Surface & Coatings Technology 261 (2015) 311–317

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Hyperthermal hydrogen induced cross-linking and fabrication of nano-wrinkle patterns in ultrathin polymer films

Liang He [a], Changyu Tang [b], Xin Xu [a], Peng Jiang [b], Woon-Ming Lau [b], Feng Chen [a],*, Qiang Fu [a],*

[a] College of Polymer Science & Engineering, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, China
[b] Chengdu Green Energy and Green Manufacturing Technology R&D Center, Chengdu Development Center of Science and Technology, China Academy of Engineering Physics, Chengdu 610207, China

ARTICLE INFO

Article history:
Received 6 September 2014
Accepted in revised form 5 November 2014
Available online 13 November 2014

Keywords:
Ultrathin film
Hyperthermal hydrogen induced cross-linking
Surface wrinkling
Nano-pattern
Polymer material

ABSTRACT

This paper presents an efficient and simple processing method for the fabrication and regulation of nano-scale wrinkle patterns. The stiff film is created through cross-linking the surface of ultrathin polymer film within twenty nanometers by using the hyperthermal hydrogen induced cross-linking (HHIC) method, and then the bilayer is heated above the glass transition temperature of the polymer before quenched to room temperature. In this way, wrinkle patterns with wavelength ranging from 150 to 300 nm are prepared. And a morphology transition between the pattern of single points (convex bumps) and the pattern of ridges (labyrinth) is observed. The formation of wrinkle patterns is systematically investigated as functions of the thickness of original ultrathin film, the time of HHIC treatment, the annealing temperature and the chemical structure of polymers. Furthermore, nano-patterned silicon wafer is used as a template to create multiscale, anisotropic wrinkle patterns.

1. Introduction

When a compressive membrane stress is applied to systems consisting of stiff films bonded to soft substrates, an elastic instability develops and leads to the spontaneous formation of intricate, highly regular wrinkle patterns [1–9]. In the past few decades, surface wrinkling has drawn much attentions for its interesting evolution mechanism and a variety of applications in getting complex and ordered topologies [1,2,4], fabricating diversified controllable functional materials [5,6], and measuring mechanical properties of thin films [1,7]. The current trend of wrinkling studies is inclined to develop more efficient and simple methods for the fabrication of wrinkle patterns, explore the formation mechanism of wrinkling as well as predict the generation of diverse wrinkle morphologies and ordered topological structures, experimentally and theoretically. Such as, Watanabe and Mizukami found that attaching a thick chemically oxidized poly(dimethylsiloxane) (PDMS) film onto a slidable belt could continuously fabricate well-ordered wrinkle patterns through bending and recovering the belt [10]. Lee et al. demonstrated that anisotropic, hierarchical surface patterns could be created by compressing nano-patterned polystyrene (PS) film bonded to compliant PDMS in different directions, such as perpendicular or parallel to the pattern orientation [11]. In the structure consisting of single-crystal silicon ribbon covalently bonded to elastomeric PDMS, Jiang et al. explored relations between the strain and the characteristic wavelength and amplitude of the wrinkles, and the special wrinkling with finite deformation and geometrical nonlinearity was also discussed [12].

Up to now, the techniques for the fabrication of wrinkles are either complicated or confined in submicrometer-thick films, i.e., they are hard to control when enforced in films with thickness in nano-scale. It is well known that a bilayer structure comprising layers with different modulus is the pre-requisite for the formation of wrinkles. In general, two methods are employed to generate a bilayer structure in polymer films. One strategy is to partially cross-link a homogenous film by ultraviolet-zone (UVO) oxidation [13], plasma irradiation [14] or chemical method [10]. The other is to mechanically stack two layers with different moduli together. However, the first method is available for limited polymers, e.g. PS and PDMS, and the cross-linking induced by these surface treatment techniques is almost impossible to be precisely controlled within several nanometers. For example, the thickness of the surface film of PDMS which is modified by using the UVO oxidation approach to create the layered structure, generally, lies in the range from 100 to 200 nm [15,16]. Accordingly, the level of the cross-linking generated by the first method is too rough for ultrathin films. For the second method, special approaches have to be employed to strengthen the interface adhesion to prevent the emergence of defects between bilayer [1,4,7]. Furthermore, it is more difficult to conduct mechanical process in films with thickness in nano-scale than the first method. Therefore, it still remains a great challenge to develop an efficient and simple method to fabricate wrinkle patterns at nano-scale in ultrathin films [1–3,14]. As the development of nanotechnology, thin films are largely used in dielectric coatings, optical reflectors and lithographic resists. Therefore, the preparation and regulation of nano-size wrinkle patterns

---

* Corresponding authors. Tel.: +86 28 85461795; fax: +86 28 85405401.
E-mail addresses: fengchen@scu.edu.cn (F. Chen), qiangfu@scu.edu.cn (Q. Fu).

http://dx.doi.org/10.1016/j.surfcoat.2014.11.013
0257-8972/

in ultrathin films are significant for the extensive, high-tech applications of surface wrinkling.

In this article, the original ultrathin polymer film with thickness in dozens of nanometers was spin-coated onto the rigid support (i.e., silicon wafer). A bilayer structure was then fabricated by using the hyperthermal hydrogen induced cross-linking (HHIC) method [17–21] to generate a stiff surface film in the homogeneous ultrathin polymer films. HHIC is a new approach to induce the cross-linking of polymer materials. Studies showed that HHIC is efficient in hydrogen-contained systems. It can induce the cross-linking of various polymer films by selectively breaking C–H bonds without the breakage of other chemical bonds [17,20]. Computer simulations and experiments also demonstrated that the cross-linking depth induced by HHIC can be as far as 11 nm for an amorphous polymer film in the premise of maintaining the functional groups of the precursor [18,19,22]. Owing to the great applicability and mildness of HHIC, this process for the preparation of a bilayer structure is potential to be applied in almost all polymer films with nano-scale thickness. After the treatment of HHIC, the bilayer was heated above the glass transition temperature of the polymer and then annealed for a selected time. Upon cooling, the film wrinkled into sophisticated patterns with nano-scale wavelength ($\lambda = 150$–300 nm). Meanwhile, the morphology of wrinkles gradually changed between the convex bumps and the labyrinth. By regulating the processing parameters, it was found that the wavelength and the morphology of wrinkles were influenced by the thickness of the original ultrathin film, the HHIC treatment time and the annealing temperature. Three typical polymers (polystyrene (PS), poly(styrene–isoprene–styrene) triblock copolymer (SIS) and crystalline polylactic acid (PLA)) were used to test the applicability of this wrinkle fabrication approach.

2. Materials and methods

2.1. Materials

Polystyrene (PS) was purchased from Polymer Source and used as received. $M_w = 100\,000$ g/mol, $M_w/M_n = 1.04$. Poly(styrene–isoprene–styrene) triblock copolymer (SIS) employed in this study was commercial SIS with trade name of Vector 4111 and 4411 (Dexco Polymers Co.). $M_w = 140\,000$ g/mol, $M_w/M_n = 1.11$. Polylactic acid (PLA) used in this study was commercially available PLLA with the trade name of 4032D (NatureWorks). $M_w = 207\,000$ g/mol, $M_w/M_n = 1.74$. It has a density of 1.25 g/cm^3 and a high stereoregularity of 1.2–1.6% $_{\text{D-isomer}}$lactide.

2.2. Experimental process

The 1.0 wt.% solution (PS, SIS solutions in solvent of toluene, and PLA solution in solvent of chloroform) was firstly ultrasonic treated about 5 min to ensure the complete dissolution of polymer. Then the solution was placed under environmental condition about 1 h. Ultrathin film was prepared by spin-coating the solution onto the silicon wafer using a KW-4A commercial spin coater (XingYouYan, China). The rotating speed varied from 1000 to 3000 r/min. The film thickness was regulated by adjusting the spin-coating speed and the concentration of solutions, and it was measured with the use of atomic force microscopy (AFM) by a scratching method. Ordered arrangement of wrinkle patterns was carried out by employing the nano-patterned silicon wafer as a template to induce the wrinkles to align parallel to the long axis of crest. Spin-coated film was placed under the vacuum condition about 24 h to affirm the solvent volatilized completely.

The HHIC method was used to generate a stiff film in the homogenous original films. The samples were placed into home-made HHIC equipment. The pressure of samples chamber during the ion exposure process was 2×10^{-8} Torr. Hydrogen gas with the purity of 99.8% was used to produce the H^+ ions. The low-energy hydrogen projectile ions extracted from H_2 plasma was carried out in the low-cost mass-separated ion beam system. After the selection, the final beam energy was controlled at ~10 eV and the energy scope was less than 0.6 eV. Then the hydrogen beam was delivered to the target samples at normal incidence. The working voltage of the equipment was varied from 100 V to 300 V with the fluence varying from 1×10^{16} to 1×10^{18} cm^{-2}. The exposure times were changed from 1 min to 10 min and the other parameters of HHIC treatment were kept unchanged. The thickness of the treated film was measured by AFM and it was roughly the same to the thickness of original film. The bilayer was placed in the oven above the glass transition temperature of the polymer (100 °C) about 6 h, then it was removed to ambient temperature environment. Upon cooling, wrinkle patterns formed.

2.3. Characterization

AFM was used to observe the surface morphology of wrinkles by operating in a tapping mode using an instrument with a SPI4000 Probe Station controller (SIINT Instruments, Japan) at room temperature. Olympus tapping mode cantilevers with the spring constants ranging from 51.2 to 87.8 N/m (as specified by the manufacturer) were used, and the scan rate ranged from 1.0 to 2.0 Hz. The images were analyzed by the software accompanying the instrument.

The chemical groups and element compositions of the film surface were confirmed by X-ray Photoelectron Spectroscopy (XPS) (as shown in Fig. S1 of the Electronic Supplementary Information) using an XSAM800 multifunctional surface analyzer instrument (Kratos, Manchester, U.K.), and they were measured at monochromatized Al Kα radiation (1486.6 eV) at 12 kV × 15 mA, room temperature and 2×10^{-7} Pa. Referenced binding energies at 284.8 eV of the hydrocarbon peak and adopted the takeoff angle of 20. The measured depth of this experimental condition ranged from 6 to 10 nm. The high-resolution C 1s spectra of films were decomposed into different carbon atoms contributions corresponding to the various chemical structures.

3. Results and discussion

A schematic diagram of the experimental procedure is illustrated in Fig. 1. The original ultrathin film was fabricated by using a spin-coating method. The film thickness ranged from 30 to 60 nm, which was measured by atomic force microscopy (AFM) and controlled by changing the spin-coating speed and the concentration of solutions. The spin-coated film was placed under the vacuum condition for 24 h to affirm a complete solvent volatilization. Then the HHIC method was used to generate a stiff surface film in the homogenous original film and create a bilayer structure (see the Fig. S1 of the Electronic Supplementary Information) [17–21]. Furthermore, according to the studies of HHIC, the thickness of the stiff film was within twenty nanometers [18,19,22]. After the HHIC treatment, the thickness of the treated film was roughly the same to that of the original film by employing an appropriate HHIC radiation intensity, which was confirmed by the measurement of AFM. And the surface of the stiff film was flat without any pre-buckling or pre-wrinkling (See the Electronic Supplementary Information Fig. S2). Then the bilayer was heated above the glass transition temperature of the polymer (100 °C) and annealed about 6 h. Thermal deformation taken place in the bilayer, which in turn was bonded to the rigid support (i.e., silicon wafer). Upon cooling, the compressive stress caused by the thermal shrinkage was applied to the bilayer by the rigid support, and the film wrinkled into intricate topological patterns.

Fig. 2 shows that the morphology and wavelength of wrinkles are influenced by the thickness of the original film. In this study, the working voltage of HHIC treatment was 300 V and the exposure time was 2 min. The samples treated by HHIC method were annealed at 130 °C for about 6 h. In the experiments, original films with thickness ranging from 30 to 60 nm were adopted and HHIC treatment with the same parameters was employed, resulting in the generation of stiff films with the same