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A perturbation analysis on solid polymer surfaces

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ABSTRACT

A linear stability model was formulated to analyze the perturbation of solid polymer surfaces. Surface energy and thermal stress were considered as the main variables. The surface tends to more unstable as the temperature increase. This is interpreted as the dominancy of the lattice vacancy diffusion over surface mass diffusion and the increase in thermal stress.

1. Introduction

Nearly all processes of materials involve the use of heat. Depending on the material system of interest, the thermal action can bring forth various outcomes. In this work, we consider the morphological stability of solid polymer surfaces. Regarding the application aspects, the surface morphologies are directly related to the performance of the appliances or devices in which polymers are used [1,2]. A number of factors contribute to the morphological instability of the polymer surfaces, such as the capillary effect, residual solvent, viscosity and diffusion [3–6]. The fabrication process of polymer film applications includes a step of "baking". Thus, the thermal effect is expected to have a strong influence on the surface morphology.

Here we address the thermally induced instability on a polymer surface. The instabilities of surfaces have been a topic of interest both theoretically and experimentally [7–11]. First, to describe the change in the amplitude of the surface fluctuation, we introduce a linear stability model. To simplify the description of the fluctuation, we consider an isotropic system, in which the movement of the polymers is postulated as being diffusive. Indeed, although polymer systems have a high internal degree of freedom, studies show that the movement of polymers is diffusive, with $t^{1/2}$ kinetics [12–15]. In the diffusion framework two fluxes are important, the mass and the vacancy fluxes. To ensure the solid state of the polymer, we considered a temperature range ($T < 120$ °C) which is below the glass transition temperature of typical polymers. Second, using the fluctuation equation and realistic material parameters, we discuss the morphological instabilities of polymer surfaces. Finally, some technical strategies to suppress surface instability are suggested.

2. Experiments

To investigate the morphological changes of solid polymer surfaces, we spin-coated poly 4-vinyl phenol (PVP, Aldrich) onto a SiO_2/Si(1 0 0) surface. PVP was chosen as it is widely used in organic electronics. The spin-coating solution was prepared by dissolving PVP in *N*,*N*-dimethylformamide (Aldrich). The spin-coating was conducted at a condition of 2500 RPM-3 min. The baking temperatures (T_bs) were 50 °C, 80 °C, 100 °C and 120 °C. The surface morphologies of the PVP were obtained using atomic force microscopy (AFM). Fig. 1 shows AFM images of PVP film surfaces. As can be noticed the surface roughens significantly as T_b increases.

3. Formulations of perturbation

We consider a surface with sinusoidal waviness. Taking coordinate x parallel to the surface, the surface fluctuation is expressed as:

$$h(x,t) = h_0 + h(t)\sin(\omega x) \quad (1)$$

Here, h, t and $\omega(=2\pi/\lambda)$ denote the amplitude, the time and the wave vector, respectively. h_0 is the initial amplitude. To investigate the morphological stability, the rate change in the amplitude of the fluctuation is considered. If the rate change in the amplitude $(\partial h(x,t)/\partial t)$ is positive the fluctuation grows as time elapses. In the opposite case, the fluctuation decays as time elapses. The presence of thermal stress (σ) and curvature (κ) causes diffusion along the surface, leading to a change in the amplitude of the surface wave. In the

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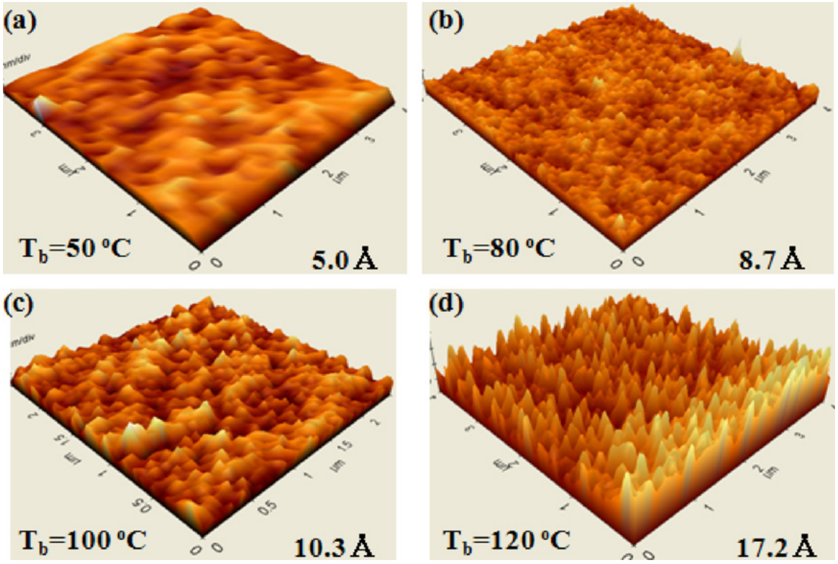

Fig. 1. AFM images of PVP surfaces. Bakings were performed at (a) 50 °C, (b) 80 °C, (c) 100 °C and (d) 120 °C.

following, we focus on formulating the fluxes of the mass and the vacancy. The mass conservation condition at a surface element dictates proportionality of the divergence to the surface velocity [16].

$$\frac{\partial h(t)\cos(\omega x)}{\partial t} = -\Omega\nabla\cdot J = -\Omega\left(J_v + \frac{\partial J_s}{\partial x}\right) \tag{2}$$

Here, Ω, J_s and J_v denote the molecular volume, surface diffusion flux and vacancy flux, respectively. Thus, the remaining task is to derive the expressions for J_s and J_v. In this work, we adopted the approach formulated by Hsia [17].

First, we consider the J_s component, which is related to the chemical potential (μ) as the follows [18]:

$$J_s = -\frac{D_sC_s}{kT}\frac{\partial\mu}{\partial x} \tag{3}$$

Here, D_s and C_s are the surface diffusivity and the number of diffusing particles per unit area, respectively. k is the Boltzmann constant and T is the absolute temperature. μ may be expressed as the linear sum of the strain energy (U) and the curvature effect [16].

$$\mu = (U - \kappa\gamma)\Omega \tag{4}$$

The variation of U along a wavy surface is in a form of a trigonometric series [19].

$$\begin{aligned} U(x,t) &= \frac{(1-\upsilon)\sigma^2}{4G}\left[1 - 8\pi\sum_{1}^{n}h_n(t)\omega\cos(\omega x)\right] \\ &\approx \frac{(1-\upsilon)\sigma^2}{4G}[1 - 4h(t)\omega\cos(\omega x)] \end{aligned} \tag{5}$$

where υ and G are the Poisson ratio (= 1/3) and the shear modulus, respectively. With Eq. (1) and κ as $(\partial h^2(x,t)/\partial x^2)$ the curvature effect is obtained as follows:

$$\gamma\frac{\partial\kappa}{\partial x} = \gamma\frac{D_sC_s}{kT}h(t)\sin(\omega x)\omega^3 \tag{6}$$

Inserting (5) and (6) into (3) gives the J_s.

$$J_s = \frac{D_sC_s}{kT}h(t)\sin(\omega x)\left[\gamma\omega^3 - \frac{(1-\upsilon)\sigma^2}{G}\omega^2\right] \tag{7}$$

Due to the presence of curvature and σ, a pressure difference (ΔP) develops beneath the surface, which induces vacancy diffusion. The vacancy concentration underneath the surface can be determined using the Gibbs–Thomson equation [20].

$$C_v = C_v^0 + \frac{\Delta P\Omega}{kT}C_v^0 \tag{8}$$

Here, C_v is the vacancy concentration beneath the wavy stressed surface, and C_v^0 is that of beneath the flat relaxed surface. The ΔP was derived under a plane strain condition [17].

$$\Delta P = -\frac{2}{3}(1+\nu)\sigma h(t)\omega\cos(\omega x) \tag{9}$$

Inserting (9) into (8) and applying the Laplace equation ($\bigtriangledown^2 C_v = 0$) gives the J_v.

$$J_v = \frac{D_vC_v}{kT}h(t)\cos(\omega x)\left[\gamma\omega^3 - \frac{2(1-\upsilon)\sigma}{3}\omega^2\right] \tag{10}$$

Inserting (7) and (10) into (2) gives the expression for the rate change in the amplitude.

$$\begin{aligned} \ln\left(\frac{h(t)}{h_0}\right) &= \frac{D_sC_s}{kT}\Omega^2\omega^3\left(\frac{1-\upsilon}{G}\sigma^2 - \gamma\omega\right) \\ &\quad + \frac{D_vC_v}{kT}\Omega\omega^2\left(\frac{2(1-\upsilon)}{3}\sigma - \gamma\omega\right) \end{aligned} \tag{11}$$

The second and the fourth terms, which contain γ, always contribute to the decay of the rate change in the amplitude. Depending on the associated diffusion, σ contributes differently to the rate change. The first term, which is related to the surface diffusion, is always positive and thus induces surface roughening. The third term, which is related to vacancy diffusion, can contribute both to the flattening and the roughening of the surface. Flattening appears when the sign of σ is negative, i.e., compressive, whereas roughening appears when the sign of σ is positive, i.e., tensile. Fig. 2 illustrates the mass transport components and the associated flow directions on a sinusoidal surface.

4. Results and discussion

Here, we analyze the morphological stability of surfaces as a function of the temperature. The coefficient of thermal expansion (C), the Young's modulus (E) and Poisson ratio (υ) are taken as C = 0.00012/K, E = 0.1 GPa and υ = 1/3 [21–23]. With such values it