

Surface Melting of Semicrystalline Polymer Thin Films Revealed by Grazing Incidence X-ray Diffraction

Chao Yan, Isao Takahashi

School of Science and Technology, Kwansei-Gakuin University, Japan

Abstract: The structure evolutions of PLLA thin film both at the surface and whole film during the heating process were in-situ followed by synchrotron grazing incidence x-ray diffraction (GIXD). The obtained GIXD results clearly show that the diffractions of the surface and the whole PLLA film disappeared at about 170°C and 180°C, respectively. That means the surface melting is prior to the whole film melting.

Keywords: surface melting, polymer thin film, grazing incidence x-ray diffraction (GIXD)

Introduction:

Melting in semicrystalline polymers can be highly complicated. More comprehensions have been achieved for polymer bulk. As thin polymer films become more desirable in technological applications such as microelectronics fabrication, liquid crystal display, photoresists for photolithography, and adhesive or passivation layers in recent years, understanding the characteristic properties of polymer thin films is of great importance. So far little attentions were been paid to the melting process of semicrystalline polymer thin films. What happens about the polymer thin film during the heating process especially at the surface is still unclear.

The present experiments clearly illustrate the structure evolution process at the surface and the whole of semicrystalline polymer thin film. The technique of grazing incidence X-ray diffraction (GIXD) also enables us to gain direct access to information of surface and bulk ordering. Moreover, synchrotron radiation and multi-axis diffractometer at BL13XU beamline of SPring-8 was employed to obtain the in-situ information. The results directly evidence the surface melting

prior to the melting of the whole film in semicrystalline polymer thin films during the heating process.

Experiment:

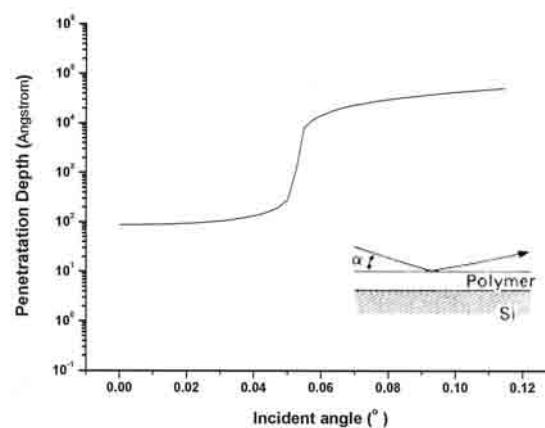


Fig. 1. Variation of X-ray penetrate depth for PLLA as a function of the angle of incidence.

The PLLA thin films were prepared by spin-coating the PLLA/chloroform solution onto the silicon (100) wafers. After sufficient crystallization, the PLLA thin films were measured by GIXD with different incident angle. As depicted in Fig. 1 the x-ray penetration depth varies with the incident angle. If the experimental incident angle less than critical incident angle, the surface information were detected. And if the experimental incident angle

bigger than the critical angle, the obtained information come from the whole film. In present experiment, the surface and the whole films were detected by using different incident angle less or bigger than the critical incident angle of GIXD separately, during the heating process of PLLA thin films.

Results and discussion:

The structure evolutions of PLLA thin film both at the surface and whole film were in-situ followed by GIXD due to the facility with strong intensity and high coherency in SPring8. As depicted in Fig. 2, the diffractions of the surface and the whole PLLA film disappeared at about 170°C and the diffractions of the whole film still presented until about 180°C. That means the crystal structure at the surface melt firstly, before the demolishment of the crystal inner the films. The results experimentally demonstrate that the crystal structure has lower melting point than that in the inner portion at the first time. The convinced experimental results may make some contribution to the comprehension of recent reports about the melting point depression in semicrystalline polymer thin films and shed more light on the

deep understanding of the melting process of semicrystalline polymer thin films.

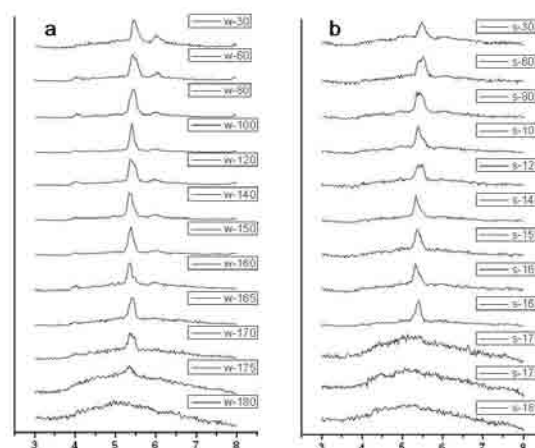


Fig. 2. In-situ measurements of GIXD of the whole PLLA thin film (a) and the surface (b) during the heating process.

Further works:

The succeeding projects are in processing for confirming current results convincingly.

Reference:

- 1) T. Nanoteku and S. Nanomura, Phys. Rev. Lett. 55 (1997) 3244.
- 2) N. Nakama, T. Nakamura and K. Komaki, J. Chem. Soc. Jpn. 32 (1999) 111.