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ORIGINAL CONTRIBUTION

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Study on the properties of a polyvinylacetate film at the air-water interface

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Abstract Isotherms of surface pressure against surface area for a polyvinylacetate (PVAc) film at the air-water interface were determined at 20.52 °C. Measurements of surface moment, hysteresis, and pressure relaxation in a constant area were subsequently conducted at appropriate area regions for elucidation of the correlation of properties and conformations of PVAc film. It is concluded that the film is stable and exhibits a perfectly reversible compression in the areas larger than 13 Å^2/repeat-unit but assumes three different conformations for three regions (70–42), (42–25), and (25–13) Å^2/repeat-unit, respectively. Finally, a twisting chain loop model is proposed for the interpretation of hysteresis and pressure relaxation occurring in the areas near and in the collapse region.

Key words Polyvinylacetate – air-water interface – surface moment – hysteresis – relaxation

Introduction

In earlier work, surface pressure – surface area (π-A) isotherms have been treated as two-dimensional analogues of pressure-volume (P-V) isotherms of materials and supposed to be in equilibrium [1, 2]. However, Harkins [3] has reported film instability for fatty acids. Langmuir [4] as well as Rabinovitch [5] have noted hysteresis in surface films. It is also well known that the shape of an isotherm depends on the rate of compression as reported by Zografi [6] and Kato et al. [1, 7]. Obviously, the time-dependent processes occurring in the film are important to determine the complete properties of film. While most polymer researchers look for the time dependence of these observations, many scientists working on Langmuir films do not.

In order to clarify the kinetic effects such as film instability, or hysteresis, some investigators [2, 8–14] have reported area changes of films at constant pressures or pressure changes at constant areas. They showed that instability of insoluble films was a rather general phenomenon in a transition region from the expanded- to condensed- liquid state or in the collapse region, which is attributed to the two-dimensional re-packing of the molecules in the film or to the collapse of film into a three-dimensional state.

Studies of PVAc film have been reported in the past [15–28]. Crisp [15] classified PVAc to be an amorphous, usually soft polymer giving stable fluid film. He has also constructed a molecular model of PVAc where all the acetyl residues are arranged on one side of the main-chain when this is set in a linear zig-zag form. Hotta [18] indicates that the molecules of PVAc are fairly loosely packed, and subject to micro-Brownian motion, thus the π-A isotherm is of an expanded type. Recently, Yu and coworkers [24–26] have measured the isotherms of surface viscoelastic parameters versus surface area for PVAc films by surface light scattering techniques. From those results, they propose the change on the molecular conformation of the film in the course of compression.

With all the work on PVAc, the time-dependent behavior of the film has been less reported. In this study, we performed measurements of surface moment, hysteresis tests, and tests of pressure relaxation at a constant area to acquire insights into correlation of properties and conformations of the film.

Experimental section

Materials

A commercially standard polyvinylacetate with a molecular weight of 113×10^3 g/mol. (Aldrich Chemical) was used. Dichloromethane (Alps Chem.) for L.C. grade was used as received. The substrate water was purified by double distillation and subsequent filtration through a Milli-Q purification system. Polyvinylacetate was dissolved in dichloromethane to prepare a spreading solution (0.50 mg/ml).

Methods

A commercially available LB 5000 Langmuir–Blodgett apparatus (KSV Instruments, Finland) with a computerized control was used. A Pt-Wilhelmy balance was used as the surface pressure sensor. A poly(tetrafluoroethylene) trough with inside dimensions of 775 mm × 120 mm and two polyoxymethylene barriers were used. It was important to use two symmetric compression barriers with the Wilhelmy plate placed in the middle of the trough facing parallel to the moving barriers to guarantee reproducible results on polymer films. Because the polymer films were viscous at high surface pressures, erroneous data were easily induced due to deflection of the Wilhelmy plate if one barrier was used. Surface potential ΔV, which is the difference in the potentials of the substrate and the film – covered substrate, was determined by a vibrating capacitor method [29–30] with an inaccuracy of less than $\pm$ 5%. Using the Helmholtz equation, $\Delta V = 4\pi n\mu$, where n is the reciprocal of surface area, the surface moment was determined from the obtained data ΔV. The water surface was cleaned by aspiration and checked before each run by compressing to 1/20 of the initial area to produce a surface pressure change of less than 0.1 mN/m. The purity of the spreading solvent was also tested. No change in the surface pressure could be detected when spreading pure solvent on the interface. Thus, remaining impurities were negligible. The spreading solution of PVAc was slowly applied by a micro-syringe onto the water surface. After the solution was spread, 30 min was allowed for the solvent to evaporate. All isotherms were run for a minimum of three times, with reproducibility errors of less than $\pm$ 1 Å^2/repeat-unit.

Results and discussion

A typical surface pressure – surface area (π-A) isotherm, obtained for the polyvinylacetate (PVAc) film, is presented in Fig. 1. It is found that the π-A isotherm is of an expanded type [15, 16]. On compression to a smaller surface area the curve rises sharply with compression. The film collapses at about 27.2 mN/m which agrees with the literature values [15, 20, 24]. The limiting area, deduced by extrapolating to $\pi = 0$ of the straight portion of the π vs. A curve at high surface pressures, was found to be 25 Å^2/repeat-unit. It is also in good agreement with the literature values [15, 21, 24].

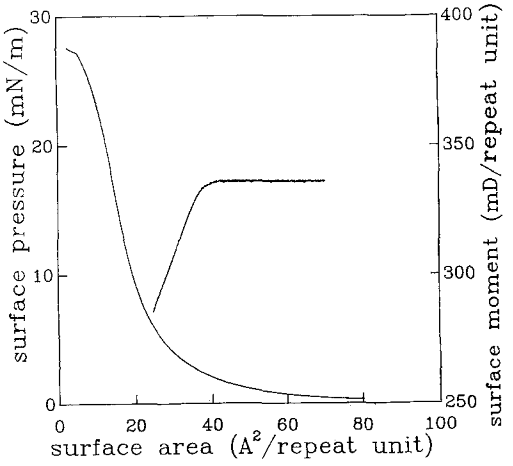
To get information on the affinity between the PVAc film and air-water interface at 20.5 °C, fitting of the isotherm was performed by the following scaling law [23, 31],

$$\pi \sim C^y \tag{1}$$

$$y = 2v/(2v - 1)\,, \tag{2}$$

where C denotes the concentration of the repeat units per area, π denotes the surface pressure, and v denotes a characteristic scaling exponent which expresses the dependence of the radius of gyration of the polymer on its molecular weight for a given solvent or, as in this case, air-water interface. As shown in Fig. 2, the double-logarithmic plot of π vs. A isotherm is linear as the film is in the specific areas larger than 35 Å^2/repeat-unit. It indicates that the isotherm of the film in this region obeys the scaling law. The value of y was found to be 2.74. Thus the v-value calculated is 0.79, which falls in the range of those reported in the literature [23, 25]. This shows that the exponent v is 0.77 for a good solvent and 0.55 for a θ-solvent [23, 32]. Therefore, the air-water interface at 20.5 °C corresponds to a good solvent condition for PVAc.

Fig. 1 Surface pressure and surface moment vs. surface area isotherms for PVAc at 20.5 °C with strain rate 1.4%/min



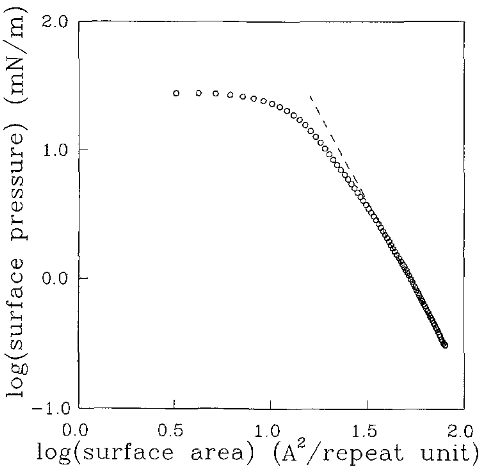


Fig. 2 Double-logarithmic plot of surface pressure and surface area for PVAc at 20.5 °C with strain rate 1.4%/min

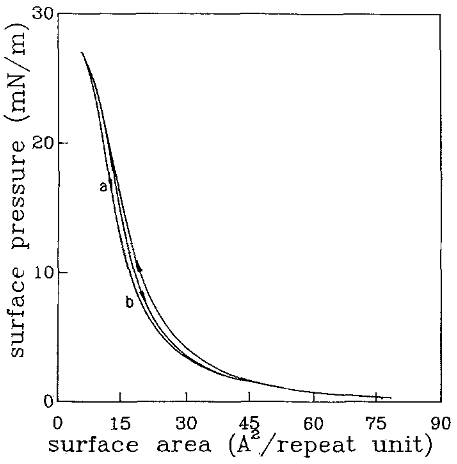
The measurement of the surface moment against surface area is a powerful method to elucidate the conformation of the polar group in the film [29–30]. When the experiment was carried out, at areas larger than 70 Å²/repeat-unit the surface moment of PVAc film varied from place to place on the surface, indicating that the film was non-homogeneous in this region. Until the surface area reached 70 Å²/repeat-unit or below, a reproducible surface moment was obtained as shown in Fig. 1. Owing to the limits of the instrument, the reproducible surface moment could be measured only up to ca. 25 Å²/repeat-unit. It was found that in the range of 70 to 42 Å²/repeat-unit, the surface moment was constant at 336 mD/repeat-unit. This reflects that the PVAc segments at the water surface assume a stable conformation and work is consumed in this range simply to shorten the distance between the segments without disturbing the orientation of the polar groups. However, in $A = (42–25)$ Å²/repeat-unit, the surface moment dropped with compression. It suggests that the polar groups are reoriented toward reducing the surface moment during compression. Following the molecular model of PVAc suggested by Crisp [15] and Hotta [18], one may surmise that the polar groups of the film at the limiting area assume a two-dimensional closest packed conformation.

Using the surface light-scattering method, Yu and coworkers [24] obtained the surface viscoelastic parameters – surface area isotherms and suggested that below the limiting area of 25 Å²/repeat-unit, the polymer chains start to have short chain loops. The number of loops increases with decreasing surface area, and reaches a saturation limit at 14.3 Å²/repeat-unit. Below 14.3 Å²/repeat-unit, the loop number remains the same, but the loop size increases up to the collapse point. In the text, we are interested in studying the reversibility of chain loop compression and the stability of chain loops in number and size at a given area using the hysteresis test and the measurement of pressure relaxation at a constant area.

Hysteresis

Hysteresis experiments were performed at various target pressures by performing compression and reexpansion operations with a constant strain rate 1.41%/min. There is no hysteresis observed as the target pressure was below 20 mN/m, corresponding to the area above 13 Å²/repeat-unit. Thus, the film compression is perfectly reversible in this range. Interestingly, the film holds reversible compression up to just below the limiting area. As mentioned above, the limiting area is the extreme of all segments residing at interface, thereby the chain loop should form as the film is confined to areas smaller than the limiting area. Therefore, the chain loops formed in the area region can release instantaneously with a reexpanding surface area. As shown in Fig. 3, as the target pressure was further compressed to 25 and 27 mN/m which are near the collapse pressure of the film, a slight hysteresis was observed. The pressure, during expansion, became slightly lower than the pressure of the compression and then recovered to the original compression isotherm as the pressure was reduced below 1.5 mN/m. Further, upon recompressing the same film, the isotherm obtained followed the first compression isotherm. Evidently, no irreversible changes had occurred in the film after the first compression run. Because the area corresponding to 25 mN/m is only 8 Å²/repeat-unit, which is about one-third of the limiting area, it is reasonable to presume that a higher stress force is

Fig. 3 Hysteresis isotherms for PVAc, temperature 20.5 °C, strain rate 1.4%/min, target pressure set at (a) 27, (b) 25 mN/m



exerted on those segments residing at the interface, such that more segments would be squeezed into three-dimensional space. As suggested by Yu and coworkers [24], the loop number remains the same as the film is confined to areas below 14.3 Å^2/repeat-unit. Therefore, the effects of squeezing segments should cause the enlargement of the chain loops existed previously. However, for taking into account on the hysteresis, the enlargement of the chain loops should be brought about by twist, instead of simply expanding the loop size. The release of twist cannot be completed instantaneously in response to expanding surface area. The facts of no irreversible change after the first compression run reveals that it takes some time for the twisted loop to release.

The results mentioned above are coincident with that discussed in the scaling law. That is, there is a good affinity of the PVAc film to the air-water interface and a weak intermolecular interaction existing in the film. Thus, the chain loops formed during compression can release and all the segments can return to the interface in the reexpansion operations.

Pressure relaxation at constant area

For the sake of further understanding the stability of chain loops in number and size, it is interesting to observe the pressure relaxation when the film is compressed to a constant area.

Figure 4(a) and (b) present the pressure behaviors of the films obtained after compression at constant areas of 17 and 13 Å^2/repeat-unit, respectively. It is found that both runs show the surface pressure retaining constant with time. Obviously, the film at these surface areas is stable, and does not bring about any relaxation process to reduce the surface pressure. As aforementioned, at these areas the polymer chain takes loops which can release instantaneously as the film is expanded. Thus, one further realizes that such loops are stable in number and size at a given area.

Figure 4(c) shows that at 8 Å^2/repeat-unit the surface pressure of film relatively rapidly decayed in the first 5 min, and then decreased slowly. Hence, the film was unstable and might bring about some relaxation process to decrease pressure. Because some chain loops in this area are twisted, as mentioned above, the mechanism of the relaxation process might enlarge loop size by twisting chain loops.

Figure 4(d) shows the pressure relaxation curve obtained at 4 Å^2/repeat-unit which is in the collapse region. The surface pressure of film decreased exponentially to an equilibrium value. This reveals that as the film was confined to areas smaller than the collapse point, the change of film conformation approached to a stable three-dimensional structure. The curve obtained is fitted well using a two-term exponential decay equation [8] as follows:

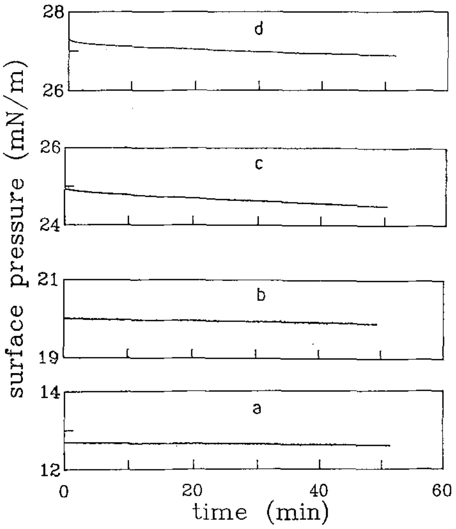


Fig. 4 Relaxation of the surface pressure after compression at constant surface area: (a) 17, (b) 13, (c) 8, (d) 4 Å^2/repeat-unit

$$\pi(t) = \pi_\infty + \sum_{i=1}^{2} \pi_{0,i} e^{-t/t_{\mathrm{C}i}} , \tag{5}$$

where $\pi(t)$ and π_∞ are the surface pressure at time t and equilibrium surface pressure, respectively. $\pi_{0,i}$ is the fraction of the pressure at $t = 0$ associated with the characteristic time $t_{\mathrm{C}i}$ in the way that $\pi_{(t=0)} = \pi_\infty + \pi_{0,1} + \pi_{0,2}$. From the best fitting the parameters $t_{\mathrm{C}1}$, $t_{\mathrm{C}2}$, $\pi_{0,1}$, and $\pi_{0,2}$ obtained are 84 s, 2.7×10^3 s, 0.09 mN/m, and 0.47 mN/m, respectively. The overall standard deviation is less than 1%. The two characteristic times obtained indicate that there are two types of relaxation occurring in the collapse region. By examining the characteristics of π-A isotherm in the collapse region (Fig. 1), the surface pressure still increases gently with decreasing area. Thus, one knows that beyond the collapse point, not all chain loops attain their critical size and collapse, but rather some still continue to grow in size. Therefore, the fast relaxation time $t_{\mathrm{C}1}$ may be considered to be the time for the unfailed loops advancing twist to reach a critical size and then lie down by gravitational force. Whereas, the slow relaxation process may come from the repulsion effects among those residue polar groups of PVAc at the interface. The effect continues to squeeze out some polar groups from the interface to seek a new stable state.

Equation (5) is also adopted to fit the curve (c) of Fig. 4. It is found that the curve could be well described by the equation with the parameters $t_{\mathrm{C}1} = 118$ s, $t_{\mathrm{C}2} = 1.2 \times 10^4$ s,

$\pi_{0,1} = 0.08$ mN/m, and $\pi_{0,2} = 1.59$ mN/m, respectively. Because the t_{C1}-value is close to that in curve (d), the fast process is associated with the increase of loop size for the twisted loops as mentioned above. Whereas, the quite slow process may be attributed to the rearrangement of the simple (untwisted) chain loops existing in the film, probably twisting the simple loops to enlarge their loop size.

Conclusions

This work has used appropriate measurements to elucidate the properties and conformations of polyvinylacetate film at air-water interface. It is concluded that the film in the region of 70 to 13 Å^2/repeat-unit is stable and exhibits a perfectly reversible compression. However, in this region the conformation of PVAc molecules varied with different area stages: I) in the region of 70 to 42 Å^2/repeat-unit, the conformation of polar group of PVAc remains unchange with compression, II) in the region of 42 to 25 Å^2/repeat-unit, the angle of polar groups related to interface significantly changes toward decreasing surface moment with decreasing area, and the film approaches to a closest packed conformation at 25 Å^2/repeat-unit, and III) in the region of 25 to 13 Å^2/repeat-unit, the molecules assume chain loops which can instantaneously release as the film is expanded.

As the film is in the areas below 13 Å^2/repeat-unit and near the collapse point, it becomes unstable and shows hysteresis in the compression/reexpansion test. The chain assumes a conformation of twisted loops and the extent of twisting depends on the surface area. Within these areas, the twisted loops can release but need to spend time.

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