Polymer 123 (2017) 179–183

Contents lists available at ScienceDirect

Polymer

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

Short communication

Stress-strain measurement of ultra-thin polystyrene films: Film thickness and molecular weight dependence of crazing stress

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ARTICLE INFO

Article history:
Received 20 April 2017
Received in revised form
3 July 2017
Accepted 6 July 2017
Available online 7 July 2017

Keywords:
Polystyrene
Ultra-thin film
Stress-strain curve
Plastic deformation
Crazing stress

ABSTRACT

In general, self-standing polymer ultra-thin films are difficult to be handled, and therefore their mechanical properties have been poorly understood. We carried out the uniaxial tensile test of ultra-thin films floating on the surface of water and measured the stress-strain curves of polystyrene (PS) ultra-thin films with thickness of around 100 nm. We found that in the stress-strain curves of PS ultra-thin films, yielding points similar to ductile materials appear. We also employed Brewster's angle reflection imaging to follow the visual appearance of ultra-thin films during tensile tests. We found that the narrow shear deformation zones (SDZs), which are 2D analogue of crazes, appear at the yield point, and both the yield and equivalently crazing stresses decrease with decreasing the film thickness. Moreover, the reduction of crazing stress is more significant for the higher molecular weight polystyrene.

Numerous studies have focused on the physical properties of thin polymer films, in particular, the glass transition temperature, T_g. It has been reported that T_g of ultra-thin films with thickness below 100 nm decrease as film becomes thinner [1–4]. It is the general consensus that highly mobile layer exists near the free surface and affects the physical properties of the whole sample in case of ultra-thin films. This surface effect may dominate the mechanical properties of ultra-thin films because the fraction of surface mobile layer for ultra-thin films is much larger than that in bulk. However, it has been technically difficult to conduct mechanical tests on ultra-thin (~100 nm) polymer films particularly under large deformation.

Bulk polystyrene (PS) undergoes craze-assisted brittle fracture. Crazes are discrete plastic deformation zones perpendicular to the tensile stress, and are composed of voids and fibrils bridging a gap between undeformed zones. It was reported that the structure of a craze in ultra-thin PS films is different from a craze in bulk. In ultra-thin films, because the thin film can deform in the thickness direction more easily than in the width direction, the shear deformation zone (SDZ), which is the micrometer wide thinner zones running perpendicular to the shear stress, has been observed [5–11]. Ductile copper grids were often used to support films and the whole grid was stretched to apply strain to investigate the SDZ in ultra-thin films [5–9,12–14]. However, in this method the stress in the film cannot be measured directly.

Many experimental methods have been developed to investigate the mechanical properties of ultra-thin films. Nanoindentation test is widely recognized but is known to be affected by the presence of substrate. Alternatively, Stafford et al. developed the Strain-Induced Elastic Buckling Instability for Mechanical Measurements (SIEBIMM) utilizing flexible PDMS as supporting substrate [15–20]. PDMS substrate can also be conveniently used to apply large deformation to thin films [21]; however, stress cannot be directly monitored due to the supporting substrate. Most of the mechanical tests for ultra-thin films require supporting substrates, which restrict the deformation of thin films; therefore, large deformation such as plastic deformation cannot be followed.

We aimed to measure directly the stress during uniaxial tensile test of ultra-thin films presenting plastic deformation before failure. We used pseudo free-standing tensile test [22], in which water surface instead of supporting substrates supports the polymer films. This method was developed by Kim et al. and the validity of this method was confirmed with thin metal and polymer films [22–25]. By this method, we successfully obtained the stress-strain curves of ultra-thin PS films during plastic deformation. This is the first report of full stress-strain curves of the ultra-thin polymer films presenting the unique plastic deformation.

Ethanol solution of poly (acrylic acid) (PAA) with molecular

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http://dx.doi.org/10.1016/j.polymer.2017.07.018

weight of 25,000 (Wako Co.) was spun-cast onto the silicon wafers (SUMCO Co., cut into square with 35 mm) pre-cleaned using UV-Ozone for 2 h. After dried in a vacuum for more than 2 h, the PS films with two different molecular weights (Polymer Source Inc., $M_w = 354$ kg/mol and $M_w = 8875$ kg/mol, polydispersity indices of less than 1.3) and thicknesses ranging from 39 nm to 229 nm were spun-cast from toluene solution on top of the PAA films on silicon wafers. The films were annealed at 110 °C in a vacuum for 18 h to remove the residual solvent and to relax the PS chains deformed during spin casting. The annealed PS on PAA films were cut into dumbbell shape with a rectangular portion of 6 mm in width and 6 mm in length using reactive ion etching with aluminum masks (Fig. 1(a)). The dumbbell-shaped PS films were peeled off from silicon wafer by dissolving PAA and floated on the surface of water (Milli-Q) in the petri dish.

Fig. 1(b) shows the illustration of pseudo free-standing tensile test. The floated films were attached to two aluminum grips with a 1.4 mm gap. Silicone rubber sheets with thickness of 0.5 mm were coated on the grips to promote good adhesion to the PS thin films. The friction between the films and the silicone rubber sheets is large enough to hold the PS thin films during tensile tests. The deformation of silicone rubber sheets estimated from the force generated during the test is small enough to be neglected. One grip was attached to the uniaxial motorized stage (Sigmakoki Co., TSDM60-20X) and the other was connected to the miniature load cell (Toyosokki Co., TCSS-0.1L). All experiments were conducted at room temperature at a fixed strain rate of 2×10^{-4} s^{-1}. The visual appearances of the films during the tensile test were captured with Brewster's angle reflection imaging (BARI), which is composed of a CCD camera (SENTECH Co., STC-MC152USB) and *p*-polarized light source set at the Brewster's angle of air/water interface. The reflectance of *p*-polarized light becomes zero at Brewster's angle, θ_B, which is given by $\theta_B = \arctan(n_2/n_1)$, where n_1 and n_2 are the refractive indices of air and the medium, respectively. We captured the images of the PS films floating on water during the tensile test at an angle of incidence of approximately 53°, which is the Brewster's angle of air/water interface but is different from that of air-PS interface, 58°. The water surface and the PS thin film appear black and white, respectively (Fig. 1(c)). After tensile test, the films were scooped up on silicon wafers and dried. Film thickness, *h*, was measured by atomic force microscope (AFM) as the difference of the height between the silicon wafer and undeformed zones of the film. Crazing was a local plastic deformation, and the thickness of all the other part of the film was the same as that before the tensile test.

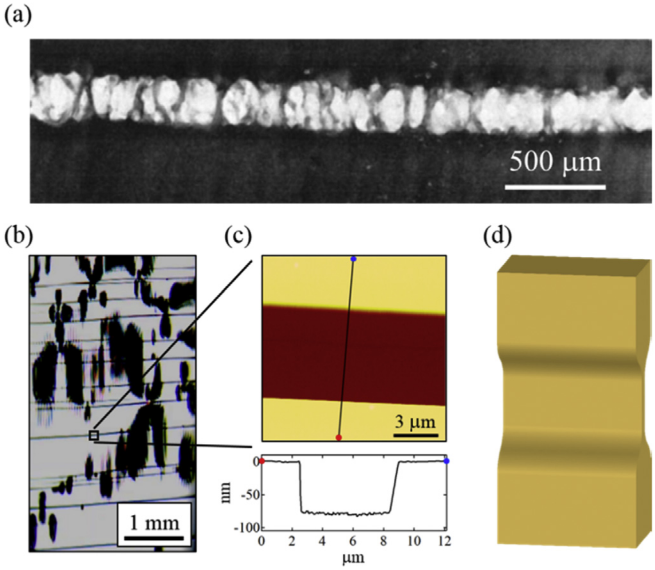

Fig. 2. Structure of the shear deformation zone (SDZ) in bulk polystyrene (PS) and in ultra-thin PS films. (a) Transmission Electron Microscope (TEM) image of craze formed in bulk PS (duplicated with permission from R.P. Kambour, R.R. Russell, Polymer (Guildf). 12 (1971) 237–246 [26]). Crazes are observed as cavities extending perpendicular to the stretching direction with fibrils bridging the cavities. (b) A BARI image of the PS ultra-thin film of $M_w = 354$ kg/mol with thickness of 105 nm during tensile test. The stretching direction is vertical direction and applied strain is 5%. The thin black lines running perpendicular to the extending direction are SDZs. The large black ellipsoidal domains are the zones where the film buckled in the direction perpendicular to the extension. (c) AFM image and height profile of the SDZ in the film of $M_w = 354$ kg/mol with thickness of 105 nm. The deep depression is the SDZ. (d) Illustration of the structure of a SDZ. SDZs are plate-like thin zones with thickness of about 23% of the original film thickness.

Fig. 2(a) is a transmission electron microscope (TEM) image of crazes. Crazes are observed as cavities extending perpendicular to the stretching direction with fibrils bridging the cavities [26]. Fig. 2(b) shows an image of ultra-thin PS film stretched in the vertical direction and captured during the tensile test using the BARI. Applied strain was 5%. The thin black lines running perpendicular to the extending direction are SDZs, which are thinner zones with different Brewster's angle. The large black ellipsoidal areas are not SDZs. They appear black because of the buckling and tilt of the films, which disappear when the stress is removed. After the tensile tests, the thin films were picked up onto a silicon wafer and then the film topology was measured using AFM. In our experiment, plate-like SDZs were observed in all the samples with thickness ranging from 39 nm to 229 nm, and the thickness of thinner zones is about 23% of the original film thickness irrespective of the original film thickness (Fig. 2(c)). For the observation by AFM, the film was picked up on to the substrate and the SDZs stuck to the silicon substrate. The films picked up onto substrates downward and upward were exactly the same. Therefore, the SDZs

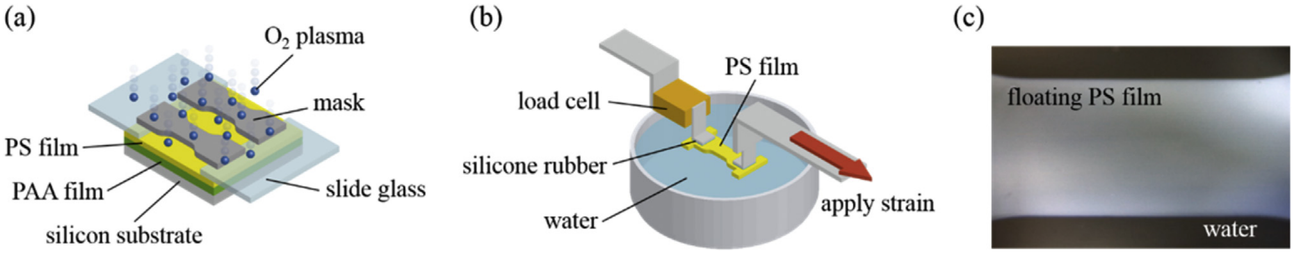

Fig. 1. Sample fabrication and tensile testing. (a) Schematic illustration of the fabrication of dumbbell-shaped polystyrene (PS) films. PS films on silicon substrate coated with poly (acrylic acid) (PAA) films were cut into dumbbell shape using O_2 reactive ion etching with aluminum masks. After etching, PS films were peeled off from silicon substrates onto water by dissolving PAA films. (b) The tensile testing system named pseudo free-standing tensile test. A PS film floating on the surface of water was attached to two grips by the friction between the films and the grips coated with silicone rubber. One grip was attached to the uniaxial motorized stage and the other was connected to the load cell. (c) A CCD image of PS thin film floating on the surface of water captured with Brewster's angle reflection imaging (BARI).