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Historical Perspective

Interfacial characteristics of binary polymer blend films spread at the air-water interface

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ABSTRACT

The interfacial characteristics of binary polymer blend films spread at the air-water interface are reviewed, focusing on their surface pressures, interfacial structures, and dilational moduli as a function of the miscibility. Miscible polymer blend films show thermodynamic, structural, and dynamic properties which are a combination of those from both components in the polymer blend present at the air-water interface. No preferential adsorption is observed and the behavior does not depend on the surface concentration regime. In contrast, for immiscible polymer blend films, preferential adsorption of one polymer phase occurs at the air-water interface and the interfacial characteristics in the semi-dilute and concentrated regimes are strongly controlled by one of the components of the adsorbed polymer.

1. Introduction

Binary polymer blend films spread at the air-water interface are of much interest for e.g. biological systems, membranes, foams, food processing, and cosmetics. Such a system can also provide important information about the thermodynamic interactions, structural orientation and packing, and dynamic dilational properties of the blended polymers. Polymer blend films are generally formed by two water-insoluble polymers and by a water-insoluble polymer and a water-soluble polymer, irrespective of their miscibility. Thus, clear difference between the corresponding polymer blend films should be observed in their interfacial properties, such as surface pressures, structural properties, and dilational moduli by plotting them as a function of total surface concentration in the polymer blends. However, the most important open physical problems have not been well understood yet in quasi-two dimensional polymer blend systems.

Commonly, in the thermodynamic studies of binary polymer blend films spread at the air-water interface, an understanding of their miscibility is one of the most important factors. The miscibility can be determined by fitting a plot of the mean surface area (A) measured at a fixed surface pressure as a function of the composition of one polymer in the blend, where the "additive line" is defined by Eq. (1).

$$A_{12} = A_1X_1 + A_2X_2 \tag{1}$$

where A_{12} is the mean surface area, A_1 and A_2 are the surface areas of polymer 1 and 2, respectively, and X_1 and X_2 are the molar fraction of the corresponding polymer films. A binary polymer blend is considered an ideal or completely immiscible mixture when the plot matches the additive line. Negative and positive deviations from the additive line correspond to miscible and immiscible binary polymer blend films, respectively. Such deviations are attributed to the intermolecular interactions between the repeating monomeric units of the polymer blends, such as hydrogen bonding, hydrophobic bonding, and steric interactions [1]. The two polymer components in miscible polymer blend films often have the same interfacial orientation at the air-water interface, whereas immiscible films they have different orientations [1–3].

Analysis of the structural properties of binary polymer blend films spread at the air-water interface should provide their interfacial orientations and changes in the conformation of the individual polymer chains at the air-water interface in the presence of other polymer chains. Since optical reflection methods and neutron reflectivity techniques have been applied to polymer films spread at the air-water interface [1,3,4], such methods could be powerful techniques for obtaining the structural properties of binary polymer blend films. Moreover, atomic force microscopy (AFM) techniques provide some morphological information of the binary polymer blend films after the films first need to be deposited on a solid surface using the Langmuir-Blodgett (LB) technique [4].

Dynamic dilational properties of the binary polymer blend films spread at the air-water interface strongly depend on relaxation processes such as polymer chain reorientation and chain conformation by variations in the surface area [5]. The dynamic dilational moduli are often measured by oscillations of barriers in Langmuir troughs and capillary wave methods that detect surface light scattering and excited wave techniques. In most oscillatory barrier measurements, the ampli-

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tudes of the surface deformation strains are $< 10\%$ and the frequencies are below 1 Hz. For the determinations of dynamic dilational moduli, it is necessary to know whether the stress-strain plot is linear or non-linear due to somewhat large strain. On the other hand, the surface light scattering and excited wave methods apply very small deformation strains ($< 10^{-3}\%$) at high frequencies (> 100 Hz).

In most previous work on binary polymer blend films spread at the air-water interface, the miscibility was one of the most studied issues and the interesting results of their thermodynamic and structural properties have been reviewed by Gabrielli et al., [3], Gaines [6], Langevin and Monroy [7], and the authors [1,4]. This review article focuses mainly on the experimental studies at equilibrium state, performed in the last two decades on the thermodynamic, structural, and dynamic dilational properties of binary polymer blend films spread at the water surface as a function of the miscibility of the polymer films. Non-equilibrium properties of polymer blend films should be important to fully understand about their physical behavior. When di- or triblock copolymers were spread at the air-water, their microsegregation provided interesting information [1,5,7] and then it should be useful to compare their interfacial behavior with the genuine blends formed by the same blocks. However, such comparisons have never been reported.

2. Measurement techniques

The interfacial characteristics of binary polymer blend films spread at the air-water interface are often discussed in terms of the miscibility of the polymer films in quasi-two dimensional spaces using surface pressure measurement techniques, fluorescence microscopy, ellipsometry, AFM, and dynamic dilational moduli measurement techniques [1,4,5,7].

2.1. Surface pressure measurements

A Langmuir trough attached to a Wilhelmy plate has been widely employed to measure surface pressure-surface area (π-A) isotherms of binary polymer blend films at the air-water interface. The polymer blend in a solution of volatile solvents is spread on the water surface in the trough and the solvent allowed evaporating. Measurements are usually undertaken at a fixed temperature by continuous or stepwise compression of the water surface, i.e. the compression method. In contrast, without compression of the water surface in the trough, the polymer blends are applied sequentially to the water surface with a fixed surface area in order to change the surface concentration Γ; this is called as the addition method. The difference between the compression method and the addition method for studying the π-A isotherms is often observed at higher Γ where the π value measured by the former method should be gradually relaxed with time at fixed A.

For polymer films spread at the air-water interface, the term A is generally expressed as the reciprocal of Γ for the spreading polymer, i.e., with unit of m^2/mg. The Γ value should correspond to the amount of adsorbed polymer at the air-water interface when neither desorption of the polymer from the interface nor dissolution of polymer into the water sub-phase occurs.

The properties of the binary polymer blend films depend on the properties of the individual polymer films spread at the air-water interface. Plots of π as a function of the total surface concentration Γ_{total} for a polymer blend film show dilute, semi-dilute, and concentrated regimes [1,4,5,7]. The surface overlapping concentration Γ^* can be estimated by extrapolating a straight line from the plot of π vs. Γ_{total} to $\pi = 0$. The dilute and semi-dilute regimes are defined as the regions of the π vs. Γ_{total} plot below and above Γ^*, respectively. As Γ_{total} increases, a semi-dilute regime in which double logarithmic plots of π vs. Γ_{total} are fitted with a power law defined by $\pi \propto \Gamma_{total}^{y}$ appears, where $y = 2\nu/(2\nu - 1)$ and ν is the critical exponent of the excluded volume of quasi-two dimensional spaces [8,9]. It is well known that the excluded volume effect depends strongly on the solvent conditions for polymer chains. The numerical values of ν under good and theta solvent conditions were calculated to be 0.77 ($y = 2.85$) [10] and 0.505 ($y = 101$) [11], respectively. When Γ_{total} further increases beyond the semi-dilute regime, the π value plateaus at a surface concentration of Γ^{**} which marks the transition from the semi-dilute to the concentrated regime.

Moreover, the π values of binary film containing polymers 1 and 2 are often plotted as a function of surface concentration, Γ_1 and Γ_2 for component 1 and 2, respectively, of the corresponding polymer blends to elucidate the influence of the surface concentration on the π values.

2.2. Measurement of structural properties

Fluorescence microscopy and ellipsometry have been applied to binary polymer blend films spread at the air-water interface for investigation of their in situ interfacial structures. Moreover, techniques such as spectroscopy or surface potential are also useful to detect changes in the in situ interfacial structures of films on water surface. However, application of the corresponding methods to binary polymer blend films was hardly reported. In contrast, AFM allows indirect interpretation of the interfacial behavior and conformation of blended polymers in the films.

2.2.1. Fluorescence microscopy

Fluorescence microscopy is used to analyze the interfacial morphology of polymer blend films spread at the air-water interface. A fluorescence probe material is added at a concentration of < 1 mol%, which is selectively soluble in the fluid (expanded) phase and insoluble in the condensed phase, in order to distinguish these phases by contrast differences in the microscopic images. However, all the polymers do not present expanded and condensed phases. Fluorescence microscopy measures the light reflected from an interface after irradiation with an excited laser beam or mercury light using a CCD (charge coupled device) or a SIT (silicon intensifier target) camera. However, as even the small amount of added fluorescence probe material can be regarded as an impurity in the spreading films, there are concerns as to whether the observed fluorescence images reflect real morphologies. In order to avoid the drawbacks of the fluorescence microscopy, Brewster angle microscopy (BAM) developed by two research groups in 1991 [12,13] is based on ellipsometry and is only governed by the refraction index.

2.2.2. Ellipsometry

Ellipsometry is often used for analyzing adsorption kinetics and layers formed at various interfaces since it simultaneously provides the refractive index and the average thickness of the adsorbed and formed layers, assuming that the corresponding layers are homogeneous [14]. For an inhomogeneous polymer layer at the air-water interface, Rottke et al. have proposed that nulling-based ellipsometric mapping can be used to characterize its morphological inhomogeneity [15]. Ellipsometry is based on the measurement of changes in the ellipticity of polarized light caused by reflection at an interface. The ellipticity can be defined by the reflective phase difference Δ and the amplitude ratio $\tan \Psi$ between two plane-polarized light waves, oscillating in parallel and perpendicular directions with respect to the incidence plane, as a function of the refractive index and the thickness of a layer. When the layer is thin, changes in Δ by the formation of layers at the interface are much easier to detect than changes in Ψ.

2.2.3. AFM

AFM is the most commonly used scanning probe microscopy technique used to characterize nanoscale surface structures since it can be applied dielectrics, insulators, and soft materials. The AFM technique measures the deflection of a cantilever due to repulsive forces generated by interactions between sharp tip and the sample surface [16]. When the tip microscopically moves over the surface (in either