Communications in Computational Chemistry
Commun. Comput. Chem., Vol. 7, No. 1, 42–49
doi: 10.4208/cicc.2025.62.01
Regular Article

Mechanism for the Inhibition of Dewetting in Polymer Thin Films by Interface Segregation of Single-Chain Nanoparticles

Zhao Qian[1,3], Rui Shi [1,*], Zhongyuan Lu[1] and Hujun Qian[1, 2,*]

[1] *State Key Laboratory of Supramolecular Structure and Materials, Institute of Theoretical Chemistry, College of Chemistry, Jilin University, Changchun 130012, China;*

[2] *Key Laboratory of Material Simulation Methods & Software of Ministry of Education, Jilin University, Changchun 130012, China;*

[3] *National Engineering Research Center for Rare Earth, Grirem Advanced Materials Co.,Ltd, Beijing 100088, China.*

[*] Corresponding authors: shirui816@jlu.edu.cn, hjqian@jlu.edu.cn

Received on 03 March 2025; Accepted on 05 April 2025

Abstract: The inhibition of dewetting in polymer thin films (PTFs) is crucial for their practical applications. Through molecular dynamics simulations, we elucidate the mechanism of interface segregation of single-chain nanoparticles (SCNPs) in inhibiting PTF dewetting. Our study provides atomic-level insights into three key aspects: (1) how SCNP segregation affects the contact angle, (2) how it influences the orientation of matrix chains at the interface, and (3) how the interaction between solvent molecules and cross-linkers within SCNPs influences the dewetting behavior. By employing static droplet and dynamic pre-punched film models, we systematically investigate the effects of SCNP doping concentration and cross-linker-solvent interaction strength. Our results demonstrate that SCNP segregation significantly alters the orientation of linear polymer chains at the interface. In pure polymer films, chain ends preferentially accumulate at the interface due to entropic effects, leading to parallel chain conformations. However, SCNP segregation suppresses this effect, promoting more vertical chain orientations. Furthermore, we find that weaker cross-linker-solvent interactions promote SCNP segregation at the substrate interface, leading to more effective dewetting inhibition. These findings provide fundamental understanding and practical guidance for designing stable polymer thin films through nanoparticle doping.

Key words: polymer thin films, single-chain nanoparticle, dewetting inhibition.

1. Introduction

Polymer thin films (PTFs) on solid substrates have become indispensable in various technological applications, ranging from protective coatings to optoelectronic devices [1-9]. A fundamental challenge in these applications is maintaining film stability and preventing dewetting, particularly for thin films where molecular forces dominate [10-12]. Recent experimental studies have highlighted the potential of nanoparticle doping as an effective strategy for dewetting inhibition [13-22]. Among various nanoparticles, single-chain nanoparticles (SCNPs) have shown particular promise due to their unique structure and compatibility with polymer matrices.[17] However, while experimental observations have established the correlation between SCNP interface segregation and dewetting inhibition, the underlying atomic-level mechanisms remain poorly understood.

Here, by performing comprehensive molecular dynamics simulation, we address this knowledge gap by providing detailed insights into three crucial aspects of SCNP-induced dewetting inhibition. First, we elucidate how SCNP segregation at the interface affects the macroscopic contact angle. Second, we reveal a significant effect on the microscopic orientation of matrix polymer chains. In pure polymer films, chain ends preferentially accumulate at the interface due to entropic effects, resulting in parallel chain conformations. However, SCNP segregation dramatically alters this behavior, promoting more vertical chain orientations at the interface. Third, we investigate the often-overlooked but critical role of solvent/cross-linker interactions in the dewetting process. Specifically, we examine how the interaction strength between solvent molecules and cross-linkers within SCNPs influences the segregation behavior and subsequent dewetting inhibition.

Building upon our previous simulation studies [23,24], as shown in Figure 1, we employ all-polymer nanocomposite films doped with SCNPs, where the chemical similarity between SCNP monomers and polymer matrix components allows us to isolate and examine the specific effects of cross-linker-solvent interactions. Our simulation results reveal that weaker cross-linker-solvent interactions promote more effective SCNP segregation at the substrate interface, leading to enhanced dewetting inhibition. These findings not only provide fundamental understanding of the dewetting inhibition mechanism but also offer practical guidance for optimizing nanoparticle-doped polymer thin films through careful control of solvent-cross-linker interactions and manipulation of chain orientations at interfaces.

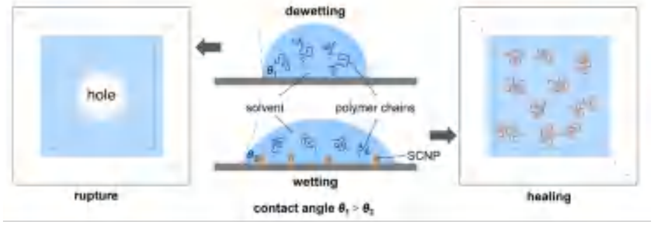

Figure 1. Schematic diagram of polymer film dewetting inhibition by interface segregation of SCNPs.

2. Methods

2.1 Models and parameters

To comprehensively investigate the inhibition effect of segregated single-chain nanoparticles (SCNPs) on polymer chain dewetting, we employ both static (droplet) and dynamic (pre-punched thin film) systems. The static droplet system allows for contact angle measurement to assess wettability, while the dynamic pre-punched film system enables monitoring of hole area evolution as an indicator of dewetting behavior.

Both systems consist of the following components: substrate, linear polymer chains, SCNPs, and solvent. We employ the Kremer-Grest model [25] to simulate polymer chains and SCNPs. With non-bonded interactions described by the Lennard-Jones potential::

$$U(r) = \begin{cases} 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] & \text{for } r < r_{\mathrm{c}} \\ 0 & \text{for } r \geq r_{\mathrm{c}} \end{cases} \quad (1)$$

where ε, σ and r_{c} are the interaction strength, bead size and truncated interaction range respectively. The finitely extensible nonlinear elastic potential is used to describe the bonds in both polymer chains and SCNPs,

$$U(r) = -\frac{1}{2}kr_m^2\log\left[1 - \frac{(r)^2}{r_m^2}\right] + \left\{4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] + \varepsilon\right\} \quad (2)$$

in which k, r_{m} are attractive force strength and maximum bond length, respectively. The second Lennard-Jones term is used to avoid overlapping between bonding pairs, and it is truncated at a cutoff distance of $2^{1/6}\sigma$. All simulations are performed with reduced units, with the energy, the bead diameter, and the bead mass set as $\varepsilon_0 = \sigma_0 = m_0 = 1$. Therefore, the time has a unit of $\tau_0 = \sqrt{m\sigma_0^2/\varepsilon_0}$. In our simulation, r_{c} is fixed at $2.5\,\sigma_0$. For bond potential, k is fixed at $30\ \varepsilon_0/{\sigma_0}^2$, $r_{\mathrm{m}} = 1.5\,\sigma_0$ and $r_0 = 1.0\,\sigma_0$. Interaction strength parameter ε used in our simulation between different components are listed in Table 1.

The values of ε between the different components are determined by the modified Lorentz-Berthelot combination rule [26-28], i.e., $\varepsilon_{ij} = \lambda_{ij}\sqrt{\varepsilon_{ii}\,\varepsilon_{jj}}$. Here, λ is a tunable parameter, typically ranging from 0.2 to 2 [28]. In our simulations, we select values for λ_{SX} within the range [0.5, 1.5], which corresponds to an effective Flory χ approximately spanning from –3 to 3. This interval covers conditions from very good to poor solubility, allowing for reasonable extrapolation of the behavior. All the simulations are performed under *NVT* condition with a time step of $dt = 0.005\,\tau_0$, Nosé-Hoover thermostat is used to control the temperature. All simulations in this work are performed with the GALAMOST package [29].

Table 1. Interaction strength between different bead types in the system.

E	P	X	S	W
P	1.0	1.0	1.5	0.5
X		1.0	0.5~1.5[a]	1.5
S			1.0	0.5
W				

[a] The specific values of ε_{SX} are shown in the following simulations. Here P, X, S, W stand for matrix linear polymer monomers, cross-linkers in SCNP, solvent, and wall particles, respectively.