Nonequilibrium behavior of polymer nano films cast from different solvents

Xiao Fan, Jinghong Ma and Yu Ma*

State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, P.R. China

*Corresponding author’s e-mail: yma@dhu.edu.cn

Abstract. Properties of materials are largely determined by the processing conditions. This is especially true of polymers, which typically have much longer relaxation times than processing times and therefore possess out-of-equilibrium chain conformations. Here, we demonstrate that the nonequilibrium behavior of polymer nano films can be tuned by controlling the processing pathways. Films cast from different quality of solvents were aged at room temperature for various times, and then carried out the dewetting experiment above the glass transition temperature. The residual stress and relaxation time strongly depend on the quality of the solvents, and the differences may be caused by the boiling point and interaction parameter. This work offered a pathway for preparing a stable nano film, which is crucial for the durability of nanomaterials and devices.

1. Introduction

The processing condition is believed to have a huge impact on the behavior of polymeric samples, especially in the film processing field, which resulting in residual stresses due to fast solvent loss, leading to a nonequilibrium state of the chain conformations[1-3]. This in turn affects macroscopic properties of matters, such as viscoelastic properties. Film thickness, which is controlled by different spin speed or concentration of the polymer solutions, has been considered as one of the most significant aspect for the difference of out-of-equilibrium states[4]. Besides, the characteristic aging time varied strongly with the quality of the solvents, which may be attributed to distorted chain conformations in the as-cast films[5].

Dewetting experiments have been proven to be a simple and high-efficiency method for providing the detailed rheological properties of polymer films. Dewetting, as a prevailing phenomenon for thin films or coatings, occurs when the thin films are heated above its glass transition temperature Tg or placed in the solvent vapor atmosphere. It is generally believed that the dewetting velocity is derived from the balance between the viscoelastic and capillary stresses, and the variations in dewetting velocity are caused by preparation-induced differences.

In this work, we focus on revealing effects of quality of solvents on nonequilibrium behavior of polystyrene (PS) nano films via dewetting experiments[1, 4, 6-8]. To this end, spin-coating method was employed to form PS nano films on a hydrophobic substrate polydimethylsiloxane (PDMS), and different quality of solvents were used. For quantitatively studying the film properties caused by the preparation, we relied on dewetting experiments after aging for different periods to realize the nonequilibrium behavior of polymer films.
2. Physics of dewetting of polymer films

The spreading coefficient, $S$, describes the ability of the drop to spread on or dewet from a surface, and can be obtained by calculation[9]. For a film A, on a substrate B, $S$ is given by Young’s equation: $S = \gamma_B - \gamma_{AB} - \gamma_A$, where $\gamma_A$, $\gamma_B$, and $\gamma_{AB}$ are the energies of the A and B surfaces and the AB interface, respectively. Equation 1 was used to calculate the interface tension, $\gamma_{AB}$:

$$\gamma_{AB} = \sqrt{\left(\gamma_A^d\right)^2 - \left(\gamma_A^p\right)^2} + \sqrt{\left(\gamma_B^d\right)^2 - \left(\gamma_B^p\right)^2}$$

(1)

Where $\gamma^d$, $\gamma^p$ are the dispersion force and polarity force, respectively. For PS/PDMS system, the value of PS and PDMS were shown in Table 1[10]. Therefore, the calculated $S$ was -25.68 mN/m. The negative spreading coefficient indicated the instability of the nanofilms and had the tendency to dewetting.

| Material | $\gamma$ | $\gamma^d$ | $\gamma^p$ |
|----------|----------|------------|------------|
| PS       | 40.7     | 34.5       | 6.1        |
| PDMS     | 19.8     | 19.0       | 0.8        |

3. Experimental section

Materials. PS (Mw = 192000 g mol$^{-1}$) were purchased from Sigma-Aldrich. Ethyl acetate (EA), Methyl Ethyl Ketone (MEK), 1,3-Dioxolane and 3-Pentanone were used to prepare PS solutions. All reagents were analytical grade and used without further purification. The detailed cleaning pathways of glass substrates and silicon wafers were described in our previous works[9].

PDMS (Sylgard 184, Dow Corning Corporation) kit with base and curing agent was used as received. The PDMS base and curing agent of w/w ratio 10:1 was firstly mixed vigorously and then degassed in vacuum for 15 min. PDMS substrates with smooth surfaces were prepared by coating mixtures onto glass substrates and then cured in the oven at 85 ℃ for 3 h.

Film preparation. In current work, we focused on the films of thickness $h = \text{ca. 100 nm}$ that prepared by spin-coating PS solution on PDMS substrates. Film thicknesses were controlled by changing the initial concentration of the solution, while the spin rate was fixed at $\omega = 3000$ rotations per minute (rpm). Thicknesses of films were measured by the ellipsometer (ELLIP/SR). In the period of spin-coating process, the substrates rotated at high speeds, and the centrifugation force dominates the thinning of the film in the early stage (hydrodynamic thinning), followed by evaporation in the later stage. It should be noted that, there was no significant difference between the air-dried and vacuum-dried samples[4-5]. Therefore, the non-equilibrium effects observed in this work were not due to the possible trapped solvent molecules, and the experiments were performed without further vacuum drying.

Dewetting experiment. Dewetting of PS films was induced by heating samples to 140 ℃ on a hot stage (Simplex Scientific), i.e., to a temperature above the glass transition temperature. The dewetting process was captured in situ and in real time by optical microscopy (BK-POLR-TR). A series of images were captured with a CCD camera (Figure 1).

Figure 1. Optical micrographs showing the time evolution of dewetting for the films of thickness $h \approx 100$ nm cast from EA. The dewetting experiments were performed at $T_{\text{dew}} = 140$ ℃. Scale bars are 100 µm.
4. Results and discussion

In the first series of experiments, films were spin-coated from EA at 25 ℃, then stored (aged) at room temperature for different periods, followed by dewetting experiments above Tg. Figure 2A presents typical graphs for the radius (R) of a dewetting hole as a function of dewetting time (t\textsubscript{dew}) at various values of aging time (t\textsubscript{aging}). An increase in t\textsubscript{aging} led to a slowing down of the growth of dewetting holes in 100 nm PS films. At the beginning of dewetting, in Figure 2B, it is observed that the initial dewetting velocity is approximately constant over a period of time, which arise from that a mature rim has not yet formed, a constant dewetting velocity is expected. After the constant region, V\textsubscript{dew} decreased according to a power-law V\textsubscript{dew} \sim t\textsubscript{dew}^{-\alpha} with an exponent \alpha \approx -1, which agreed with the value reported by Reiter[8]. To quantify the changes caused by aging, we measured R for a given dewetting time as a function of t\textsubscript{aging}. As shown in Figure 2C, R showed a decay with aging time that could be fitted by a single exponential. Meanwhile, we present additional curves of the initial dewetting velocity as a function of t\textsubscript{aging}, which suggested an exponential decay (Figure 2D). Thus, we fitted an exponential function to the measured values of R and V using the following form

\[ y(t) = (y(0) - y(\infty)) \exp\left(-\frac{t}{\tau}\right) + y(\infty) \]  

(2)

with y(t) = R(t) = V(t), or y0 = R(0) = V(0), or y\infty = R(\infty) = V(\infty). The resulting relaxation times (\tau\textsubscript{res}) were very similar (\tau\textsubscript{res} = 21.6 h from Figure 2C and 23.7 h from Figure 2D). This decrease in dewetting dynamics reflects a reduction of the driving forces for dewetting and strongly suggests a decrease in the amount of residual stress within the film caused by physical aging.

Assuming that all residual stresses (\sigma\textsubscript{res}) were released, the ratio of dewetting velocity in as-prepared film and fully aged film V(0)/V(\infty) should be equal to the ratio of total stresses and capillary stress (\sigma\textsubscript{cap})[8-9].

\[ \frac{V(0)}{V(\infty)} = \frac{\sigma_{\text{res}} + \sigma_{\text{cap}}}{\sigma_{\text{cap}}} \]  

(3)

\sigma\textsubscript{cap} was 256.8 kPa based on \sigma\textsubscript{cap} = |S|/h. Thus, \sigma\textsubscript{res} in PS nano film cast from EA was 188.8 kPa.

Figure 2. (A) Hole radius (R) as a function of dewetting time (t\textsubscript{dew}) after being aged at room temperature for different periods (t\textsubscript{aging}). The PS nano film was cast from EA. The operating temperature of the dewetting experiment is 140 ℃. (B) Dewetting velocity V\textsubscript{dew} (t\textsubscript{dew}) on logarithmic scales as a function of dewetting time t\textsubscript{dew} for different aging times. (C) Hole radii taken at three constant times (dashed lines in part A) follow an exponential decay as a function of aging time. (D) Semi-logarithmic representation of the initial dewetting velocities vs t\textsubscript{aging}. Red solid lines represent fits to Equation 2.
After that, the experiment in Figure 2 was repeated, and the characteristic relaxation times for aging at room temperature was determined for all sample series.

Figure 3. Semi-logarithmic representation of the initial dewetting velocities $v$ vs $t_{aging}$ prepared by different solvents: (A) MEK, (B) 1,3-dioxolanem and (C) 3-pentanone. Solid lines represent fits to Equation 2.

As shown in Figure 3, all samples follow the exponential decay in the aging experiment at room temperature, and the residual stress and relaxation time calculated by Equation 2 and Equation 3 were shown in the figure, indicating that the PS nano films cast from different solvents led to the difference in the equilibrium state. For PS nano films cast from 1,3-dioxolane, a relatively high residual stress and short relaxation time were found.

For further understand the sources of diverse non-equilibrium states of polymer nano films prepared by different solvents, boiling point of solvent and the Flory-Huggins interaction parameter between PS and solvent were introduced to explain the diversity. Figure 4A shows that PS nano film cast from different quality of solvent possesses dissimilar residual stress, i.e., locates in different equilibrium states. The drying time of the film during spin-coating varied and is governed by the boiling point of the solvent. A higher boiling point determines the relatively low evaporation rate, and a longer film formation time allows more time for the chains to equilibrate during the solvent evaporation process[11]. Besides, the Flory-Huggins parameter $\chi$ has been one of the most widely used quantities, characterizing a variety of polymer-solvent and polymer-polymer interactions, and was calculated by Equation 4. If $\chi < 0.5$, the polymer should be soluble.

$$\chi = \frac{V_{mol}[(\delta_{D2}\delta_{D1})^2+0.25(\delta_{D2}\delta_{P1})^2+0.25(\delta_{H2}\delta_{H1})^2]}{RT}$$

where $V_{mol}$, $R$ and $T$ represent the molar volume of the solvent (mL mol$^{-1}$), the gas constant and temperature (K), respectively. The detailed solubility parameters come from HSPiP software.

Figure 4. The interrelation between residual stress ($\sigma_{res}$) and (A) boiling point, (B) interaction parameter $\chi$ and (C) relaxation time $\tau_{res}$. The dashed lines are for eye guide only.

As can be seen in Figure 4B, the smaller value means a more stretchable chain in the solution. The larger the swollen coil size, the stronger the deformation of the coils in the film, the higher the in-plane tensile stress in the film[5]. Figure 4C illustrates an approximate linear relationship between residual stress and relaxation time, revealing the faster relaxation with a higher residual stress.
5. Conclusions
In summary, four kinds of solvents with different boiling point and interaction parameter with PS were adopted to explored the processing induced nonequilibrium behavior in PS nano films by dewetting experiment. Although the same preparation method, the seemingly identical films are in different non-equilibrium states caused by utilizing various quality of solvent, which arise from the difference in boiling point and interaction parameters, causing the difference in the chain conformations. This work demonstrates the role of the quality of the solvent on the nonequilibrium conformation in the film, and provides a strategy for getting a thermodynamically stable thin film.

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