure-area per molecule (π-A) isotherms and excess area showed that mixed monolayers exhibit intermolecular interaction. When the pressure increases, the deviation can change from positive to negative. The mixed PS-b-PMMA monolayers exhibited mostly negative excess area among three studied PS-PMMA. The results of the mixed PS-co-PMMA monolayers were similar to those of mixed PS-r-PMMA likely because of close chain arrangements. Phr was found to be in the majority miscible with PS-PMMA at the air/water interface likely because of hydrogen bonding between Phr and PS-PMMA and confinement inducement.

Keywords: PS-PMMA, Phenoxy resin, Monolayer.

1. INTRODUCTION

Polymer blends in the thin film states are of special interest for both fundamental studies and practical applications. There are lots of studies of mixed polymer monolayers spread at the air/water surface [1-4]. In particular, Gabrielli *et al*. [5-8] have made a significant contribution to the investigation of various mixed polymer films in obtaining information regarding the aspect of their miscibility in the two-dimensional state. One of their vital conclusions is that the miscibility of mixed polymers spread at the air/water interface strongly depends on the interfacial orientation of the polymer chains, such as a predominantly horizontal orientation, with the hydrophobic chains parallel to the interface, and a predominantly vertical orientation, with the hydrophobic chains perpendicular to the interface. The components that show miscibility have the same interfacial orientation, and the immiscible ones have a different orientation. However, the work of Kawaguchi and Nishida [2] seems to demonstrate that the thermodynamic interaction between the two polymers plays an important role besides orientational conditions.

In general, the miscibility of the mixed polymer monolayers is determined from the plot of the mean areas at a constant surface pressure as a function of composition of one component in the binary mixture. If the plot obeys a linear relationship, *i.e.* the surface areas are additive, the mixed films can be regarded as an ideal mixture or as a completely immiscible mixture. The deviation from the linear relation stems from the contribution of intermolecular interaction between two components. A negative deviation means that the mixtures are considered to be stable and miscible, whereas a positive deviation indicates that the mixtures are less stable than components alone at the interface.

On the other hand, determining the miscibility of two polymers in the bulk state (polymer blends) is one of the central problems in polymer science and engineering. Few pairs of polymers were found to be miscible [9]. Not all polymers form stable films at the air/water interface, therefore it is not easy to determine good pairs to compare the miscibility in the bulk state with that in a film spread at the air/water interface.

The poly(styrene-b methyl methacrylate) (PS-b-PMMA) was reported by this laboratory [10]. In that article, PMAs(PMMA, PEMA, PPMA and PBMA) are predicted by the mean field theory to be immiscible with poly(styrene-b-methyl methacrylate) (PS-b-PMMA) in the bulk state. However, the miscibility of PMAs with PS-b-PMMA may be different in the two dimensional state. Therefore the mixed monolayer behavior of PMAs and PS-b-PMMA was investigated from the measurements of surface pressure-area per molecule (π-A) isotherms at three different temperatures (10℃, 25℃ and 40℃). Calculation of compressibility from isotherms provided the inflection data from maximum and minimum peaks. The miscibility and non-ideality of the mixed monolayers were examined by calculating

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the excess area as a function of composition. Mostly negative deviations from ideality were observed in the mixed monolayers. This is likely because of favorable interaction between PMMA and PMAs in the monolayer state. The positive deviations occurred at 40℃ with PBMA at a high surface pressure. Therefore with confinement in the two dimensional state, the miscibility between PMAs and PS-b-PMMA was greatly improved in comparison with the bulk state.

To the best of our knowledge, there is no report on the mixed monolayer behavior of different PS-PMMA/Phenoxy resin. Phr was found to be miscible with PMMA and not miscible with PS. PS and PMMA are known to be immiscible. Phr was predicted to be immiscible with PS-PMMA in the bulk state based on the mean field theory. There are three kinds of PS-PMMA used in this study, PS-b-PMMA, PS-co-PMMA and PS-r-PMMA. The carbonyl groups of PMMA can form hydrogen bonds with OH groups of Phenoxy resins. This can be the driving force to make the mixed monolayers miscible at the air/water interface. The surface pressure-area per molecule(π-A) isotherms of the prepared mixed films was measured. On the basis of the results of π-A isotherms, miscibility was investigated. The effects of copolymer chain arrangement, temperature and Phenoxy composition on the mixed monolayer was expounded and reported in detail in this report.

2. EXPERIMENTAL

2.1. Materials

Phenoxy resin (abbreviated as Phr) was purchased from Scientific Polymer Products, Inc., with a molecular weight (M_w) of 50,000 g/mol. The molecular weight (M_n) of PS-b-PMMA obtained from Polymer Source, Inc., is about 10,000 g/mol for each block. PS-co-PMMA had a M_w = 100,000-150,000 g/mol with a 40 mol% of styrene supplied by Aldrich Chemical Company, Inc. PS-r-PMMA with a 50 mol% of styrene from Polymer Source, Inc. had a M_w = 16,100 g/mol. and M_n = 11,500 g/mol.

Chloroform purchased from Tedia Company Inc. or 2-butanone from Seed Chemical Inc. was used as the spreading solvent for the polymer films. Phenoxy resin was dissolved in chloroform. The 2-butanone solvent was chosen to co-dissolve PS-PMMA /Phr in three different weight (3/1. 1/1,1/3) ratios. PS-PMMA solution was also prepared using 2-butanone. Only highly pure water, which was purified by means of a Milli-Q plus water purification system, with a resistivity of 18.2 MΩ-cm was used in all experiments. Blank experiments using the spreading solvent were carried out that there were no surface-active impurities.

2.2. Surface Pressure Measurements

A model minitrough (M 1200) was purchased from KSV Instruments Ltd., Finland. The Teflon trough was 320 mm long and 75 mm wide. Regulation of the trough temperature was controlled by circulating constant temperature water. The trough was placed on an isolated vibration-free table and was enclosed in a glass chamber to avoid contaminants from the air. One of the important characteristics of the trough system is that two barriers confining a monolayer at the interface are driven symmetrically during the compression of the monolayer. The surface pressure was measured by the Wilhelmy plate method. The resolution for surface measurement is 0.004 mN/m, and the inaccuracy of surface area regulation is less than 1%, according to the specifications of the instruments. A surface pressure-area per molecule (π-A) isotherm was obtained by a continuous compression of a monolayer at the interface by two barriers.

For starting the experiment, the freshly cleaned trough was placed into position in the apparatus first, then it was filled with purified water as the subphase with temperatures controlled at 10±0.5℃, 25±0.5℃ and 40±0.5℃. The clean platinum plate was hanged in the appropriate position for surface pressure measurements. The surface pressure fluctuation was estimated to be less than 0.2 mN/m during the compression. Then, the two barriers were moved back to their initial positions. The sample concentration of solution of polymer and solvent was set at 0.5 mg/mL. A 50 μL sample containing monolayer-forming polymeric materials was spread on the subphase by using a Hamilton microsyringe to make the deposition of polymer molecules at almost the same condition. At least 40 min was allowed for evaporation of the spreading solvent. After evaporation, the monolayer was compressed continuously at a rate of 3.5 mm/min to obtain a single π-A isotherm. The π-A isotherms of our studied polymers are dependent on the compression rate therefore the results were performed at the same compression speed.

3. RESULTS AND DISCUSSION

3.1. π-A isotherms of Polymers at Three Different Temperatures

Figures **1-4** illustrate the π-A isotherms of polymers at 10℃, 25℃ and 40℃ in the order of Phr, PS-b-

PMMA, PS-co-PMMA and PS-r-PMMA, respectively. For Phr in Figure **1**, the surface areas decrease with the elevation of temperature likely because of dominant enthalpic contribution. The collapse pressure of Phr was observed to decrease with increasing temperature. For PS-b-PMMA in Figure **2**, the π-A isotherms at 10℃, 25℃ 40℃ were shifted to the left slightly and demonstrated also enthalpic contribution. The π-A isotherms of PS-co-PMMA in Figure **3** behaved similar to those in Figure **2**. Except the difference between the isotherm at 25℃ and 40℃ is much smaller. The surface areas of PS-r-PMMA in Figure **4** decrease mostly with increasing temperature probably because of enthalpic contribution. The collapse pressure of the three copolymers was observed to decrease mostly with increasing temperature.

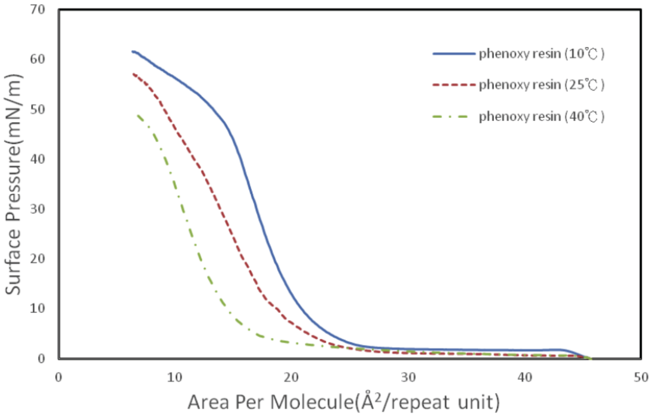


Figure 1: π-A isotherms of Phr.

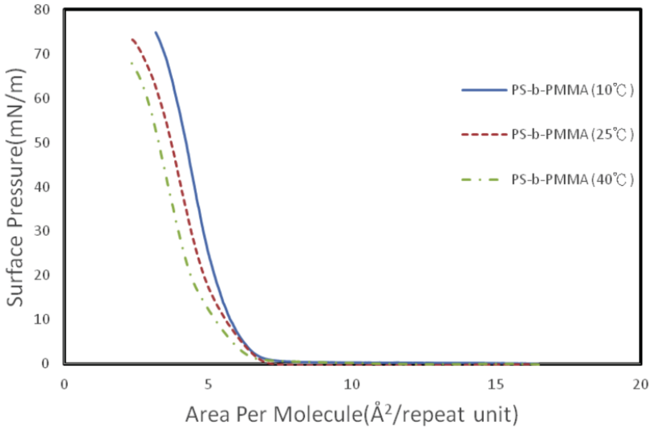


Figure 2: π-A isotherms of PS-b-PMMA.

Monolayer characteristics were calculated from Figures **1-4** and tabulated in Table **1**. The solid limiting area of Phr is greatest likely because of biggest repeating unit. The lift-off areas of Phr, PS-b-PMMA, PS-co-PMMA and PS-r-PMMA were estimated to be almost temperature independent. The lift-off areas of PS-co-PMMA and PS-r-PMMA were nearly the same because of similarity in structure. The solid limiting areas of the three copolymers are nearly temperature independent. The collapse pressures of the three copolymers are higher than Phr likely due to amphiphilic nature.

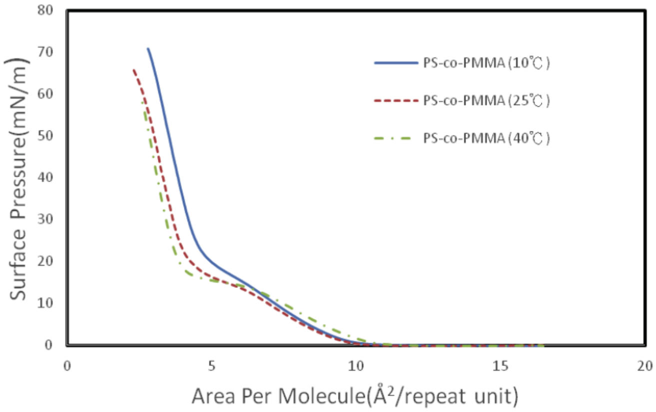


Figure 3: π-A isotherms of PS-co-PMMA.

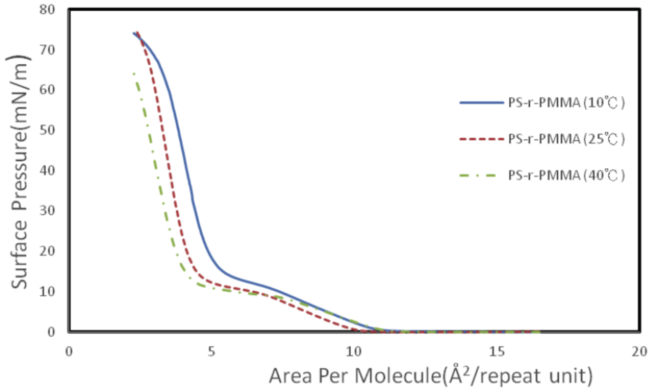


Figure 4: π-A isotherms of PS-r-PMMA.

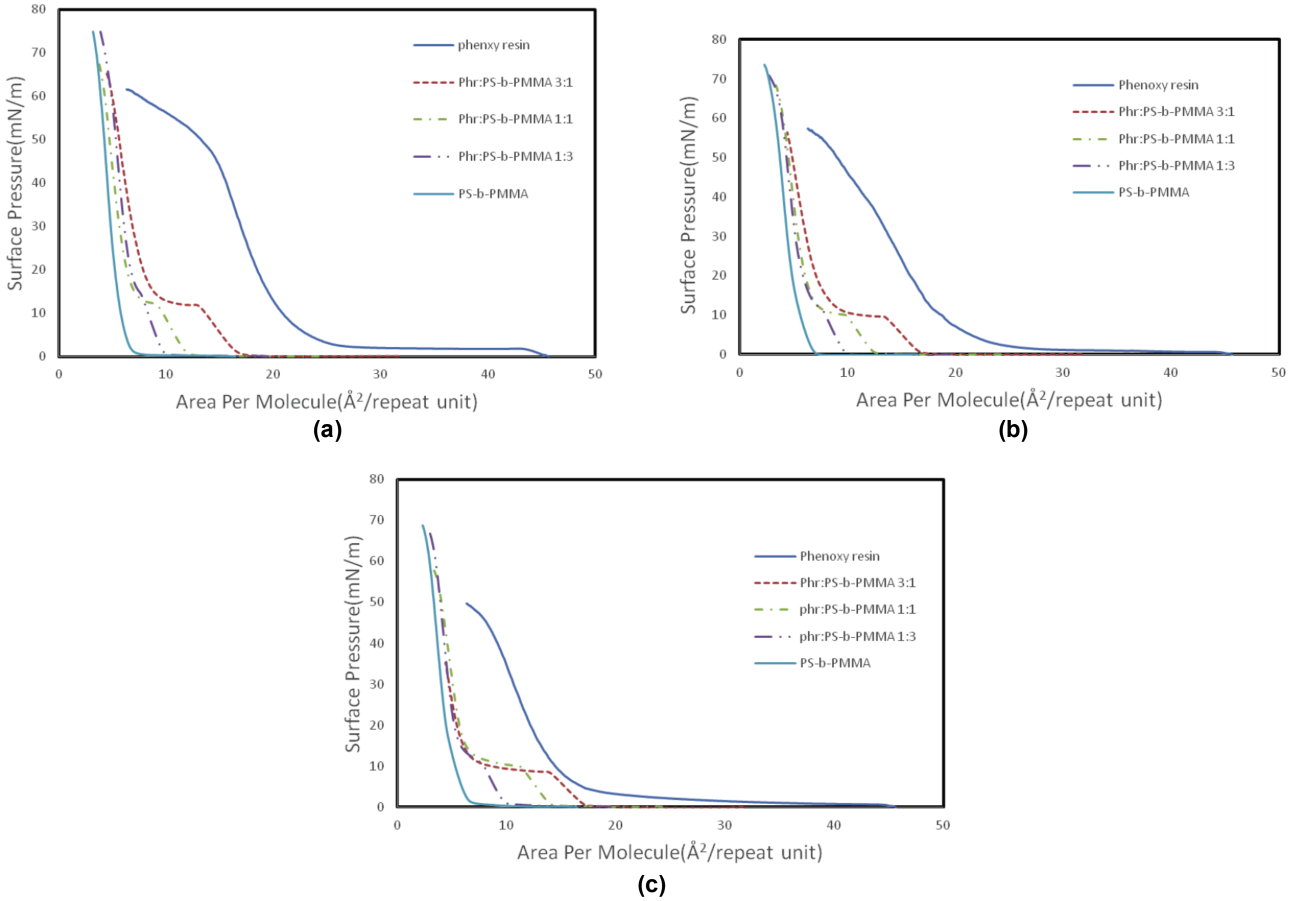
3.2. π-A Isotherms of Mixed Monolayers at Three Different Temperatures

The π-A isotherms of mixed Phr/PS-b-PMMA monolayers at 10℃, 25℃ and 40℃ are shown in the order of Figure **5**(**a**), Figure **5**(**b**) and Figure **5**(**c**), respectively. The π-A isotherms of the mixed monolayers increase mostly with increasing Phr composition.

The π-A isotherms of mixed Phr/PS-co-PMMA monolayers at 10℃, 25℃ and 40℃ are plotted in the order of Figure **6**(**a**), Figure **6**(**b**) and Figure **6**(**c**), respectively. The π-A isotherms of the mixed monolayers increase mostly with increasing Phr composition. The cross-over phenomenon was

Table 1: Characteristics of π-A Isotherms of Polymers

	Lift-off Point (Å^2/repeat unit)	Inflection Point (mN/m)	Limiting Area (Å^2/repeat unit)	π Collapse (mN/m)
Phenoxy resin				
10℃	45.6	2.2	21.2	61.5
25℃	45.6	2.1	19.9	57.2
40℃	45.6	2.8	15.1	49.7
PS-b-PMMA				
10℃	7.0	---	5.8	74.9
25℃	7.2	---	5.6	73.7
40℃	6.7	---	5.1	68.7
PS-co-PMMA				
10℃	11.2	18.3	5.2	74.8
25℃	10.7	15.6	4.6	66.3
40℃	11.8	15.8	4.3	59.6
PS-r-PMMA				
10℃	11.6	12.5	5.3	74.2
25℃	10.7	10.3	4.5	74.8
40℃	11.4	9.7	4.2	64.1



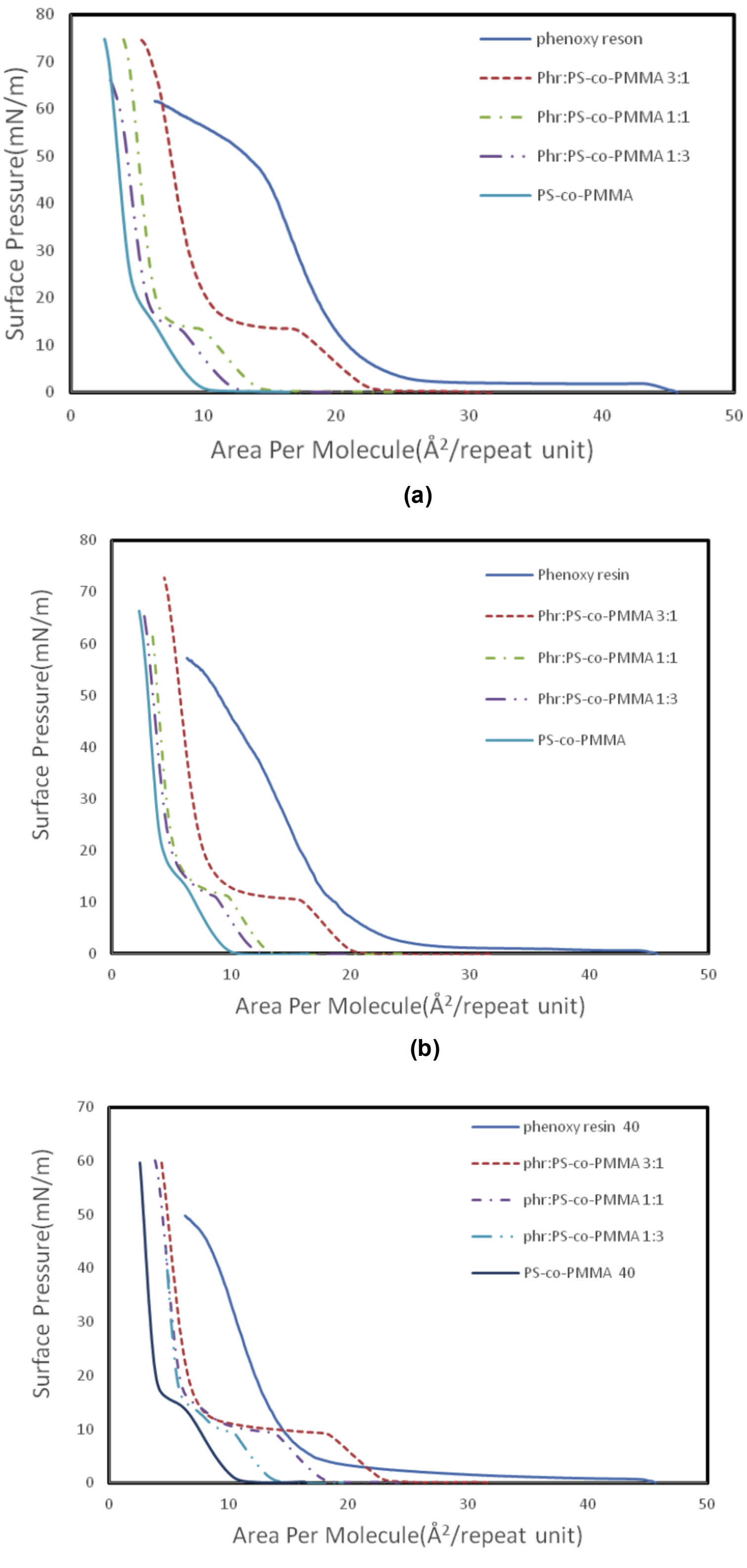
(a) **(b)**

(c)

Figure 5: π-A isotherms of PS-b-PMMA/Phr at (**a**) 10℃ (**b**) 25℃ (**c**) 40℃.

observed at the highest Phr composition at 40℃ in Figure **6**(**c**).

The π-A isotherms of mixed Phr/PS-r-PMMA monolayers at 10℃, 25℃ and 40℃ are plotted in the



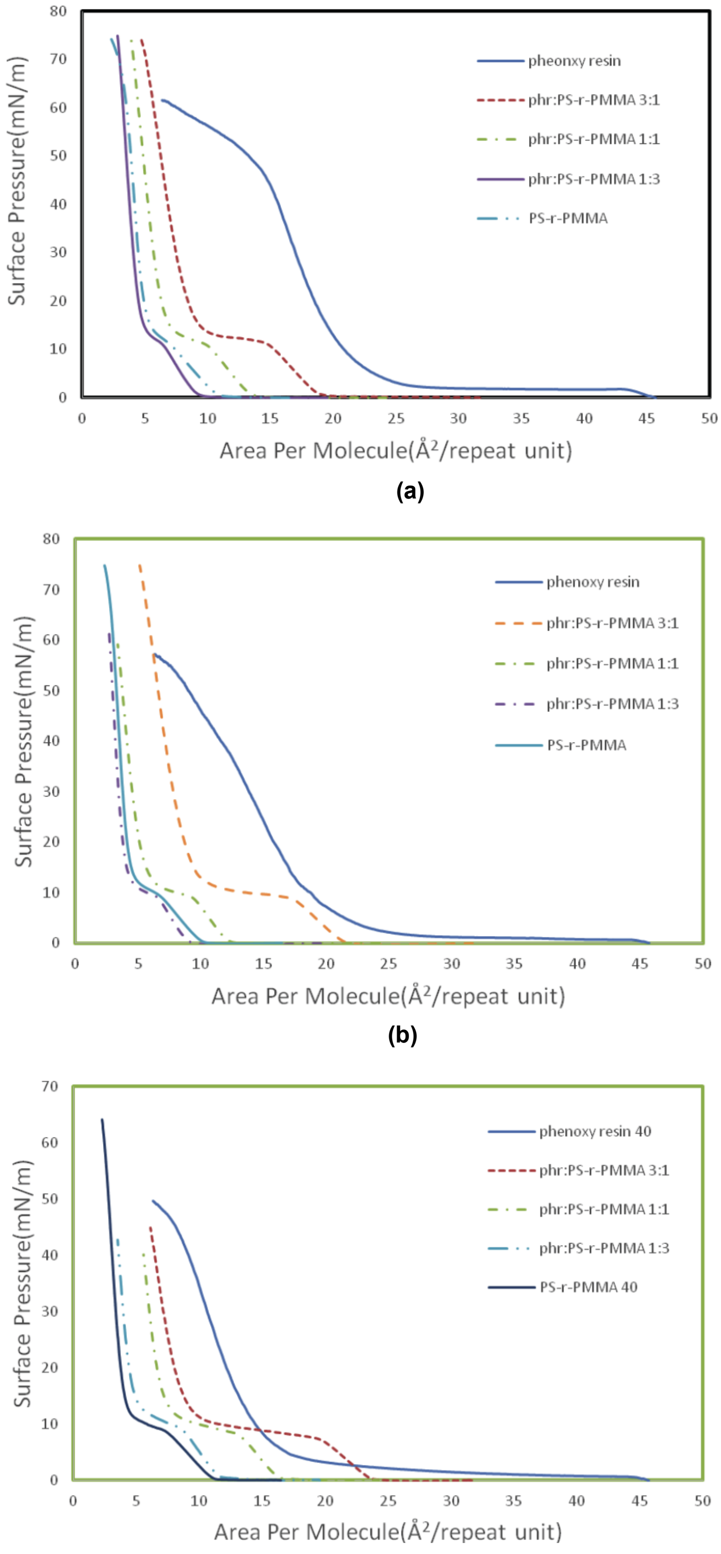
(a)

(b)

(c)

Figure 6: π-A isotherms of PS-co-PMMA/Phr at (**a**) 10℃ (**b**) 25℃ (**c**) 40℃.

order of Figure **7**(**a**), Figure **7**(**b**) and Figure **7**(**c**), respectively. The π-A isotherms of the mixed monolayers increase mostly with increasing Phr composition. A similar cross-over phenomenon was also observed at the highest Phr composition at 40℃ in Figure **7**(**c**).



(a)

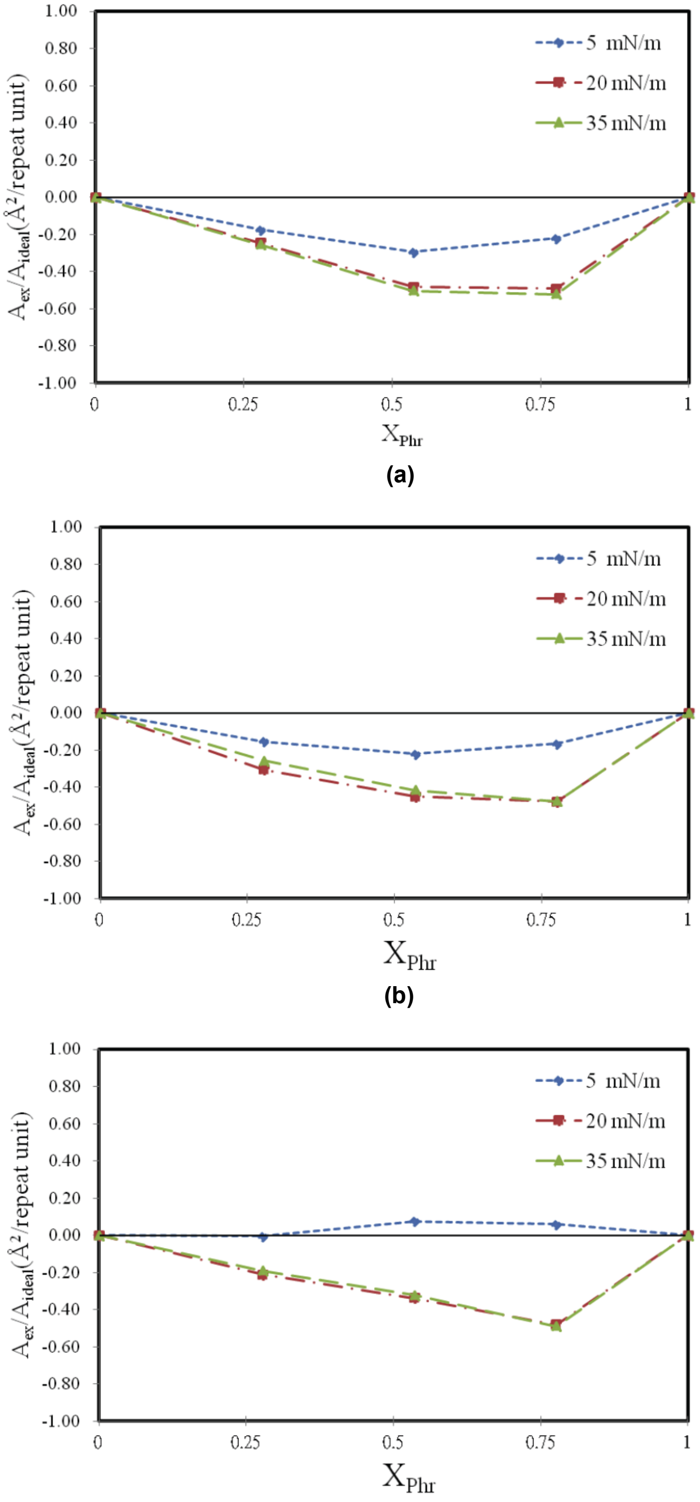
(b)

(c)

Figure 7: π-A isotherms of PS-r-PMMA/Phr at (**a**) 10℃ (**b**) 25℃ (**c**) 40℃.

3.3. The Excess Areas of Mixed Monolayers at Three Different Temperatures

A study of Monroy *et al*. [11] on monolayers of hydrogen-bonded polymer blends indicated that the calculation of the excess Gibbs energy provides a similar result as the excess area. Therefore in this study only the excess areas were calculated. At a given surface pressure, the excess area is defined as the



(a)

(b)

(c)

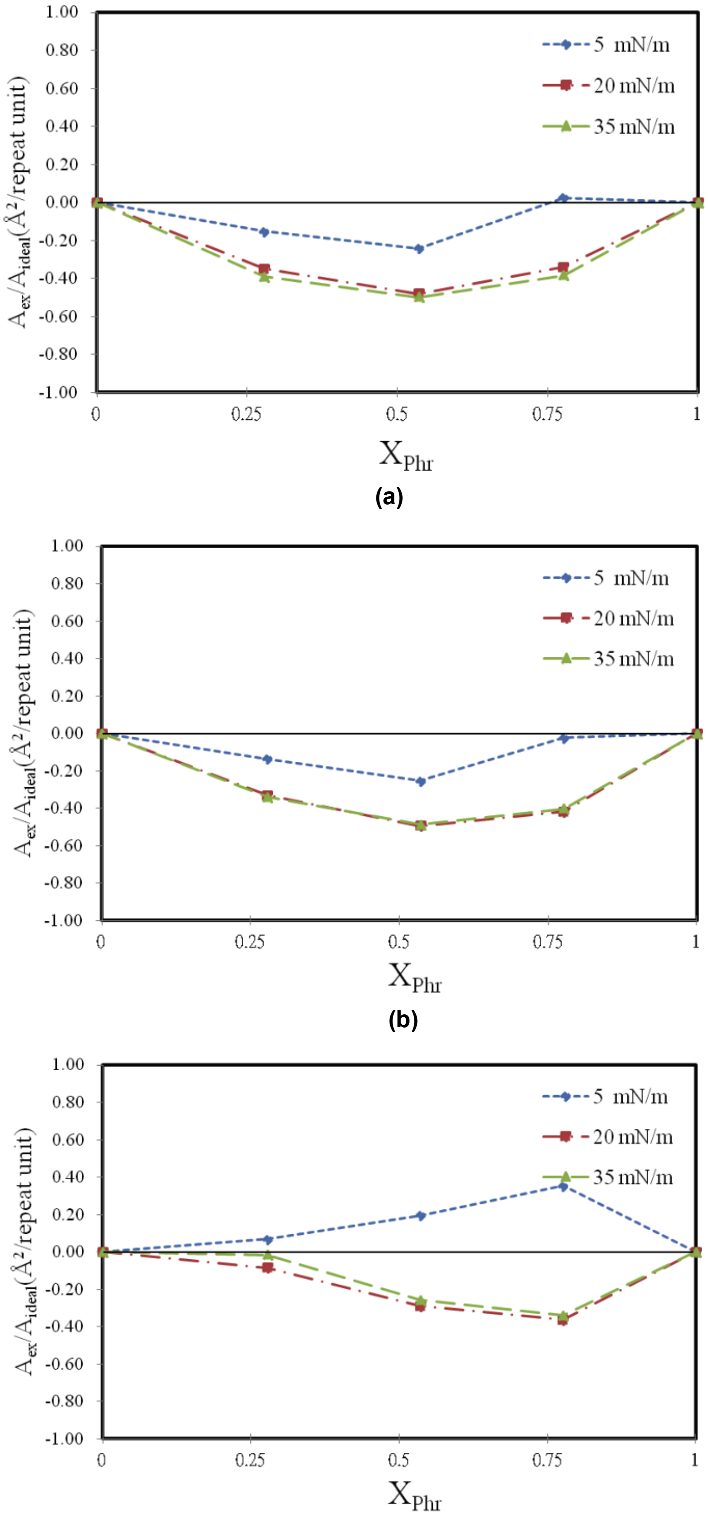
Figure 8: Excess areas of mixed PS-b-PMMA/Phr at (**a**) 10℃ (**b**) 25℃ (**c**) 40℃.

difference between the average area per molecule of a mixed monolayer consisting of components 1 and 2 and that of an ideal mixed monolayer [1].

$$A_{ex} = A_{12} - A_{ideal} = A_{12} - (X_1A_1 + X_2A_2) \quad (1)$$

where A_{12} and A_{ideal} are the mean and ideal areas per molecule of the mixed monolayer at a given surface pressure, respectively, X_1 and X_2 imply the mole fractions of components 1 and 2, respectively, and A_1 and A_2 are the areas per molecule of each pure monolayer at the same surface pressure. Based on eq.(1), the A_{ex} values of mixed monolayers can be estimated from the data shown in Figures **5**(**a**)-**5**(**c**), **6**(**a**)-**6**(**c**) and **7**(**a**)-**7**(**c**), individually.

In Figures **8**(**a**)-(**c**), **9**(**a**)-(**c**) and **10**(**a**)-(**c**) the normalized quantities, A_{ex}/A_{ideal} are shown as a function of Phr mole fraction at 10℃, 25℃ and 40℃, respectively. For Figure **8** the A_{ex}/A_{ideal} values of the mixed Phr/PS-b-PMMA monolayers are mostly negative at three temperatures. Positive excess area deviations were detected at a surface pressure of 5 mN/m and 40℃ to show unfavorable interaction



(a)

(b)

(c)

Figure 9: Excess areas of mixed PS-co-PMMA/Phr at (**a**) 10℃ (**b**) 25℃ (**c**)40℃.

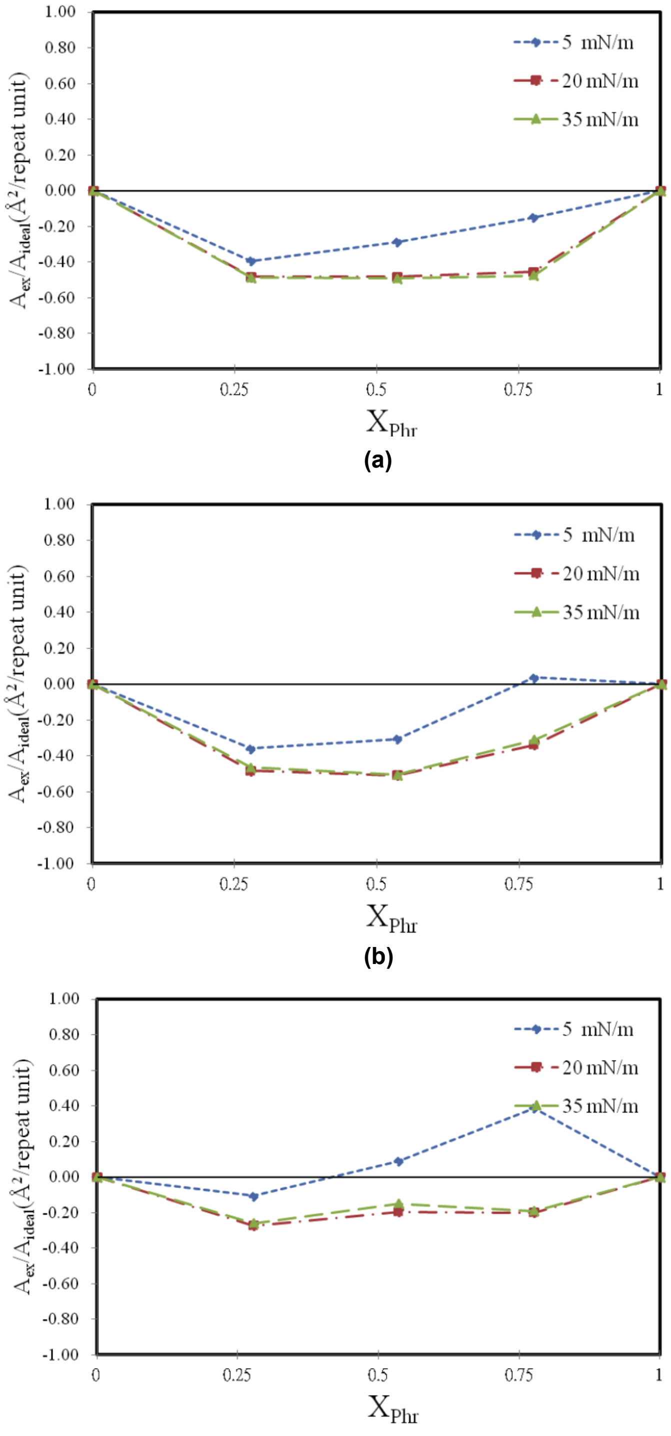


Figure 10: Excess areas of mixed PS-r-PMMA/Phr at (**a**) 10℃ (**b**) 25℃ (**c**)40℃.

between Phr and PS-b-PMMA. Surface pressure increase in the majority causes a more negative excess area. The A_{ex}/A_{ideal} values of the mixed Phr/PS-co-PMMA monolayers in Figure **9** are in the majority negative at three temperatures. Positive excess surface areas were estimated at a surface pressure of 5 mN/m and 40℃. Especially at the highest Phr composition also indicating unfavorable interaction between Phr and PS-co-PMMA. The A_{ex}/A_{ideal} values of the mixed Phr/PS-r-PMMA monolayers are shown in Figure **10**. The excess surface areas of Phr/PS-r-PMMA are similar to those of Phr/PS-co-PMMA at the same temperatures. A slight difference is that a partially negative surface area was observed in the high PVPh composition at a surface pressure of 5 mN/m and 40℃ in Figure **10**(**c**).

On the basis of the excess surface areas estimation of the mixed Phr/PS-PMMA monolayers, Phr was found to be in the majority miscible with PS-PMMA at the air/water interface. The reason was likely hydrogen bonding between Phr and PS-PMMA and confinement inducement.

4. CONCLUSIONS

Miscibility deduced from the π-A isotherms of the mixed Phr/PS-PMMA monolayers are quite different from that in the bulk state. Phr was found to be miscible with PMMA and not miscible with PS. PS and PMMA are known to be immiscible. Phr was predicted to be immiscible with PS-PMMA in the bulk state based on the mean field theory. However, on the basis of the excess surface areas estimation of the mixed Phr/PS-PMMA monolayers, Phr was found to be in the majority miscible with PS-PMMA at the air/water interface likely because of hydrogen bonding between Phr and PS-PMMA and confinement inducement.

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