In situ observation of surface deformation of polymer films by atomic force microscopy

Nishino, Takashi
Nozawa, Akiko
Kotera, Masaru
Nakamae, Katsuhiko

(Citation)
Review of Scientific Instruments,71(5):2094-2096

(Issue Date)
2000

(Resource Type)
journal article

(Version)
Version of Record

(URL)
https://hdl.handle.net/20.500.14094/90001326

REVIEW OF SCIENTIFIC INSTRUMENTS VOLUME 71, NUMBER 5 MAY 2000

In situ observation of surface deformation of polymer films by atomic force microscopy

Takashi Nishino, Akiko Nozawa, Masaru Kotera, and Katsuhiko Nakamae[a)]
Department of Chemical Science and Engineering, Faculty of Engineering, Kobe University, Rokko, Nada, Kobe 657-8501, Japan

(Received 16 November 1999; accepted for publication 12 January 2000)

The tensile $X-Y$ stage, providing a load cell and a stretching device, has been constructed to observe the surface deformation of polymer film *in situ* by using an atomic force microscope (AFM). From the three-dimensional AFM images, the streak-like bumps were observed on a polyethylene terephalate (PET) film surface. By monitoring the change in the distance between them by the tensile load, the strain was evaluated in the direction both parallel and perpendicular to the tensile direction. The microscopic stress–strain relationship by AFM coincided with the macroscopic one, which indicates so-called affine deformation of PET film. Young's modulus was obtained as 2.3 GPa for PET from the initial slope of the stress–strain curve by AFM. The apparent Poisson ratio of the PET film surface could be also evaluated. © *2000 American Institute of Physics.* [S0034-6748(00)01605-1]

I. INTRODUCTION

The mechanical property of polymers is one of the most important properties in a variety of utilizing fields, so it becomes very essential to investigate the deformation process of polymeric materials. Recently, with the development of microscopic processing techniques, precise measurements of the deformation within a very small area have been required. Many techniques have been reported for the measurement of mechanical properties of polymers.[1–4] An Instron type tensile tester is the most popular. Scanning electron microscope is also used from the microscopic viewpoint,[5] however, vacuum conditions and an electron conducting coating on a polymer surface are needed for the observation.

Scanning probe microscopy techniques have recently developed,[6–8] and they can give an atomic image,[9] mechanical stiffness[10,11] and chemical species[12,13] of the polymer surface. Among them, an atomic force microscope (AFM) is a very useful tool for observing a polymer surface with three-dimensional (3D) images under various ambient conditions without pretreatment. Especially, AFM has an advantage in high space resolution from the micrometer down to the nanometer scale.

In this study, a tensile stage was developed to attach to an AFM probe head, and we here proposed a novel technique of *in situ* observation of the tensile deformation of a commercial polyethylene terephthalate (PET) film surface by AFM. The microscopic relationship between stress and strain by AFM was compared with the macroscopic deformation behavior. In addition, the apparent Poisson ratio of the film surface was also investigated.

II. EXPERIMENT

Figure 1 shows a schematic illustration of the stretching device specially designed for *in situ* AFM observations of the film surface. A rectangular sample (width 5 mm ×initial length 20 mm) was clumped in a stretching device and stretched in the direction perpendicular to the machine direction of the film with a constant dead load.

Atomic force micrographs were taken by a contact mode in air using AFM (Topo Metrix, Explorer, TMX2100). A V-shaped Si_3N_4 cantilever (a spring constant 0.032 N/m) was scanned on the film surface. Scan speed was 200 μm/s.

Commercial PET films (Toray Co., Ltd.) with a thickness of 100 μm were used. The density of this film was 1.398 g/cm^3 measured by a flotation method (benzene-carbon tetrachloride system, 30 °C), which corresponds to the crystallinity of 43%.[14,15] The film was rinsed with methanol in an ultrasonic bath for 30 min, after that the film was dried at room temperature for 24 h prior to the AFM observation.

Figure 2 shows the photograph of the experimental setup. An AFM cantilever was set on the film attached to the stretching device, and deformation images were observed *in situ*. Both the stretching device and the AFM probe were mobile with $X-Y$ stages manipulated by micrometers. A

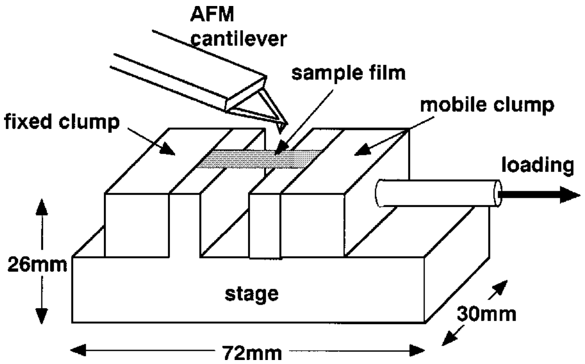

FIG. 1. Schematic illustration of the stretching device attached to the AFM.

[a)] Author to whom correspondence should be addressed; electronic mail: nakamae@cx.kobe-u.ac.jp

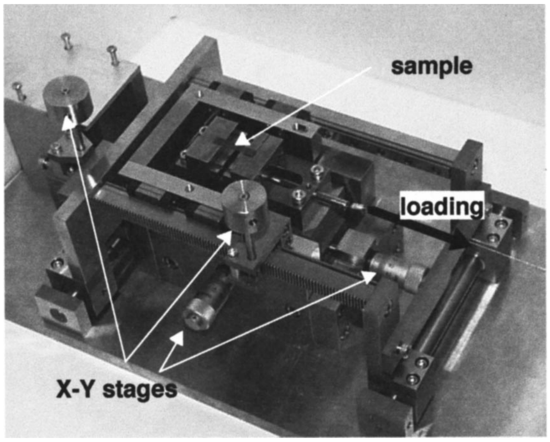

FIG. 2. Photograph of the stretching device and $X-Y$ stages attached to the AFM.

stretching device for a single fiber is also available by alternating the clumping system into a screw type.

The stress on the film was monitored through the load cell and an amplifier. The macroscopic strain of the whole sample was also measured by monitoring the displacement of the clump with an experimental error of ±0.25%.

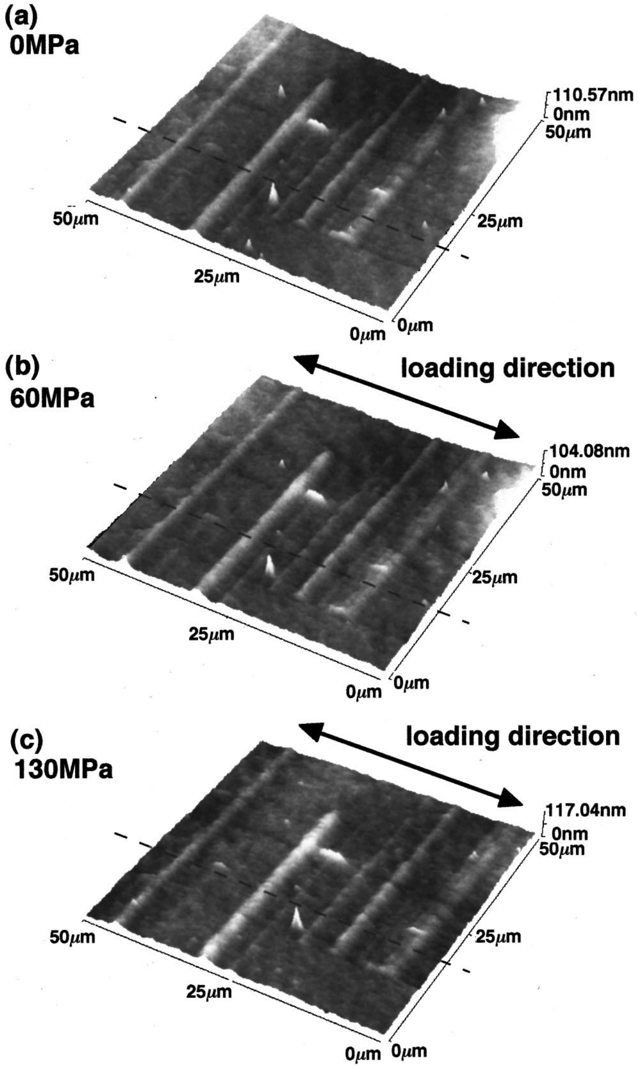

FIG. 3. AFM 3D images of polyethylene terephthalate film surface (50 μm×50 μm). The arrows indicate loading direction.

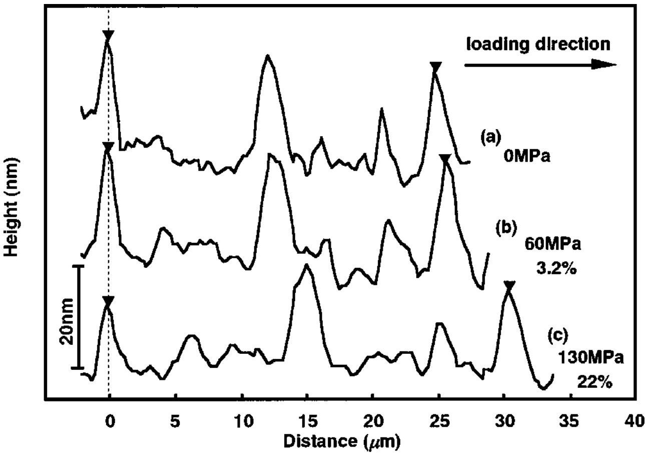

FIG. 4. One-dimensional height profiles of polyethylene terephthalate film surface in the direction parallel to the loading axis (along the broken line in Fig. 3).

III. RESULTS AND DISCUSSION

Figure 3 shows the typical three-dimensional surface images (50 μm×50 μm) of a PET film (a) before loading, and under loading at (b) 60 MPa, and (c) 130 MPa. Loading direction was shown with arrows. Some streak-like bumps, ~20 nm in height, could be observed parallel to the machine direction of the film. These bumps could hardly be observed by the scanning electron microscope because their heights were very small in comparison with the scanning area. They would be produced during processing (extruding) and drawing. By utilizing them as markers, the strain could be evaluated by monitoring the distance between the streak-like bumps on the surface AFM images. By increasing the stress, the distance between the streaks was getting longer in the tensile loading direction.

Figure 4 shows the one-dimensional height profiles (a) before loading, (b), and (c) under loading along the broken lines in Fig. 3. It was clear that the pattern of bumps was elongated to the loading direction. The height of bumps

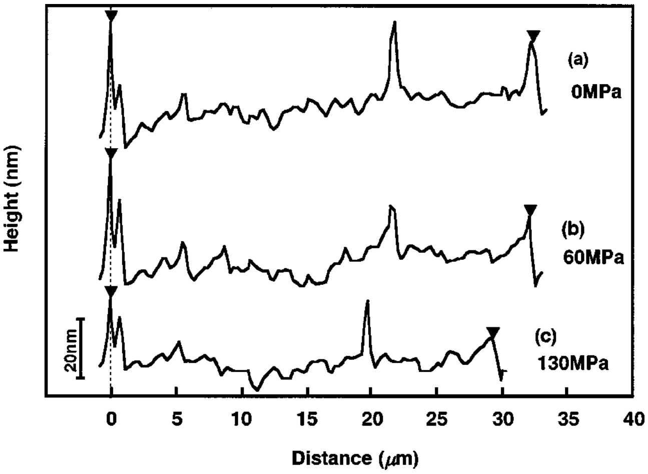

FIG. 5. One-dimensional height profiles of polyethylene terephthalate film surface in the direction perpendicular to the loading axis.

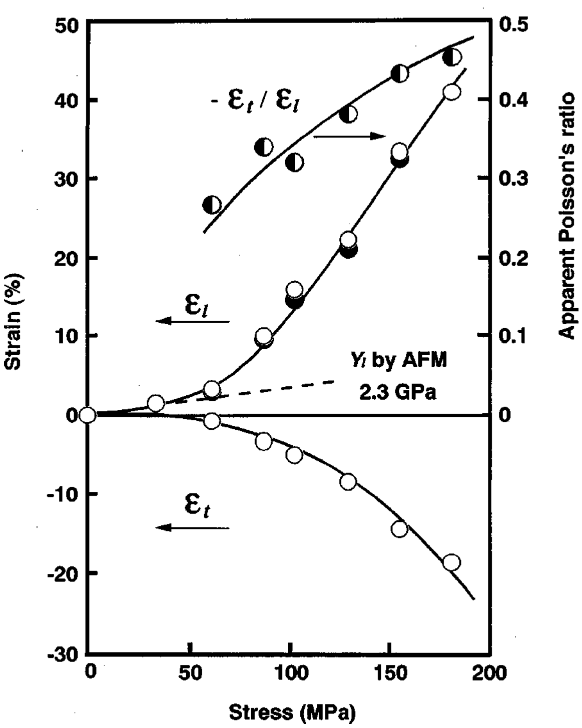

FIG. 6. Stress–strain curves of polyethylene terephthalate film, and the stress dependence of the apparent Poisson ratio. ○ Microscopic strain by AFM, ● macroscopic strain, and ◐ apparent Poisson's ratio.

peaks (▼) at 130 MPa became lower compared with those at 0 and 60 MPa. This indicates the roughness decreased and the surface tended to become smoother with the increase of the stress. From the distance (l) between two filled triangles (▼) of each profile, the microscopic surface strain (ε_l) could be calculated with the following equation:

$$\varepsilon_l = \Delta l / l_0,$$

where, l_0 is the initial distance at 0 MPa, and Δl is the change in the distance. The image in Fig. 3 consists of 300 $\times$300 pixels, which corresponds to the space resolution of 0.167 μm. This amounts to the experimental error of $\pm 0.3\%$ for the strain evaluation. The experimental error can be reduced by increasing the pixels, whereas it takes a long time for the observation. The reproducibility of the strain was found to be within $\pm 0.3\%$ for five experiments. From Fig. 4, though the stress increased from 60 to 130 MPa stepwisely, the strain ε_l increased from 3.2% to 22%, respectively.

When the film is stretched, the film was not only stretched to the loading direction, but also shrunk to the perpendicular direction of the load.

Figure 5 shows the one-dimensional height profiles of (a) before loading, (b), and (c) under loading in the direction perpendicular to the load. The distance between two triangles (▼) was shrunk with the increase of the load.

Figure 6 shows the stress and strain curves of PET film in the direction both parallel and perpendicular to the loading axis by AFM. The macroscopic stress–strain curve was also superposed on the figure with the filled circles. The microscopic deformation process of the PET film surface could be *in situ* observed by AFM images. The stress–strain curve showed that the deformation is elastic up to 60 MPa, followed by yielding. Microscopic Young's modulus (Y_l) was obtained as 2.3 GPa from the initial slope of the stress–strain curve by AFM. The microscopic stress–strain relationship by AFM coincided with the macroscopic one, which indicates that the deformation process of the PET film is a so-called affine one.

The strain, ε_t, perpendicular to the loading direction decreased with loading. From the ratio of the stains ε_l to ε_t, the apparent Poisson ratio ($\nu = -\varepsilon_t/\varepsilon_l$) could be evaluated, which is shown with half filled circles in Fig. 6. The ν value increased from 0.3 up to 0.5 with the increase of the stress. The polymeric materials usually possess the ν value of 0.35–0.5,[1] and the ν value of 0.5 means the isovolumeric deformation, such as ideal elastomers. The ν value close to 0.5 will be influenced by an irreversible plastic deformation after yielding of the film. Further investigations on various films and fibers are now going on.

ACKNOWLEDGMENT

The work was partly supported by the Hyogo Science and Technology Association.

[1] L. E. Nielsen, *Mechanical Property of Polymers and Composites* (Marcel Dekker, New York, 1975).
[2] I. M. Ward, *Structure and Properties of Oriented Polymers* (Applied Science, London, 1975).
[3] I. M. Ward, *Mechanical Properties of Solid Polymers* (Wiley, New York, 1983).
[4] K. Nakamae and T. Nishino, Adv. X-Ray Anal. **35**, 545 (1992).
[5] B. J. Briscoe, E. Pelillo, F. Ragazzi, and S. K. Sinha, Polymer **39**, 2161 (1998).
[6] G. Binnig, H. Rohrer, Ch. Gerber, and E. Weibel, Phys. Rev. Lett. **49**, 57 (1982).
[7] G. Binnig and C. F. Quate, Phys. Rev. Lett. **56**, 930 (1986).
[8] S. N. Magonov and M.-H. Whangbo, *Surface Analysis with STM and AFM* (VCH, Weinheim, Germany, 1996).
[9] D. Snetivy and G. J. Vancso, Macromolecules **25**, 7037 (1992).
[10] J. Domke and M. Radmacher, Langmuir **14**, 3320 (1998).
[11] N. A. Burnham, and R. J. Colton, J. Vac. Sci. Technol. A **7**, 2906 (1989).
[12] E. W. van der Vegte and G. Hadziioannou, Langmuir **13**, 4357 (1997).
[13] C. D. Frisbie, L. F. Rozsnyai, A. Noy, M. S. Wrighton, and C. M. Lieber, Science **265**, 2071 (1994).
[14] R. de P. Daubeny, C. W. Bunn, and C. J. Brown, Proc. R. Soc. London, Ser. A **226**, 531 (1954).
[15] A. B. Thomson and D. W. Woods, Nature (London) **176**, 78 (1955).