

Spreading Kinetics of Poly(diisobutylene maleic acid) at the Air–water Interface

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Abstract : The surface rheological properties of polymer monolayer show complicated non-linear viscoelastic flow phenomena when they are subjected to spreading flow. These spreading flow properties are controlled by the characteristics of flow units. The kinetics of the formation of an interfacial film obtained after spreading poly(diisobutylene maleic acid) at air–water interface were studied by measuring of the surface pressure with time. The experimental data were analyzed theoretically according to a nonlinear surface viscoelastic model. The values of dynamic modulus, static modulus, surface viscosities and rheological parameters in various area/ monomer were obtained by applying experimental data to the equation of nonlinear surface viscoelastic model.

Keywords : surface rheological properties, non-linear surface viscoelastic model, poly(diisobutylene maleic acid), spreading kinetics, air–water interface

1. Introduction

The study of spreading rates at high surface pressures is important to obtain information about the stabilities of insoluble monolayers[1]. Polymer film desorption is also important to the establishment of an equilibrium, in surfactant solution[2]. In addition to this dissolution process, the instantaneous, non equilibrium, molecular configurations reached by a continuous compression, also contribute to the monolayer metastability[3]. After a sudden interruption of the compression, the molecules in the film will reorganize spontaneously into a state of lower Gibbs energy, at a lower surface pressure or area.

Reorganization rates may therefore yield important information on molecular conformations in monolayers subject to different perturbations. Unlike dissolution, the magnitude of reorganization strongly increases with the compression speed[4]. The surface rheological properties of polymer monolayer show complicated nonlinear viscoelastic flow phenomena when they are subjected to spreading flow. These spreading flow properties are controlled by the characteristics of flow units.

The stability and rheology of many complex fluids depends on the physical properties of interfacial films. C. Cicuta investigate the surface viscoelasticity of proteins spread surface monolayers using a recently discovered method[5]. Surface viscoelasticity is known to play a key role in slowing down or preventing

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droplet coalescence. Coalescence is a process that reduces the interfacial area, thus if a film is present, it will be compressed[6]. The kinetics and equilibrium properties of a variety of monolayer penetration systems have been investigated and were the subject of a recent review[7]. Interfacial shear rheology is powerful tool for investigating the structure of Langmuir monolayers at the air-water interface. It can also provide valuable information about the formation and structure of adsorbed layers at that interface[8].

In this study, the kinetics of the formation of an interfacial film obtained after spreading poly(diisobutylene maleic acid) at air-water interface were studied by measuring the evolution of the surface pressure with time. The experimental data were analyzed theoretically according to a nonlinear surface viscoelastic model. The values of dynamic modulus, static modulus, surface viscosities and rheological parameters in various area/monomer were obtained by applying experimental data to the equation of nonlinear surface viscoelastic model.

2. Theory

The non-linear surface viscoelastic model and the model of surface hole for the activation free energy curves of flow unit put forward by Hahn and his colleagues, shown in Figure 1 and Figure 2[9]. This model consists of a spring and infinite number of non-Newtonian Maxwell elements coupled in parallel. As can be seen, it necessarily possesses many relaxation times and surface shear modulus. For real viscoelastic polymeric materials, we postulate the existence of a continuous spectrum of relaxation times. The concept that a continuous distribution of relaxation times should be required to represent the behavior of real system would seem to follow quite naturally since we already know real polymeric systems also

exhibit distribution in molecular weight, hole distance of flow segments, crystallite size, conformational size, etc. In this model, the dashpots follow a hyperbolic sine law of non-Newtonian viscosity. If the number of hyperbolic sine law non-Newtonian elements is allowed to become infinite with the characteristic parameter becoming continuous function of relaxation time, the summation over the differential elements of the model can be replaced by an integration over all relaxation times. Assuming that relaxation times τ_i are continuous distribution, the following integral equation of nonlinear surface viscoelastic model is obtained.

$$\Pi(t) = \Pi_e + \int \tanh^{-1} \left[\tanh \left\{ \frac{1}{2} \alpha (\Pi_0 - \Pi_e) \right\} \exp \left(- \frac{\alpha G}{\beta} t \right) \right] d\beta \quad (1)$$

The surface rheological parameters, dynamic elastic modulus G_1 , static elastic modulus G_e , surface shear modulus α , surface viscosity η , surface diffusion coefficient D and relaxation time τ was calculated by the following equations.

$$G_1 = \frac{\Pi_0 - \Pi_e}{S_c} \quad (2)$$

$$G_e = \frac{\Pi_e}{S_c} \quad (3)$$

$$\alpha = \frac{\lambda \lambda_2 \lambda_3}{2kT} \quad (4)$$

$$\eta = \frac{\beta \Pi_e}{\sinh \alpha \Pi_e} \quad (5)$$

$$D = \frac{\lambda_1 kT \sinh \alpha \Pi_e}{\lambda_2 \lambda_3 \beta \Pi_e} \quad (6)$$

$$\tau = \frac{\beta}{\alpha G_1} \quad (7)$$

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$$\frac{1}{\beta} = \frac{2\lambda k'}{\lambda_1} = \left(\frac{2\lambda}{\lambda_1}\right)\left(\frac{kT}{h}\right)\exp\left(-\frac{\Delta G^\ddagger}{RT}\right) \tag{8}$$

$$\begin{aligned} \ln \beta T &= \left(\frac{\Delta G^\ddagger}{RT}\right) + \ln\left(\frac{\lambda_1}{2\lambda}\right)\left(\frac{h}{k}\right) \\ &= \left(\frac{\Delta H^\ddagger}{RT}\right) - \left(\frac{\Delta S^\ddagger}{R}\right) + \ln\left(\frac{\lambda_1}{2\lambda}\right)\left(\frac{h}{k}\right) \end{aligned} \tag{9}$$

Here, λ , λ_1 , λ_2 and λ_3 are customary parameters in Eyring's theory of spreading flow, λ , and λ_1 , are the length of hole swept out by the motion of spreading flow segments and the length of the flowing segment, respectively. $\lambda \lambda_1 \lambda_2$ is surface shear volume. From equation (9), the activation free energy, activation entropy and activation enthalpy for the surface flow process was obtained. Derivation of the equation of nonlinear surface viscoelastic model is flowing.

In this model, dashpots strain rate

$$\frac{dS}{dt} = \frac{1}{\beta_i} \sinh(\alpha_i \Pi_i) \tag{10}$$

springs strain rate

$$\frac{dS}{dt} = \frac{1}{G_i} \frac{d\Pi_i}{dt} \tag{11}$$

for the non-linear surface viscoelastic model

$$\frac{dS}{dt} = \sum_{i=1}^N \frac{1}{G_i} \frac{d\Pi_i}{dt} + \sum_{i=1}^N \frac{1}{\beta_i} \sinh(\alpha_i \Pi_i) \tag{12}$$

strain rate for the spring of equilibrium surface pressure

$$\frac{dS}{dt} = \frac{1}{G_e} \frac{d\Pi_e}{dt} \tag{13}$$

total surface pressure

$$\Pi(t) = \Pi_e + \sum_{i=1}^N \Pi_i \tag{14}$$

on differentiation by time t

$$\begin{aligned} \frac{d\Pi(t)}{dt} &= \frac{d\Pi_e}{dt} + \frac{d\sum_{i=1}^N \Pi_i}{dt} \\ &= G_e \frac{dS}{dt} + \sum_{i=1}^N G_i \frac{dS}{dt} - \sum_{i=1}^N \frac{G_i}{\beta_i} \sinh(\alpha_i \Pi_i) \end{aligned} \tag{15}$$

$$\begin{aligned} \frac{d\Pi(t)}{dt} &= \left(G_e + \sum_{i=1}^N G_i\right) \frac{dS}{dt} \\ &\quad - \sum_{i=1}^N \frac{G_i}{\beta_i} \sinh \alpha_i (\Pi(t) - \Pi_e) \end{aligned} \tag{16}$$

In constant strain S_c , $dS/dt = 0$

$$\frac{d\Pi(t)}{dt} = -\sum_{i=1}^N \frac{G_i}{\beta_i} \sinh \alpha_i (\Pi(t) - G_e S_c) \tag{17}$$

$$\sum_{i=1}^N \frac{d\Pi(t)}{\sinh \alpha_i (\Pi(t) - G_e S_c)} = -\sum_{i=1}^N \frac{G_i}{\beta_i} dt \tag{18}$$

on integration

$$\sum_{i=1}^N \ln \tanh \alpha_i \frac{(\Pi(t) - G_e S_c)}{2} = -\sum_{i=1}^N \frac{G_i}{\beta_i} t + C \tag{19}$$

as boundary condition, initial surface pressure

$$\Pi_0 = \left(G_e + \sum_{i=1}^N G_i\right) S_c \quad (t = 0)$$

at $t=\infty$, $\Pi_e = G_e S_c (t = \infty)$

The integral constant is given by the boundary conditions

$$C = \sum_{i=0}^N \ln \tanh \alpha_i \left(\frac{\Pi_0 - \Pi_e}{2}\right) \tag{20}$$

By substituting Eq.(11) into Eq.(10), we obtain the equation for relaxation

$$\Pi(t) = \Pi_e + \sum_{i=1}^N \frac{2}{\alpha_i} \tanh^{-1} \left[\tanh \left\{ \frac{1}{2} \alpha_i (\Pi_0 - \Pi_e) \right\} \exp \left(- \frac{\alpha_i G_i}{\beta_i} t \right) \right] \quad (21)$$

For monodisperse

$$\Pi(t) = \Pi_e + \int \tanh^{-1} \left[\tanh \left\{ \frac{1}{2} \alpha (\Pi_0 - \Pi_e) \right\} \exp \left(- \frac{\alpha G}{\beta} t \right) \right] d\beta \quad (22)$$

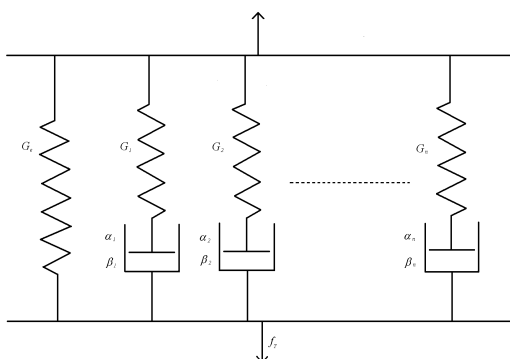


Fig. 1. Nonlinear surface viscoelastic model.

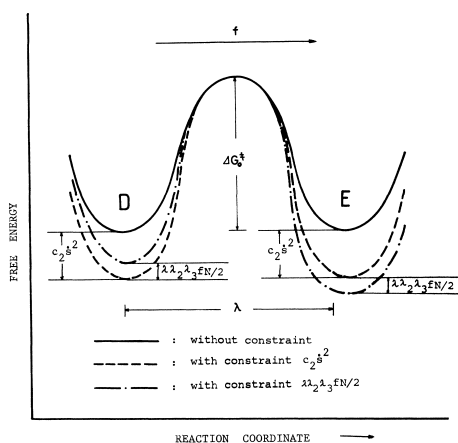


Fig. 2. The model of surface hole for the activation free energy curves of flow unit.

3. Experimental

Spreading was performed during a period of about 10 sec using a micro syringe. Kinetics of surface film formation were recorded by following the variations with time of the surface pressure. Zero time corresponds to the beginning of the spreading procedure. The surface pressure of monolayer surfaces until the time reached an apparent equilibrium state was measured by the Wilhelmy plate technique using a sand-blasted platinum plate attached to a Cahn 2000 electrobalance (Cahn Co., Paramount, CA) and a Teflon trough that was mounted on an aluminum base and enclosed in a box to reduce drafts and dust and to maintain a high relative humidity (>80%). The temperature in the box for all experiments was 23–25 °C and the temperature of the aqueous subphase was controlled with a thermostated water bath (Lauda model RM6) which circulated water through a glass coil at the bottom of the trough. A mixed spreading technique, where polymer was dissolved into a single spreading solution, was used to spread the lipid mixtures. The equilibrium surface tension was determined when the change in mass of the plate was less than 1 mg (or less than 0.2 mN/m) in 1 h. The area per molecule was varied by three methods: (i) continuous addition of lipid molecules (after the attainment of equilibrium) to a surface of constant area, (ii) stepwise reduction of surface area with a movable barrier with a fixed amount of deposited material (compression method), and (iii) repeated cleaning and spreading of the monolayer film to a given surface concentration (single-shot method). Spreading monolayers required equilibration times after spreading that ranged from a few hours at surface pressures less than 8 mN/m to 18–24 h at higher surface pressures.

4. Results and Discussion

Relaxation kinetics was studied in systems at 298 K, after compressing the polymer monolayers at a constant speed up to target surface area. Then the compression was stopped, and the π - t relaxation were recorded. The π - t relaxation has been used to study reorganization kinetics[10, 11] and icollapse kinetics[12] in some instances. The surface pressure relaxation curves of poly(diisobutylene maleic acid) at air–water interface of various surface areas are shown in Figure 3–8. As shown in the figures, the surface pressure decays gradually to equilibrium value, Π_e , with time at a constant strain. The quantity, Π_e , is defined as the surface pressure at $t = \infty$. Then final surface pressure Π_e is obtained by extrapolating the straight line portion of the Π vs. $1/t$ to zero. The surface pressure on the low surface area increase to Π_e very slowly, whereas on the high surface area decay to Π_e and if a limiting surface pressure is really reached it must be due to the crystallite segments. The observed decay of surface pressure is, therefore, due to the relaxation of bonds in air–water interface. Of course it will be shown that the suitable distribution of relaxation times and the molecular weight distribution, which have a natural basis in terms of molecular behavior, can also explain the observed data. The surface pressure–area curve of poly(diisobutylene maleic acid) at air–water interface of equilibrium is shown in Figure 9.

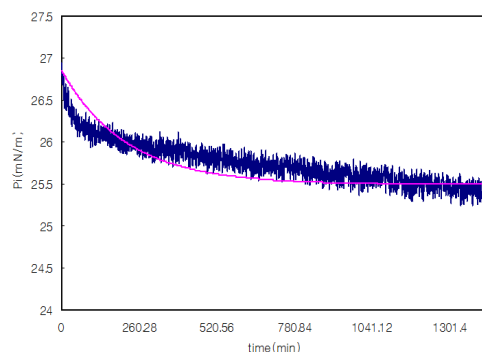


Fig. 3. Surface pressure–time curve of spreading poly(diisobutylene maleic acid) at air–water interface of 0.3756 nm^2 area/monomer.

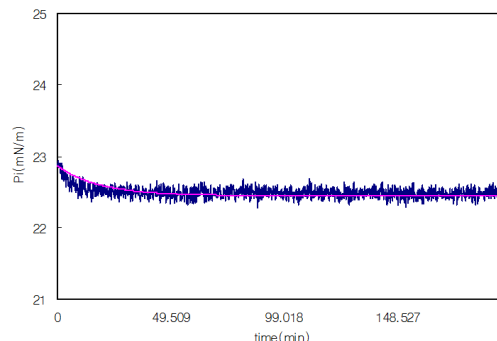


Fig. 4. Surface pressure–time curve of spreading poly(diisobutylene maleic acid) at air–water interface of 0.4198 nm^2 area/monomer.

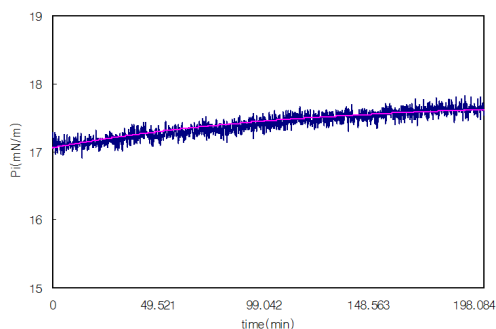


Fig. 5. Surface pressure–time curve of spreading poly(diisobutylene maleic acid) at air–water interface of 0.4686 nm^2 area/monomer.

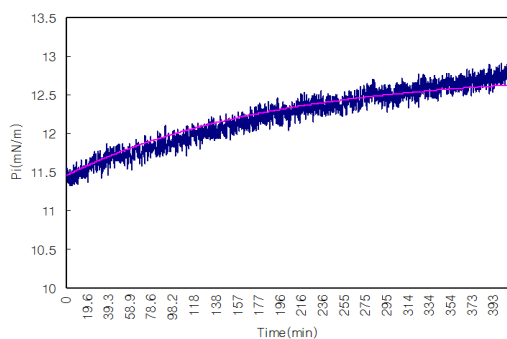


Fig. 6. Surface pressure–time curve of spreading poly(diisobutylene maleic acid) at air–water interface of 0.5200 nm^2 area/monomer.

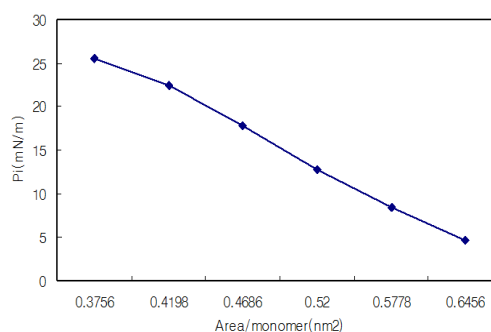


Fig. 9. Surface pressure–area curve of spreading poly(diisobutylene maleic acid) at air–water interface.

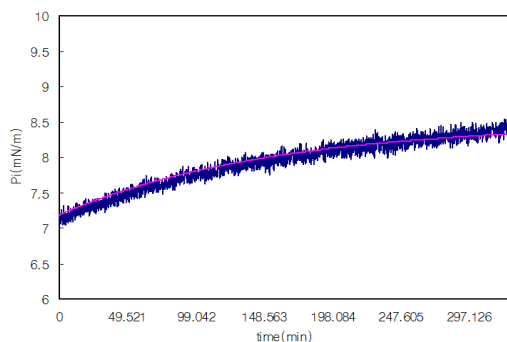


Fig. 7. Surface pressure–time curve of spreading poly(diisobutylene maleic acid) at air–water interface of 0.5778 nm^2 area/monomer.

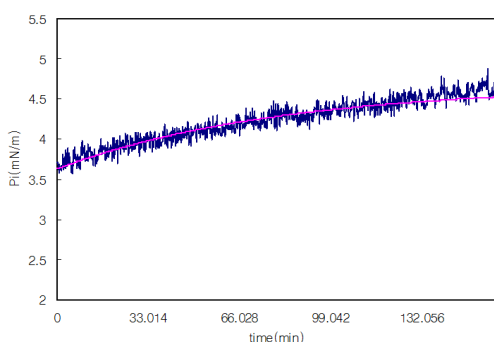


Fig. 8. Surface pressure–time curve of spreading poly(diisobutylene maleic acid) at air–water interface of 0.6456 nm^2 area/monomer.

The values of dynamic modulus, static modulus, surface viscosities and rheological parameters in various area/monomer were obtained by applying experimental data to the equation of nonlinear surface viscoelastic model as shown in Table 1. The static elastic modulus decreases with increasing surface area. At higher surface area, the surface tension developed at given spreading extension becomes smaller, in keeping with the reduction in relaxation modulus with rise in surface area. The change in the free energy of activation would be small because of the heat absorbed by the liberated water molecules. In spreading of polymer solution, there are two relaxation processes superimposed upon each other, one due to thermal agitation and the other due to absorption of extra moisture as the polymer solution is spreaded. The time at which there is a rapid change in slope of the relaxation curve indicates the completion of relaxation caused by the extra moisture absorbed on spreading the polymer, and it is assumed that any further relaxation is due solely to thermal agitation.

Table 1. The values of dynamic modulus G_1 , static modulus G_2 , viscosity modulus α and relaxation time β in various area/monomer

Parameters	Area/monomer (nm ²)					
	0,6456	0,5778	0,52	0,4686	0,4198	0,3756
G_1 (mN/m)	-10.338	-12.936	-13.210	-6.780	4.162	14.570
G_2 (mN/m)	26.819	33.818	38.775	45.430	43.496	27.060
$\alpha \times 10^2$ (m/mN)	-7.13	-6.847	-5.866	-5.445	4.950	4.500
β (min)	58.475	134.794	146.850	42.2436	3.7531	4.9662 232.724

5. Conclusion

The theoretical equation for the nonlinear surface viscoelastic spreading kinetics was derived from the Ree-Eyring and Maxwell non-Newtonian model. This model consists of infinite number of hyperbolic sine law Maxwell elements coupled in paralleled plus a spring. The kinetics of the formation of an interfacial film obtained after spreading poly(diisobutylene maleic acid) at air-water interface were studied by measuring the evolution of the surface pressure with time. The values of dynamic modulus, static modulus, surface viscosities and rheological parameters in various area/monomer were obtained by applying experimental data to the equation of nonlinear surface viscoelastic model. The static elastic modulus decreases with increasing surface area. At higher surface area, the surface tension developed at given spreading extension becomes smaller, in keeping with the reduction in relaxation modulus with rise in surface area.

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