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Miscibility of PEO-b-PCL and its Component Polymers with PVPh at the Air/Water Interface

Hui-Ting Pan and Wen-Ping Hsu*

Department of Chemical Engineering, National United University, Miao-Li, Taiwan 360, R.O.C

Abstract: The mixed monolayer behavior of polyethylene-block-polycaprolactone (PEO-b-PCL) and its component polymers (PEO or PCL) with poly(vinyl phenol)(PVPh) was investigated from the measurements of surface pressure-area per molecule (π-A) isotherms at three different temperatures(10℃, 25℃ and 40℃). The miscibility and nonideality of the mixed monolayers were examined by calculating the excess surface area as a function of composition.

Interestingly, PEO and PCL were shown to have different interactions with PVPh at the air/water interface from in the bulk state on the solid substrate. PE O demonstrated mostly positive excess surface area with PVPh. Negative excess surface areas were in the majority observed in the PCL/PVPh monolayers. A scheme of differences in interaction sites between PEO (or PCL) and PVPh at the air/water interface was proposed to explain the negative or positive deviations of surface areas successfully.

Keywords: Miscibility, PEO-b-PCL, PVPh.

1. INTRODUCTION

Polymer blends in the thin film states are of particular interest for both fundamental studies and practical applications. 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 component composition 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 or 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 one indicates that the mixtures are less stable than components alone.

Recently, Okumura [1] published an article of surface pressure–area isotherms and surface dilational moduli of poly(N-isopropyl acrylamide) monolayers spread at air–water interface. The surface pressure–area isotherms and surface dilational moduli of poly (N-isopropyl acrylamide) (PNI-PAM) monolayers spread at the air–water interface were measured during the compression–expansion cycles as a function of surface pressure and frequency at a fixed strain of 10%. The isotherms of the monolayers clearly showed a negative hysteresis, *i.e*., the decrease in the surface pressure increased with increasing number of cycles. However, the isotherm of an expansion process was in good agreement with that of the following compression process. Therefore, the Lissajous orbits of the monolayers exhibited a negative hysteresis loop with the repeating cycles, and then, the corresponding surface dilational moduli were determined from the first loop of Lissajous orbits. The resulting surface moduli were much larger than those of poly (ethylene oxide) and poly (vinyl acetate) monolayers, while their magnitudes were the same as those of poly (methyl methacrylate) monolayer. Such larger surface moduli may be attributed to the chain entanglements of loops and trains of spread PNIPAM chains in the monolayers The stereocomplex formation between isotactic and syndiotactic poly(methyl methacrylate) in a Langmuir monolayer investigated by surface pressure-area isotherms and atomic force microscopy(AFM) was reported by Aiba *et al*. [2] . Their results indicated that the stereocomplex formation was highly sensitive to the compression rate of the monolayer. Other current references include the molecularly detailed modeling of surface pressure isotherms of poly-L-lactic acid, poly(dimethylsiloxane), PMMA and poly(isobutylene) [3] at the air/water interface.

Monolayers of poly(vinyl phenol)(PVPh) at 25℃ were reported previously [4] by this laboratory. The mixed monolayer behavior of stereoregualr PMMA and PVPh was investigated from the measurements of surface pressure-area per molecule(π-A) isotherms. The miscibility and non-ideality of the mixed monolayers were examined by calculating the excess area as a function of composition, and negative deviations from ideality were observed, which suggest the existence of attractive interactions between iPMMA and PVPh. However, the π–A isotherms of mixed syndiotactic

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*Address correspondence to this author at the Department of Chemical Engineering, National United University, Miao-Li, Taiwan 360, R.O.C; Tel: +886-37-382213; Fax: +886-37-382223; E-mail: mjkr.hsu@msa.hinet.net

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PMMA (sPMMA)/PVPh monolayers showed positive deviation from ideality, which might suggest that non-favorable interactions exist between sPMMA and PVPh.

Surface pressure measurements of binary mixtures containing poly(ethylene oxide)(PEO) were performed by Kawaguchi *et al*. [5]. PEO with a molecular weight M_w = 180,000 g/mol was shown to exhibit an expanded structure. Low molecular weight PEO cannot exist as a stable film at the air/water interface because of its strong hydrophilicity. Surface pressure-induced crystallization of poly (ε-caprolactone) from a metastable region of the surface pressure-area per monomer (π–A) isotherms in Langmuir monolayer at the air/water interface has been captured in real time by Brewster angle microscopy(BAM) [6]. A kink or a dynamic "collapse" point at around 11.3 mN/m was observed in PCL corresponding to the transport of polymer chains from the monolayer to crystal lamellae.

PEO and PCL are known to be miscible with PVPh in the bulk state because of hydrogen bonding. Microphase separation of PEO-b-PCL/PVPh was investigated by Guo *et al*. [7]. The TEM and SAXS results show that the cubic PEO-b-PCL diblock copolymer changes into ordered hexagonal cylindrical morphology upon addition of 20 wt% PVPh followed by disordered bicontinuous phase in the blend with 40 wt% PVPh and then to homogeneous phase at 60 wt% PVPh and above blends. Up to 40 wt% PVPh there is only weak interaction between PVPh and PCL due to the selective hydrogen bonding between PVPh and PEO. However, with higher PVPh concentration, the blends become homogeneous since a sufficient amount of PVPh is available to form hydrogen bonds with both PEO and PCL.

To the best of our knowledge, there is no report on the mixed monolayer behavior of PEO-b-PCL/PVPh. The miscibility of PVPh and PEO-b-PCL in the two dimensional state (air/water interface) is probably different from the bulk state. The PEO group is hydrophilic likely penetrates more into water. The PCL group is in the majority hydrophobic probably stays more in the air. The PVPh group is also mostly hydrophobic. Therefore in this article, mixed monolayers of PEO-b-PCL and its component polymers(PEO or PCL) with PVPh were investigated at the air/water interface. The surface pressure-area per molecule(π-A) isotherms of the prepared binary films was measured. On the basis of the results of π-A isotherms, miscibility was investigated. The effects of structure, temperature and PVPh composition on the mixed monolayer was expounded and reported in detail in this report. Interestingly, PEO and PCL were shown to behave differently with PVPh at the air/water interface from in the bulk state. The interaction between PCL and PVPh (mostly hydrophobic) was found to be stronger than the interaction between PEO and PVPh.

2. EXPERIMENTAL

2.1. Materials

The molecular weight (M_n) of PEO-b-PCL obtained from Polymer Source, Inc., Montreal, Canada is about 5,000 g/mol for each block. The polydispersity index is 1.07. According to the supplier information, the glass transition temperature, melting temperature and crystallization temperature are -71℃, 50℃ and 23℃, respectively. PVPh was purchased from Polysciences, Inc., Warrington, PA with a molecular weight (M_w) of 1500-7000 g/mol. PEO with a M_v = 100,000 g/mol was supplied by Aldrich Chemical Company, Inc. PCL from Scientific Polymer Products, Inc. had a M_w = 120,000 g/mol.

Tetrahydrofuran(THF) purchased from Tedia Company Inc. was used as the spreading solvent for the polymer films. The solvent was chosen to co-dissolve PEO-b-PCL (or PCL) and PVPh. For PEO/PVPh system, 1 to 1 volume ratio of chloroform and THF was used. 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 THF 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 25 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 PEO, PCL, PEO-b-PCL and PVPh, respectively. For PEO in Figure **1**, the surface areas increase with the elevation of temperature likely because of dominant entropic contribution. The collapse pressure of PEO was observed to increase with increasing temperature. The π-A isotherms of PCL at 10℃ and 25℃ in Figure **2** are quite similar with a kink at ca. 6 mN/m. However, the results at 40℃ demonstrating higher surface areas with a kink at ca. 9 mN/m. The kink at ca. 6 mN/m at 25℃ is lower than the literature value(11.3 mN/m) at 22.5 ℃ [6] likely because of different solvent. For PEO-b-PCL in Figure **3**, the π-A isotherms at 10℃ and 25℃ are quite similar. The data at 10℃ and 25℃ demonstrate a kink at ca. 7 mN/m and 8-9 mN/m but the kink disappears at 40℃. The surface areas of PEO-b-PCL at 40℃ are larger than those at 25℃ quite reasonable from the presence of PEO and PCL. The surface areas of PVPh in Figure **4** decrease mostly with increasing temperature probably because of enthalpic contribution.

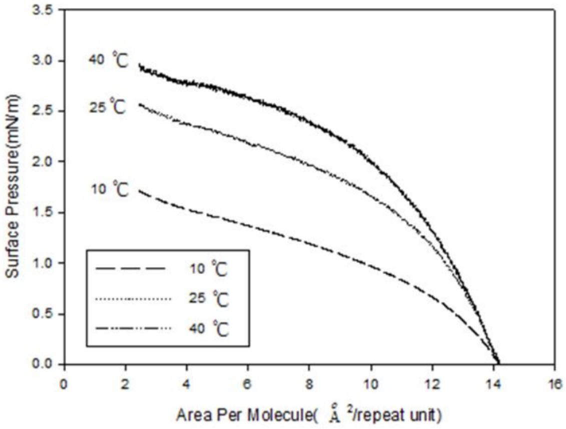


Figure 1: π-A isotherms of PEO.

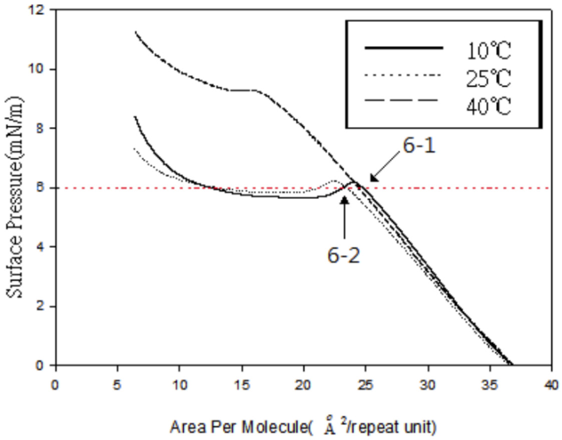


Figure 2: π-A isotherms of PCL.

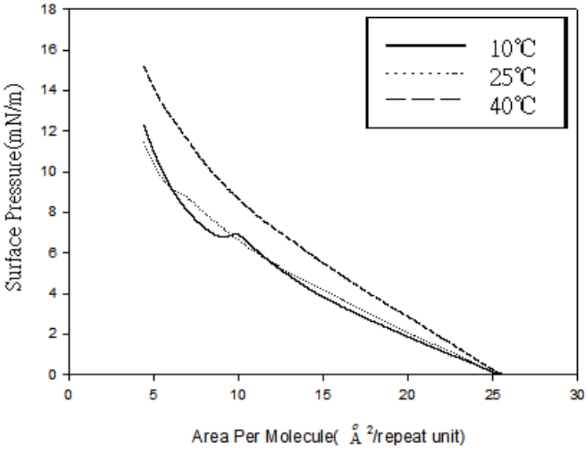


Figure 3: π-A isotherms of PEO-b-PCL.

Monolayer characteristics were calculated from Figures **1-4** and tabulated in Table **1**. The solid limiting area of PCL is greatest likely because of long alkyl chain. The lift-off areas of PEO, PCL and PEO-b-PCL were estimated to be almost temperature independent. For PVPh, the lift-off area at 40℃ is larger than those at 10℃ and 25℃. The solid limiting areas of PEO and

Table 1: Characteristics of π-A Isotherms of Polymers

	Lift-off point	Inflection point	Limiting area	π collapse
	($Å^2$/repeat unit)	(mN/m)	($Å^2$/repeat unit)	(mN/m)
PEO				
10℃	14.2		12.2	1.6
25℃	14.2		12.9	2.5
40℃	14.2		14.2	2.8
PCL				
10℃	36.7	6.4	36.3	8.4
25℃	36.6	6.2	37.5	7.6
40℃	36.7	9.1	37.5	11.4
PEO-b-PCL				
10℃	25.5	7.0	20.0	12.5
25℃	25.5	8.8	20.5	11.1
40℃	25.5		14.2	15.0
PVPh				
10℃	24.8	1.5 13.3	11.7	35.5
25℃	22.6	2.0 11.1	9.5	25.0
40℃	36.7	2.0	14.8	25.3

PCL are nearly temperature independent. The collapse pressure of PVPh is highest likely due to rigid styrene structure and hydrogen bond interaction of PVPh with water. The collapse pressure of PEO is lowest probably because of strong hydrophilicity of PEO segments.

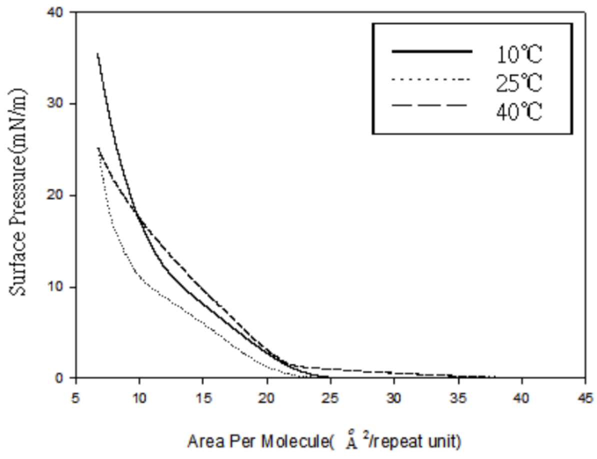


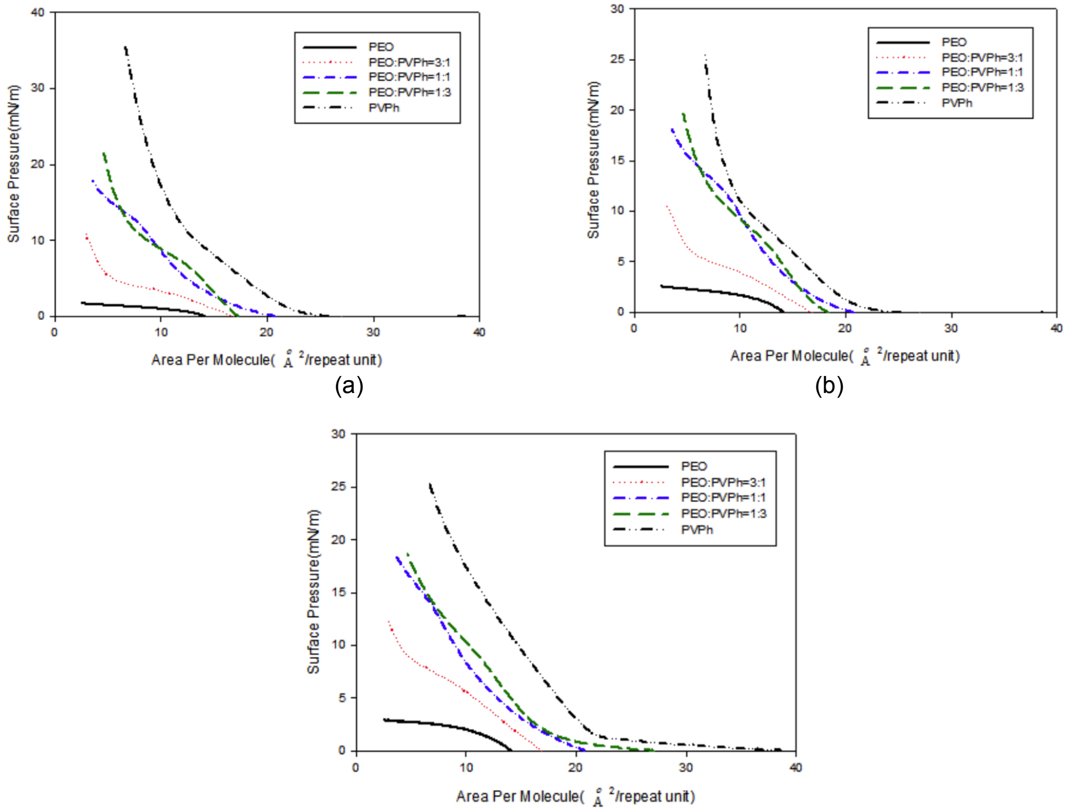
Figure 4: π-A isotherms of PVPh.

3.2. π-A isotherms of mixed monolayers at three different temperatures

The π-A isotherms of mixed PEO/PVPh 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 PVPh composition. The cross-over phenomena were observed at high PVPh composition (50% and 75%) at three temperatures.

The π-A isotherms of mixed PCL/PVPh monolayers at 10℃, 25℃ and 40℃ are plotted in the order of Figure **6**(**a**), Figure **6**(**b**) and Figure **6**(**c**), respectively. The results at 10℃ are quite similar to those at 25℃. The surface areas increase with increasing PCL composition at lower surface pressure regions. The surface areas increase more or less with increasing PVPh composition at higher surface pressure regions. For the π-A isotherms at 40℃, the PCL/PVPh(1/3) monolayers demonstrate smaller surface areas than PVPh indicating probably favorable interaction between PCL and PVPh.

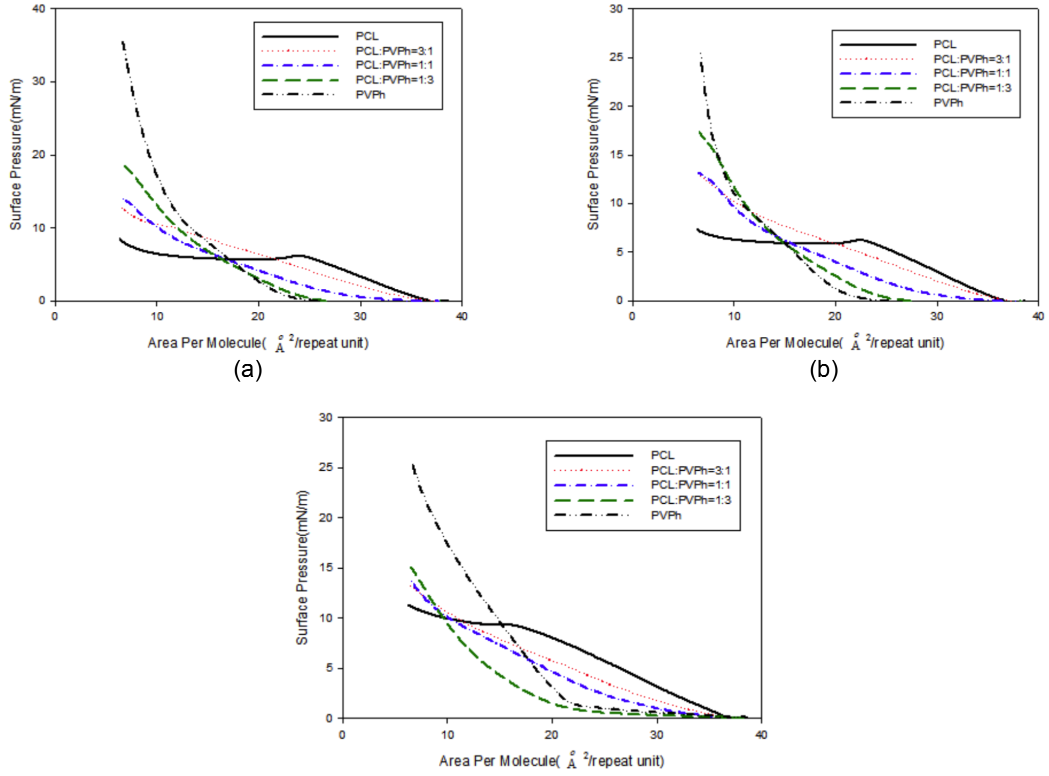
The π-A isotherms of mixed PEO-b-PCL/PVPh monolayers at 10℃, 25℃ and 40℃ are depicted in the order of Figure **7**(**a**), Figure **7**(**b**) and Figure **7**(**c**), individually. The results at 25℃ and 40℃ are quite similar to each other. The π-A isotherms of mixed PEO-b-PCL / PVPh monolayers at 25℃ and 40℃ show smaller surface areas than average of those of PEO-b-PCL and PVPh in comparison with those at 10℃. The



(a) (b)

(c)

Figure 5: π-A isotherms of PEO/PVPh at (a) 10℃ (b) 25℃ (c) 40℃.

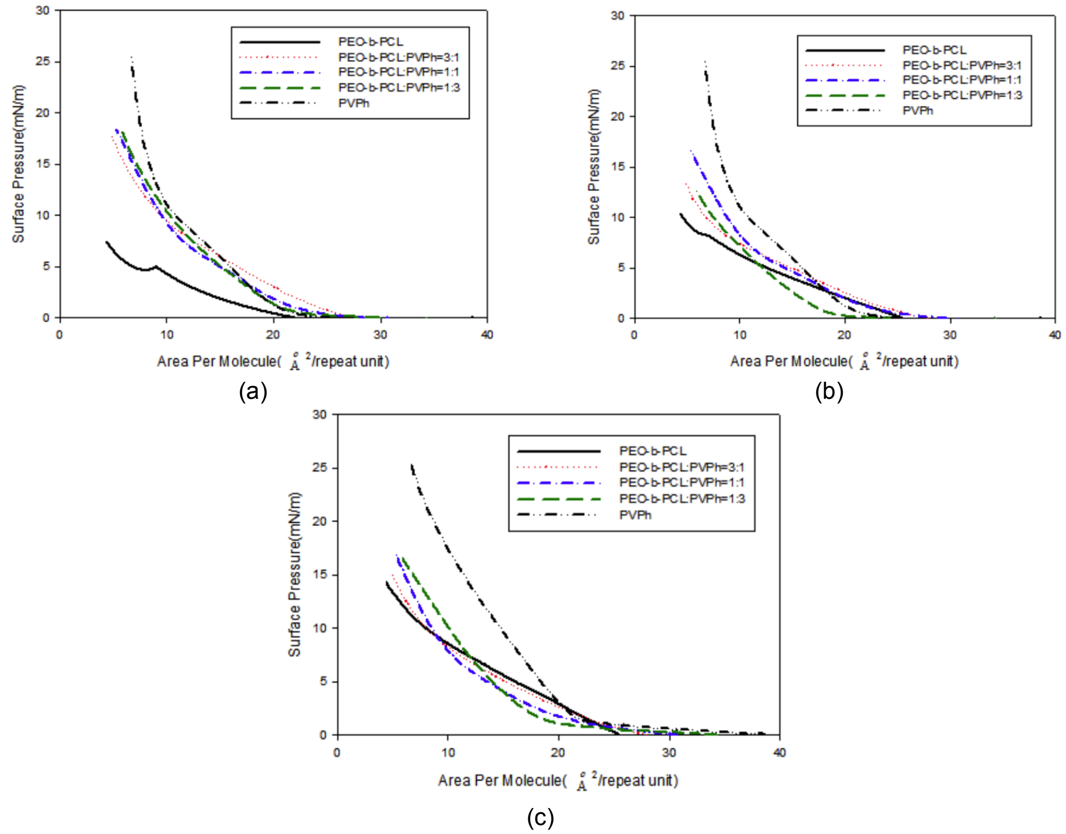


(a) (b)

(c)

Figure 6: π-A isotherms of PCL/PVPh at (a) 10℃ (b) 25℃ (c) 40℃.

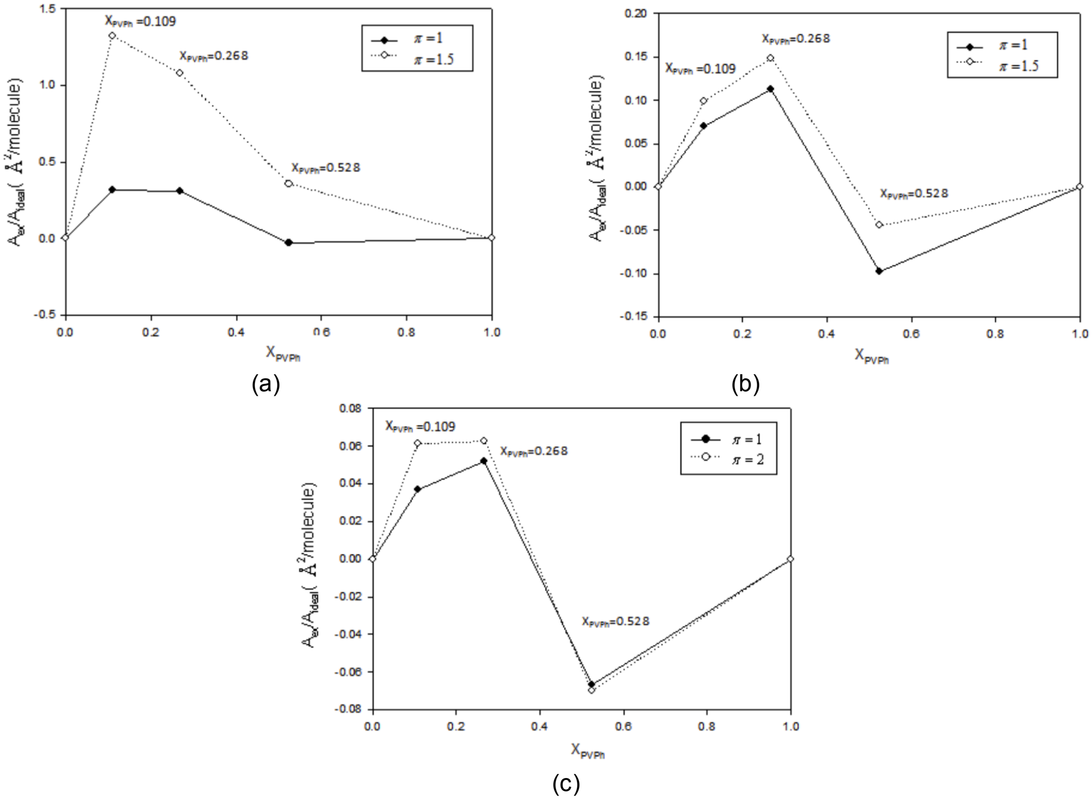
collapse pressures of the mixed PEO-b-PCL/PVPh monolayers were found to be composition dependent and increase with increasing PVPh composition.



(a) (b)

(c)

Figure 7: π-A isotherms of PEO-b-PCL /PVPh at (a) 10℃ (b) 25℃ (c) 40℃.



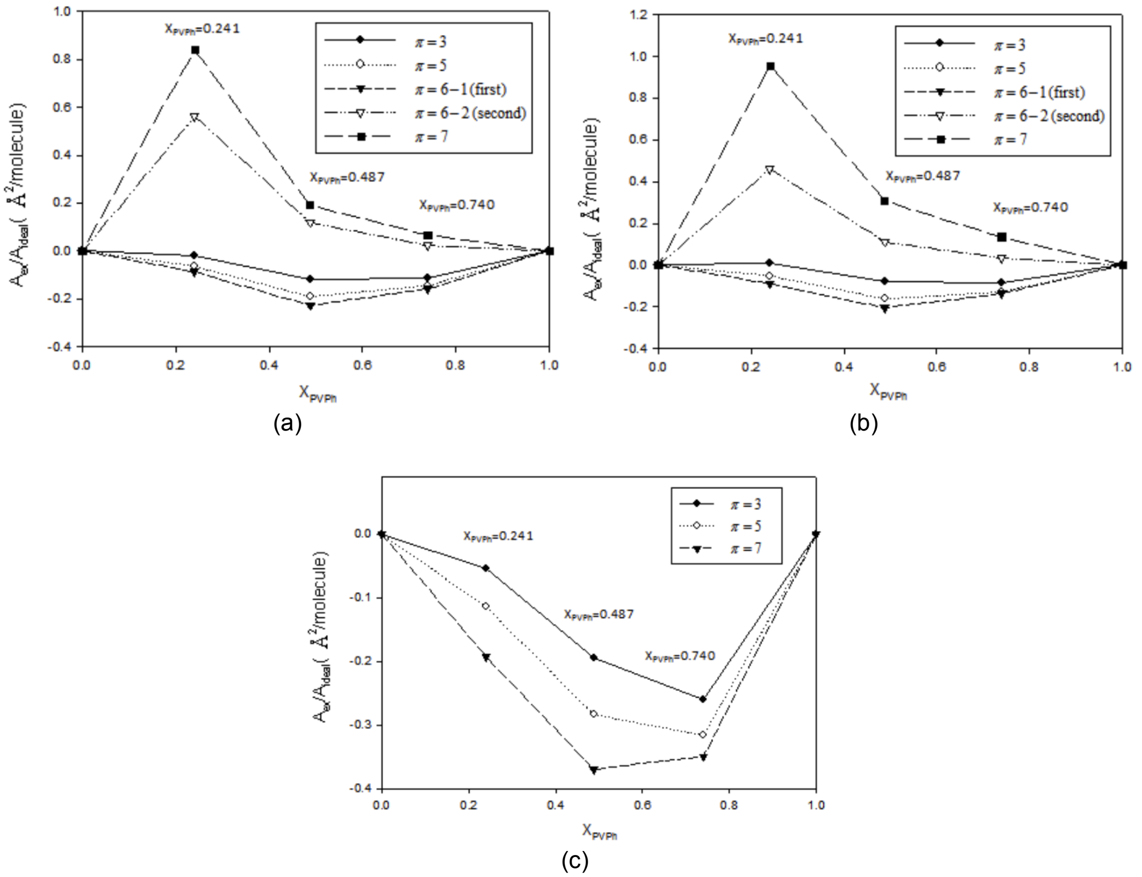
(a) (b)

(c)

Figure 8: Excess areas of mixed PEO/PVPh 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*. [8] on monolayers of hydrogen-bonded polymer blends indicated that the



(a) (b)

(c)

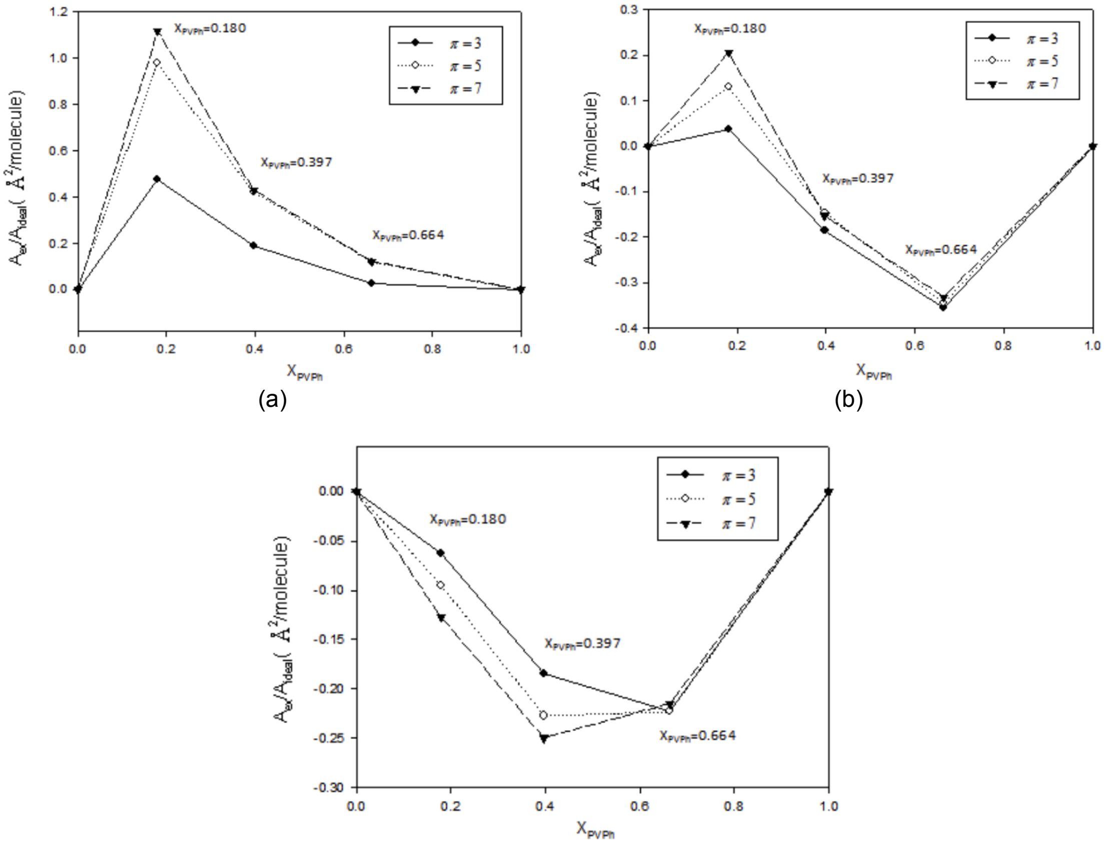
Figure 9: Excess areas of mixed PCL/PVPh at (**a**) 10℃ (**b**) 25℃ (**c**) 40℃.

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 difference between the average area per molecule of a mixed monolayer consisting of components 1 and 2 and that of an ideal mixed monolayer [9].

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

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 PVPh mole fraction at 10℃, 25℃ and 40℃, respectively. Because of a low collapse pressure of PEO, the excess surface areas were reported at surface pressures at 1, 1.5 mN/m(or 2mN/m). For Figure **8** the A_{ex}/A_{ideal} values of the mixed PEO/PVPh monolayers are mostly positive at three temperatures. Negative excess area deviations were detected at high PVPh composition and at 25 ℃ and 40℃ to show favorable interaction between PEO and PVPh. Surface pressure increase causes an adverse effect (more positive) on the excess area especially at10 ℃. The excess areas became less negative at 40℃ in comparison with those at 25℃ The A_{ex}/A_{ideal} values of the mixed PCL/PVPh monolayers in Figure **9** are in the majority negative at surface pressures at 3 and 5 mN/m and at 10℃ and 25℃. The surface pressures at 6mN/m are denoted as 6-1 (before the kink) and 6-2(after the kink) in Figure **9**(**a**) and **9**(**b**), respectively. The excess surface areas are negative before the kink but becoming positive after the kink. Negative excess surface areas were estimated in the PCL/PVPh monolayers at 40℃ (in Figure **9**(**c**)) indicating favorable interaction between PCL and PVPh. The A_{ex}/A_{ideal} values of the mixed PEO-b-PCL/PVPh monolayers are shown in Figure **10**. The excess surface areas of PEO-b-PCL/PVPh at 10℃ and 25℃ are similar to those of PEO/PVPh at the same temperatures. A slight



(a) (b)

(c)

Figure 10: Excess areas of mixed PEO-b-PCL/PVPh at (a) 10℃ (b) 25℃ (c) 40℃.

difference is that negative surface areas were observed in the mid PVPh composition in PEO-b-PCL/PVPh not in PEO/PVPh. The results of PEO-b-PCL/PVPh at 40℃ (Figure **10**(**c**)) resemble more like PCL/PVPh (Figure **9**(**c**)) at the same temperature demonstrating negative excess surface areas.

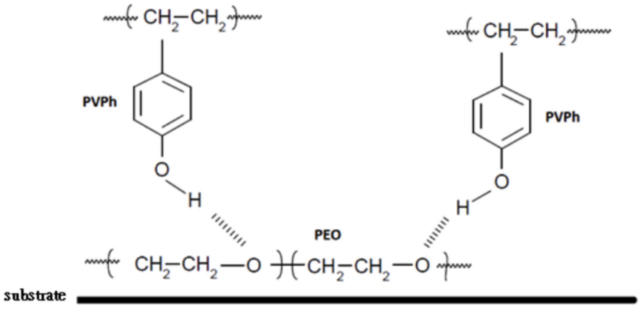


Figure 11: Interaction between PEO and PVPh on the solid substrate.

The difference in interaction between PEO and PCL with PVPh on the solid substrate and at the air/water interface can be realized and depicted in Figures **11** and **12** and Figures **13** and **14**, individually. PEO interacts favorably with PVPh on the solid substrate than PCL because of a higher degree of hydrogen bonding as shown in Figure **11**. However, on the basis of the excess area estimation in this article the behavior at the air/water interface is different from that on the solid substrate. Probably, PCL interacts favorably with PVPh at the air/water interface (Figure **14**) than PEO with PVPh (Figure **13**). PCL has a more favorable interaction with PVPh probably because of a closer proximity of its CO groups with OH groups of PVPh in the interface.

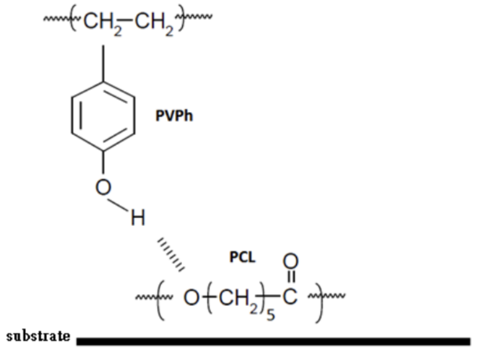


Figure 12: Interaction between PCL and PVPh on the solid substrate.

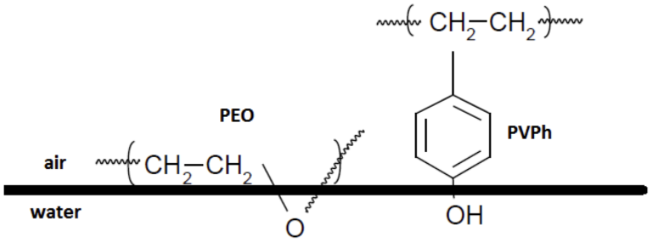


Figure 13: Interaction between PEO and PVPh at the air/water interface.

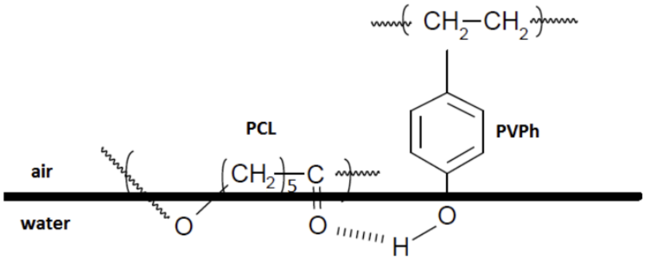


Figure 14: Interaction between PCL and PVPh at the air/water interface.

CONCLUSIONS

Miscibility deduced from the π-A isotherms of the mixed PEO/PVPh and PCL/PVPh monolayers are quite different from that in the bulk state. PEO interacts more strongly with PVPh than PCL in the bulk state. However, on the basis of the excess surface areas estimation, PCL interacts more favorably with PVPh than PEO at the air/water interface. For PEO-b-PCL/PVPh monolayers at 10 ℃ and 25℃, the behavior resemble more like PEO/PVPh at the same temperatures. However at 40℃, PEO-b-PCL/PVPh monolayers shows a similar behavior to PCL/PVPh monolayers.

A simple scheme was proposed successfully to explain the interaction difference between PEO and PCL with PVPh on the solid substrate and at the air/water interface. PCL has a more favorable interaction with PVPh probably because of a closer proximity of its CO groups with OH groups of PVPh in the interface.

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