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How does solvent annealing influence stress-driven surface undulations in polymer composite films with immobilized film-spanning nanoparticles?

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ABSTRACT

Our study on poly(methyl methacrylate) (PMMA) films with fixed nanoparticles (NPs) on the supporting substrate, where the nanoparticles span the film thickness, reveal a three-stage evolution of wavelike undulations on the film surface: early stage, intermediate stage and late stage. The wavelike height undulations are induced by the compressive stresses, which are enhanced by introducing fix constrians (NPs) that resist the in-plane thermal expansion of the polymer film. We quantified the evolution of surface undulations, in an effort to understand the effect of solvent annealing on the undulations. The polymer chains in PMMA films prepared by spin coating are not fully equilibrated due to the rapid solvent evaporation during drying. Solvent annealing increases the molecular mobility and enables relaxation of the polymer network. This solvent treatment could perhaps give rise to an increase in entanglement density and associated film modulus. The surface undulations increase with the solvent annealing time before they reach the equilibrium values. The wavelike surface undulations might be associated with the entanglement density of polymer chains.

1. Introduction

Thin polymer films are of great interest because of their technological and scientific importance. The numerous technological applications of thin films are strongly dependent on their instability, where the film instability might give rise to the formation of defects or device failure. Muller-Buschbaum et al. investigated the relaxation of conformal roughness before the onset of dewetting and the long-range interface correlation in thin polymer films [1,2]. Recently wrinkling instability induced by abrupt compressive stresses in a stiff thin film deposited on a soft compliant material has become the subject of many theoretical [3,4] and experimental investigations [5]. The mismatch strain caused by the thermal expansion, osmotic pressure or mechanical stress in bilayer films with different mechanical properties induces the abrupt compressive stress in the bilayer systems [6]. There has been much progress in understanding the formation of sinusoidal wavelike patterns (wrinkles) at micro- and nano-scales in bilayer systems, which have shown potential for stretchable electronics [6], templates [7], and thin film metrology [8,9]. The overall evolutionary process of wrinkling in bilayer systems are studied by Huang [3,10] and Yoo and Lee [11]. They suggest a three-stage evolution of wavelike patterns in bilayer systems. The wavelike surface undulations induced by the compressive stresses in polystyrene thin films has been reported [12]. Despite the intense investigations on the wavelike patterns in bilayer systems, the morphological dynamics of wavelike surface undulations in the single polymer layer systems without any surface stiff layer have yet to be fully investigated. In this study, the polymer thin films are prepared by spin coating polymer solutions on a supporting solid substrate. The spin-coating is one of primary methods for fabricating thin polymer films which involves the transition from a (dilute) solution to a dry glass. As the term of "spin-coating" suggests, a polymer solution deposited on a substrate that is rapidly spun undergoes the rapid rotation during film preparation. Owing to centrifugal forces the polymer solutions flow off the rotating substrate and a tiny amount of polymer solutions left on the substrate forms a uniform thin polymer film while simultaneously subjecting to rapid drying. As pointed out by several authors [13–17], in films prepared by spin coating polymer

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chains may not be fully equilibrated, but rather in a less entangled state due to a dramatic rise in viscosity resulting from the solvent evaporation. During spin coating at room temperature the rapid solvent evaporation is similar to a thermal quench from the melt [14]. The polymer chains are "frozen into" the poorly entangled out-of-equilibrium state. For entangled polymer solutions the strong dependence of the the entanglement molar mass, M_e, on the polymer concentration, ϕ, can be expressed by the relation, $M_e(\phi) \sim M_e(1)\phi^{-5/4}$, where $M_e(\phi)$ is the value of M_e at polymer concentration of ϕ and $M_e(1)$ is the M_e at polymer concentration of 1 (bulk) [18]. The entanglement density in the dry spin-coated films should be somewhere in between $M_e(\phi)$ and $M_e(1)$. We can then reasonably expect that the strongly out of equilibrium chain conformations and a reduced entanglement density resulting from film preparation by spin coating influences the overall evolution of the wavelike surface undulations. However, the effect of far from equilibrium chain conformations in polymer thin film system with fixed lateral constraints (NPs) has not been previously emphasized as a means of controlling the characteristic wavelength and amplitude of the surface undulations when there are large nanoparticles within the film, as in the case of lithographically etched structures such as posts and functional elements protruding the polymer film. In spite of the complexity of the physical processes, the instability of polymer thin film containing spanning NPs can be considered as a probe to study chain conformations and entanglements in polymer thin films prepared by spin coating. By controlling the chain conformations and entanglements using solvent annealing process we gain information on the temporal evolution of the wavelike surface undulations of polymer thin films. These surface undulations also potentially provide valuable information about the chain entanglements and associated film elastic moduli in polymer films.

2. Experimental

2.1. Preparation of NP-coated substrate

The particle coverage depends on the nanoparticle solution concentration and spin coating velocity. By adjusting the concentration of the NP solution and spin speed during preparation of NP-coated substrates, we can control the distribution of nanoparticles. The silica nanoparticles were spin-coated onto the plasma-treated Si substrates for 60 s at the spin speed of 1800 rpm from 0.01% nanoparticle solution by mass in water. The NP-coated substrates with $2 \times 10^5/\text{mm}^2$ nanoparticle density and the distance between nanoparticles in the range from 1 μm to 7.5 μm were obtained. The substrates used in this study are polished atomically-flat silicon wafers cleaned using warm piranha solution. Due to the relatively strong affinity between nanoparticles and the plasma-treated Si substrate, the silica nanoparticles are bound to the underlying substrate through the physical adorption and only removed by the extended sonication. The silica nanoparticles with diameters of 150 nm in a colloidal dispersion (mass fraction 10%, suspension in water) were purchased from Polysciences Inc. The size of the nanoparticles is 150 ±30 nm. The NPs adsorb to the underlying silicon wafer substrate first, and then the polymer film is spin-coated on the NP-coated substrate. The silica NPs penetrate through the film. In the present work the nanoparticles are considered as fixed constraints within the films.

2.2. Preparation of PMMA thin films

The homopolymer was poly(methyl methacrylate) (PMMA) with a relative molecular mass of 996 kg mol^{-1} and polydispersity of 1.06 (Sigma–Aldrich). All of the PMMA films were prepared *via* spin coating at the spin speed of 2000 rpm from a 1% polymer solution by mass (having very low viscosity) in toluene onto the NP-coated silicon wafer. Before starting the spin-coater a polymer solution was first deposited on a substrate and covered the whole substrate. In order to let the polymer solution wet the substrate or increase the interaction between polymer solution and substrate, the polymer solution was kept on the substrate for approximately 5 s before initiating the spin-coater. During spin coating, most solution flows off the rotating substrate owing to centrifugal forces and the solution wetting the substrate forms a uniform film. The fixed nanoparticles might arrest the solution near the nanoparticles during spin coating, which would lead to the lack of solution at the back side of the nanoparticles (like the formation of the shadow). Due to the relatively low concentration solution (low viscosity) and the solution wetting the substrate prior to rapid rotation of substrate the thickness of polymer film prepared *via* spin coating is uniform. The shadowing effect did not show obvious influence on the film thickness. The film thickness was characterized with ultraviolet (UV)-visible interferometry (uncertainty ± 1 nm). The samples were placed in a vacuum oven for annealing.

The schematic of the solvent treatment of polymer thin films is shown in Fig. S1. The experimental procedure for solvent treatment of polymer thin films is outlined as follows. A desiccator with the valve-controlled vent in the lid was used as a solvent annealing chamber. A vacuum pump was connected to the vent in the lid of the desiccator. A glass Petri-dish filled with approximately 35 ml of solvent was placed in the desiccator. After vacuum-pumping the desiccator for 2 min, the vent was closed to seal the desiccator. The saturated vapor was created by a solvent reservoir placed inside the desiccator. The sample kept inside the desiccator was solvent annealed for different times.

2.3. Atomic force microscopy (AFM)

Atomic force microscopy (AFM) is a technique to probe the surface features at a high resolution. Sample surfaces were imaged using atomic force microscopy (AFM) (Asylum MFP3D) in the tapping mode, in which the lateral forces in the tip-sample interaction are significantly reduced as compared to the contact mode. The AFM scanning in the tapping mode significantly lessens the damage to the surface of sample. AFM images in both height and phase contrast modes were obtained in the ambient atmosphere. The tapping mode cantilevers with spring constant 3 N/m and resonance frequency ranging from 50 to 100 kHz were used.

2.4. Scanning electron microscopy (SEM)

SEM image was obtained using a Hitachi S-4700 scanning electron microscope (Hitachi Inc.).

3. Result and discussion

Representative AFM images of spin-coated PMMA films with the thickness of 75 nm are shown in Fig. 1. After annealing the PMMA film containing spanning NPs at temperature of 189 °C in a vacuum oven for 2 h, the AFM height image shown in Fig. 1a reveals a small variation in the local film height with a peak to valley distance of ~2 nm. The 3D view of the surface structure of the AFM height image is provided below the corresponding 1D height trace. The color-scale in 3D view is adjusted so that the smaller features of the surface undulations can be observed. Due to the relatively large-z features of the NPs the adjustment in vertical false color-scale "saturates" the NPs. In this study the power spectrum density (PSD) is used to quantify the evolution of wavelike surface undulations, which gives the statistical information on the surface undulations. By calculating the power spectrum density of the AFM height image, the characteristic wave vector, q^*, is