Dynamic Measurement of the Surface Viscoelastic Properties of a Polymer-Solvent System Using the Ripplon Surface Laser-Light Scattering Method

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Abstract

Since drying determines the final qualities of polymer-solvent-coated films, it is of considerable importance to understand the drying behavior and surface properties of coated films. Surface properties of polymer-solvent films at the air–solvent interface can be deduced from the propagation characteristics of high-frequency capillary waves generated by thermal fluctuation of the liquid displacement called "ripplon." The characteristics are probed by the ripplon surface laser-light scattering (SLLS) method. The purpose of the present study is to develop a highly sensitive and accurate surface viscoelasticity measurement method and observe the dynamic molecular adsorption/desorption processes near the surface of polymer-solvent films. As a first step, we tried to quantitatively evaluate the surface viscoelastic properties of a dilute polymer-solvent system using ripplon SLLS. The surface properties of polymer solutions and some surfactants mixed with methyl ethyl ketone at the air–solvent interface have also been investigated.

Introduction

Drying conditions significantly affect the qualities of polymer-solvent-coated films. The characteristics of diffusion and heat transfer, and surface properties during drying are very important in controlling the quality of coated film. In this work, we measure the surface properties at the liquid surface of polymer-solvent films using the ripplon surface laser-light scattering (SLLS) method[1]. Ripplon is a thermally excited capillary wave whose propagation is determined by the surface tension and shear viscosity of polymer-solvent films. Measuring the surface properties of polymer-solvent films by ripplon SLLS has two main advantages:

1) Because ripplon SLLS is a completely non-contact measurement method of a liquid surface, it is possible to monitor the change of surface properties continually during drying.

2)   Since ripplon is a small amplitude wave (~nm) and is influenced by the surface viscoelastic properties of adsorbed molecules on the liquid surface, ripplon SLLS is a suitable and sensitive technique for measuring surface viscoelasticity.

Many experimental studies of measuring surface viscoelastic behaviors of polymer solutions have been carried out using a monolayer film of polymer aqueous solution, but the viscoelastic behavior of dilute polymer organic-solvent systems, which are often used for industrial production, is still not clear. In this work, we made a quantitative evaluation of the surface viscoelastic properties of dilute polymer-solvent systems using ripplon SLLS.

Ripplon Surface Laser-Light Scattering Spectroscopy

A schematic diagram of the ripplon SLLS experimental apparatus is shown in Fig. 1. The light source is an Nd:YVO$_4$-YAG laser with a wavelength of 532 nm, and an output power of 20 mW. The output of the laser is divided into incident and reference lights by a beam splitter and is then superimposed onto the sample surface, with the crossing angle θ, which determines the scattering wave number. The frequency of the scattered light is modulated by the Doppler effect through the interaction with the moving wave. We can obtain the power spectrum of ripplon by FFT analysis of the spectrum of scattered light using an optical heterodyne technique. The propagation of ripplon is described as the decay oscillation in the form of $A\exp\{i(kx-\omega_0 t)-\Gamma t\}$, and the angular frequency ω_0 and damping constant Γ is approximated by Eqs. (1) and (2). The basic idea of the experimental setup is the same as Sugahara's report[2], but we established a new arrangement of the optical system in this work. As a result, the intensity of the scattered light of ripplons detected by PMT becomes 100 times larger than that of the previous setup. In this way, the sensitivity and accuracy of the light-scattering measurement were improved considerably.
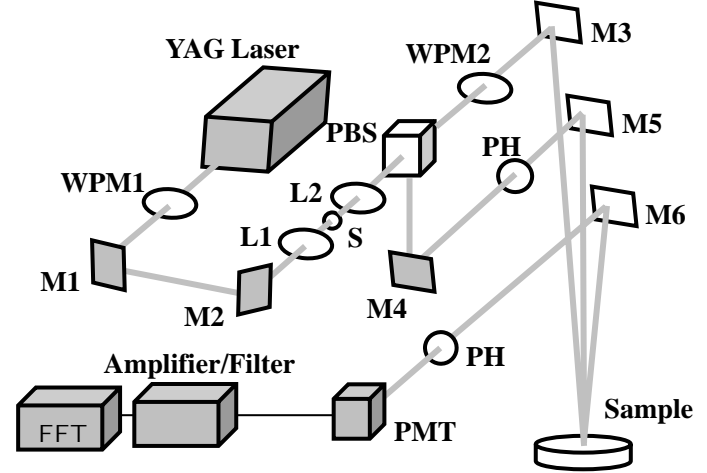

Fig. 1. Schematic diagram of experimental apparatus

The typical ripplon spectrum observed by ripplon SLLS is shown in Fig. 2. Figure 3 shows the measured surface tension of an aqueous methanol solution. Ripplon SLLS enables us to measure a wide range of surface tensions.

$$\omega_0^2 = \frac{\sigma}{\rho}k^3 \qquad (1) \qquad\qquad \Gamma = 2\frac{\eta}{\rho}k^2 \qquad (2)$$
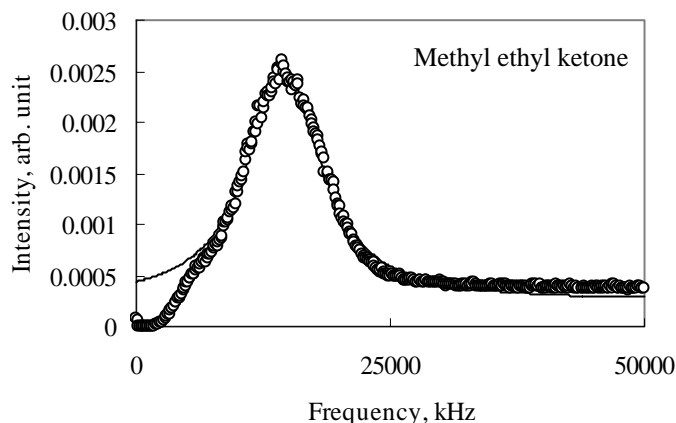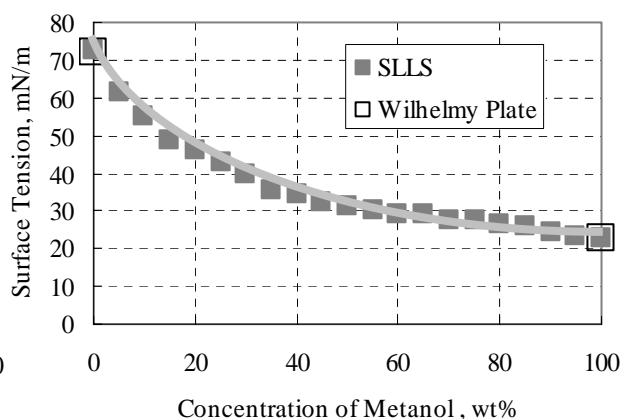
Fig. 2. Typical ripplon spectrum

Fig. 3. Surface tension as a function of methanol concentration.

Results and Discussion

Basic hydrodynamics model: Surface tension and kinematic viscosity of dilute surfactant solution mixed with MEK, measured and evaluated by Eqs. (1) and (2), are shown in Figs. 4 and 5. Static values measured by traditional methods are also shown in the same figures. Figure 4 shows that both the surface tensions decrease when the surfactant concentration is increased up to 0.2 wt%, although there is a systematic discrepancy between them. At a concentration above 0.2 wt%, however, the surface concentration appears to reach an equilibrium balance, resulting in a plateau. The surface tensions by ripplon SLLS show good agreement with the static values only with pure MEK, and tend to be smaller than those using the static method. Note that the kinematic viscosities from the falling ball method do not change with surfactant concentration, but they increase with ripplon SLLS. This discrepancy can be explained as follows. The surfactant concentration on the surface is higher than the bulk concentration, and the values measured by ripplon SLLS are affected
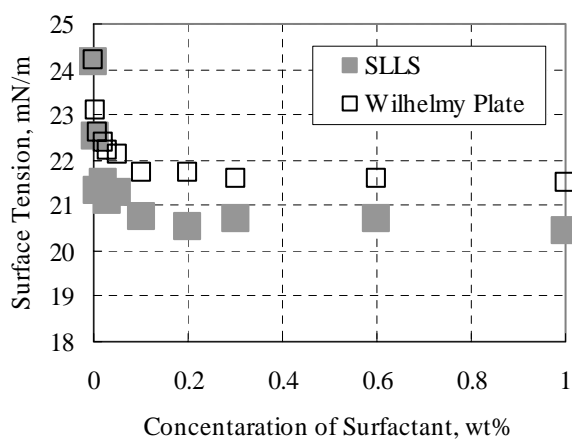

Fig. 4. Measured surface tension as a function of surfactant concentration in MEK.
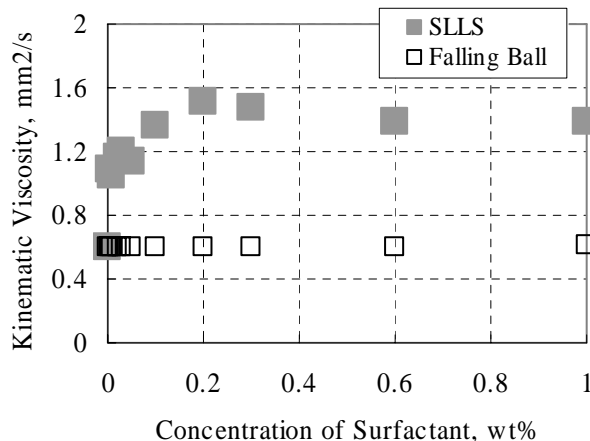

Fig. 5. Measured kinematic viscosity as a function of surfactant concentration in MEK.

by only this surface concentration. This is because ripplon SLLS observes small waves (~nm) only near the surface.

Surface viscoelastic model: Several hydrodynamics models were developed to described the motion of the molecular monolayer-covered interface. The Langevin[4] dispersion relation is used here to extract viscoelastic parameters from the ripplon SLLS power spectrum as follows.

$$\left[(k+m)-\frac{Kk^2}{i\omega\eta}\right]\left[(k+m)\frac{m}{k}-\frac{\sigma k^2}{i\omega\eta}\right]-(k-m)^2=0 \qquad (3)$$

$$m=\sqrt{k^2-i\omega\rho/\eta}, \qquad K=\varepsilon+i\omega\kappa, \qquad \omega=\omega_0+i\Gamma \qquad (4)$$

ω_0, Γ are determined experimentally from the ripplon spectrum. Both ε and κ are determined from Eqs. (3) and (4) by using a numerical technique. Figures 6 and 7 show the surface elasticity and surface viscosity measured under the same conditions as Figs. 4 and 5. The figures show that both the surface elasticity and viscosity increase with a surfactant concentration up to 0.2wt%, and then saturate. The values and changes of surface elasticity and viscosity are very small, but the data in the region of ~0.2wt% is clearly affected by the molecular adsorption of surfactant to the surface. This visocoelascity should have an influence on the results observed in Figs. 4 and 5. The surface viscoelastic characteristics with different kinds of polymers will be investigated more closely, and they will confirm the accuracy of the observed values quantitatively.
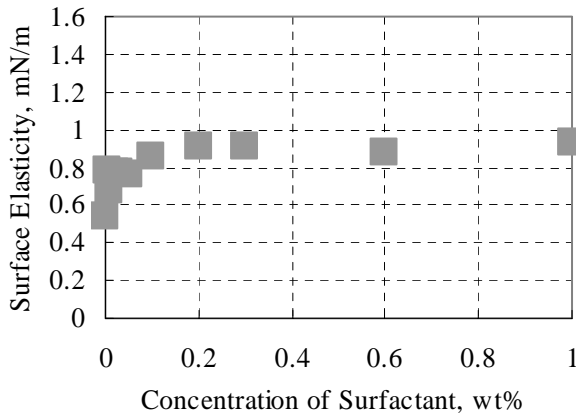

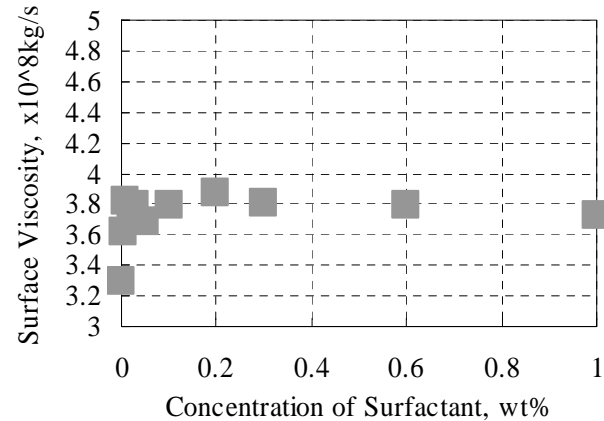Fig. 6. Measured surface elasticity of MEK-surfactant solutions.

Fig. 7. Measured surface viscosity of MEK-surfactant solutions.

References
1. T. Nishio and Y. Nagasaka, *Int. J. Thermophys.*, 16(5), (1995), 1087.
2. Y. Sugahara and Y. Nagasaka, *Proc. 7th Asian Thermophys. Prop. Conf.*, Hefei (China), (2004), 116.
3 E. H. Lucassen-Reynders and J. Lucassen, *J. Adv. Colloid Interface Sci.*, 2, (1969), 347.
4. Dominque Langevin, *Light Scattering by liquid surfaces and complementary techniques*, Marcel Dekker, Inc, New York, (1992).