Wide-Angle X-ray Scattering Instrument

NANOPIX-WE

1. Introduction

In recent years, many countries have become increasingly concerned about environmental issues, and are accelerating their efforts to reduce their environmental impact by reducing dependence on fossil fuels (coal and oil) to achieve the carbon neutral. Developed countries and manufacturers are creating social policies and manufacturing strategies for low environmental load. Thus, the demand for advanced polymer materials has increased annually for use in products related to energy conservation, such as electric vehicles, fuel cells and biodegradable plastics. Structural control at the crystal structure scale (nanoscale) is one of the most important issues in their development and manufacturing of functional polymer materials for polymer electrolyte membranes for fuel cells, battery separators, biodegradable polymers, and bulk reinforced plastics, as well as films and fibers.

Wide-Angle X-ray Scattering (WAXS) / Wide Angle X-ray Diffraction (WAXD) is widely used for structural analysis of functional polymer materials. In particular, 2D-WAXS measurements using a two-dimensional (2D) detector are widely used for the identification of crystal structures, evaluation of selected orientations, and measurement of crystallinity of polymers. In general, the periodic structure of polymers has a spacing size of 0.2 nm to 1.8 nm, and diffraction peaks are observed in a scattering angle 2θ range between 5° and 45° when using Cu Kα radiation (λ=0.15418 nm). Therefore it is necessary to measure a wide region with a large scattering angle.

In this paper, we introduce the latest wide-angle X-ray scattering measurement system NANOPIX-WE. While NANOPIX is designed for advanced small-angle X-ray scattering measurements (SAXS), NANOPIX-WE is optimized for WAXS measurements, with a scattering angle of 2θ between 3° and 65°. Its high-intensity X-rays enable not only static measurements but also in situ measurements with controlled temperature and external fields, and high-speed time-resolved measurements. This new product has been developed to allow structural evaluation of polymeric materials such as films, fibers and bulk materials in various environments, but it can also perform 2D-WAXS measurements on inorganic materials such as powders and metallic materials.

2. Features of NANOPIX-WE

2.1. Optimized for 2D-WAXS measurement

The NANOPIX-WE supports both transmission and GI-WAXS (reflection) measurement arrangements (Fig. 1). In particular, the optical system optimized for 2D-WAXS measurements uses a high-brightness rotating anode X-ray generator MicroMax-007 HF with a rated output power of 1.2 kW and an effective focal spot size of 70 µm diameter, and a high-performance VariMax confocal multilayer mirror with a focal length of 600 mm to provide maximum X-ray intensity. This combination achieves X-ray intensity exceeding 10^9 cps and a beam size with a half width of 220 µm at the sample position.

In general, the shape of the diffraction peaks in the transmission measurement arrangement is affected by the monochromatic nature of the incident X-ray beam, divergence angle, irradiation area, sample geometry (thickness, width), and spatial resolution of the detector. The injection optics of the NANOPIX-WE not only combine the above-mentioned small beam size and high intensity, but also provide advanced beam shaping. The X-ray beam irradiated onto the sample is shaped by a combination of a collimator and an anti-scattering pinhole slit. In addition, an anti-scattering cylinder suppresses parasitic scattering between the collimator and the de-scattering pinhole/slit. The beamstop is a flying type that does not allow the shadows of wires or other fixtures to enter the measurement field of view, enabling measurement over the entire 360° azimuthal range.

2.2. Large area hybrid photon-counting detector: HyPix-6000

The detector is one of the most important components of a 2D-WAXS measurement system, and the NANOPIX-WE is equipped with a large-area hybrid photon-counting detector, HyPix-6000, as a standard feature (Fig. 2). The HyPix-6000 has 775×770 pixels with 100 µm squared size, and a detection area of 77.5 mm×80.3 mm, including the blind area between detection modules. In addition, the NANOPIX-WE is equipped with a motorized two-axis stage (horizontal and vertical) and a function to automatically integrate single large-area measurement images from multiple measurement images (we call this the "extended measurement function") using dedicated control software. The extended measurement function enables measurement images with an effective detection area of 200 mm square or more to be obtained and, in combination with the minimum sample-detector distance (camera length) of 40 mm, it is possible to measure scattering angles of 60° or more (Fig. 3).

2.3. Wide variety of sample environment attachment

The NANOPIX-WE is used for measurements under a variety of conditions by controlling external conditions such as temperature, humidity, mechanical deformations; stretching and compressing, and by using various sample attachment options such as simultaneous measurement with a differential scanning calorimeter in transmission configuration, measurements under shear stress, and measurements under ultra-high pressure using a diamond anvil cell. The combination of a kinematic base mount and a motorized 2-axis sample stage (100 mm horizontal and 20 mm vertical travel range, 1 µm accuracy) makes it easy to change sample attachments. In addition, measurements from each attachment can be controlled by dedicated control software. Figure 4 shows an example of the Modular Force Stage (MFS) with temperature control

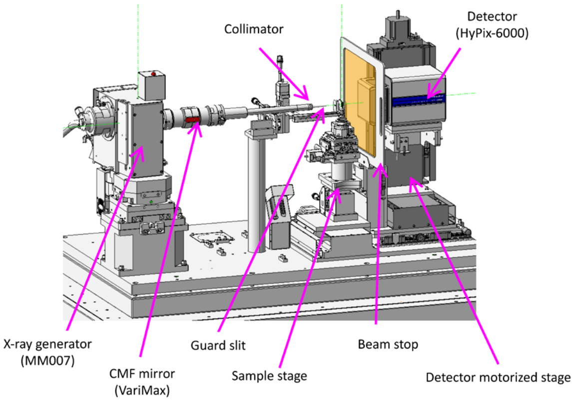

Fig. 1. Optical system of NANOPIX-WE.

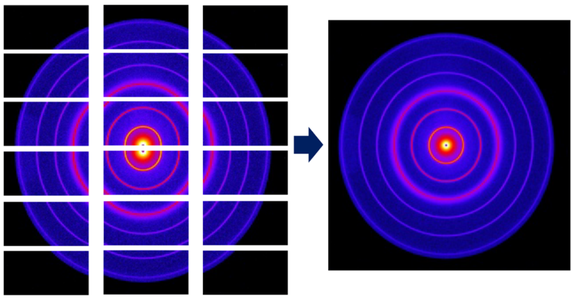

Fig. 3. Schematic diagram of the extended measurement function when using HyPix-3000. Extended measurement function integrates the image data of different measurement positions to generate a single image data of a wide range of 2θ.

Fig. 2. Large area hybrid photon counting detector HyPix-6000 and wide range YZ direction motorized stages.

Fig. 4. General-purpose attachments for mounting various sample environment stages and Linkam's Modular Force Stage (MFS).

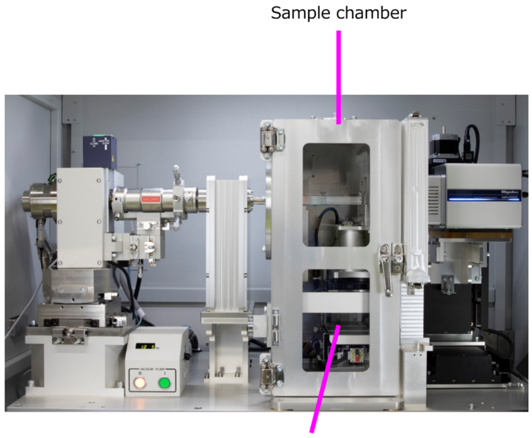

Fig. 5. Full vacuum optical system (Large vacuum chamber)

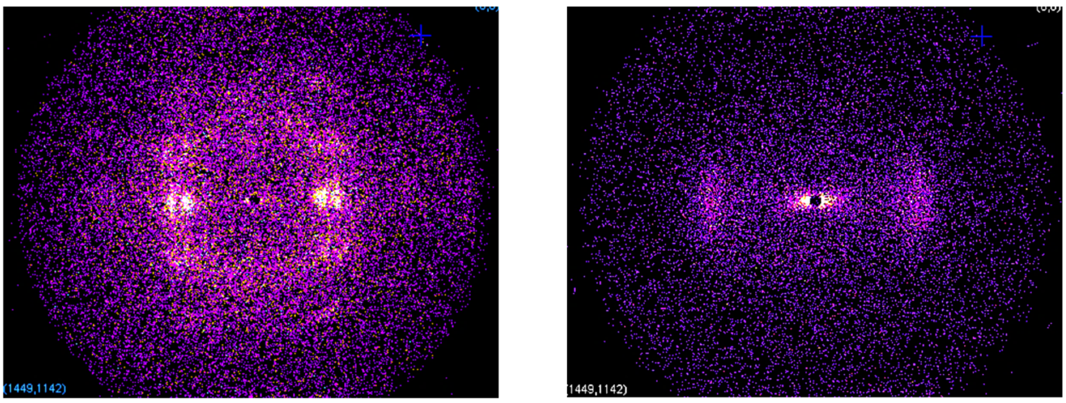

Fig. 6. Single fiber samples measured using the large vacuum chamber option, (a) silk, (b) carbon fiber, each with an exposure time of 10 seconds.

manufactured by Linkam Scientific, UK, mounted on a multi-purpose attachment.

2.4. Vacuum chamber for sample stage.

When conducting 2D-WAXS measurements on ultra-thin polymer films or single fibers, it is necessary to reduce air scattering as much as possible. This air scattering is caused by the interaction of the incident X-ray beam with the air between the incident collimator and the detector. Especially when the scattering intensity from the sample itself is weak, background data reduction from the measurement data often can't be processed.

Therefore, the NANOPIX-WE has a large vacuum chamber option (Fig. 5), which consists of a full vacuum from the incident optical system to just before the detector, including the motorized sample stage, with no other scattering sources other than the sample. The large vacuum chamber option is also equipped with a motorized 2-axis sample stage as a standard feature to control the sample attachment position under vacuum. Figure 6 shows a 2D-WAXS image from a single fiber. By using the large vacuum chamber option, it is possible to clearly observe the structure of even a single fiber with low regularity.

3. Applications

3.1. Polymer film sample

Polyethylene (PE, polyethylene) is a well-known polymer material that is widely used industrially. Figure 7(a) shows a 2D-WAXS image obtained by extended measurement. The scattering angle 2θ covers the range from 3° to 65°, realizing a complete azimuthal measurement of 360°. The 1D scattering data obtained by circular averaging of the image in Fig. 7(a) is shown in Fig. 7(b). Due to the high-intensity source and high-resolution detection system of NANOPIX-WE, the diffraction peaks are sharp and the higher order diffraction peaks with weak scattering intensity can be observed (Fig. 7(b)).

3.2. Time resolved measurement with temperature control device/tensile device

In-situ observation and operando measurements are

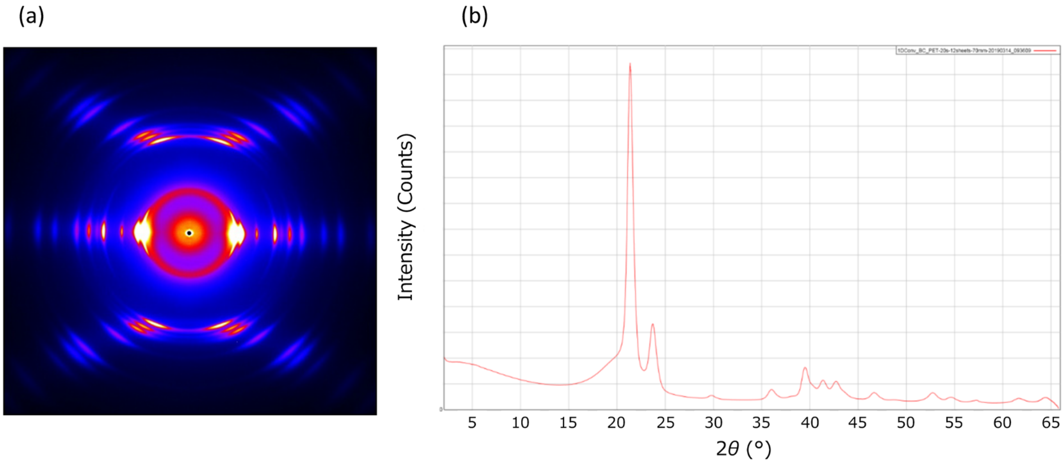

Fig. 7. Diffraction image from PE film (exposure time 40 s), (a) 2D measurement data, (b) 1D profile after circular averaging process.

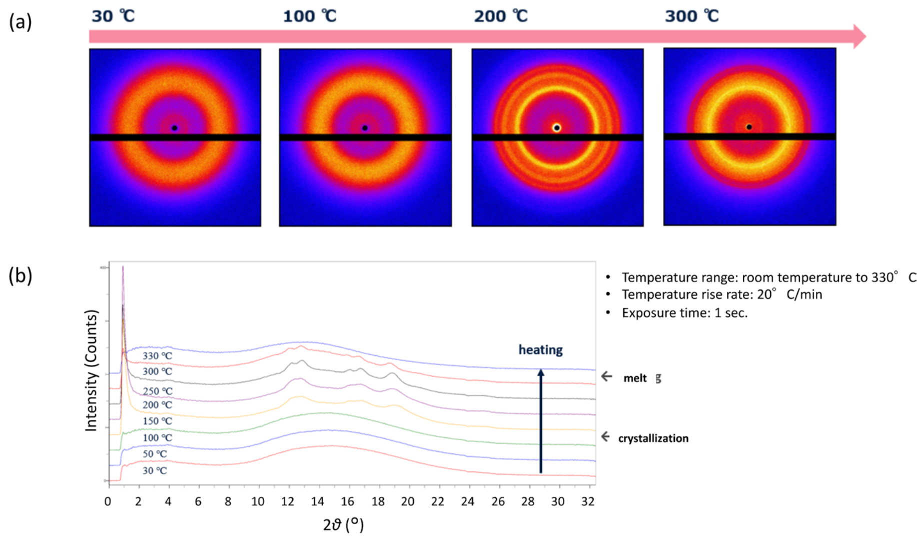

Fig. 8. High-speed time-resolved 2D diffraction measurement of PET film during heating. (a) 2D measurement data, (b) 1D profile after circular averaging (vertical axis is shifted)

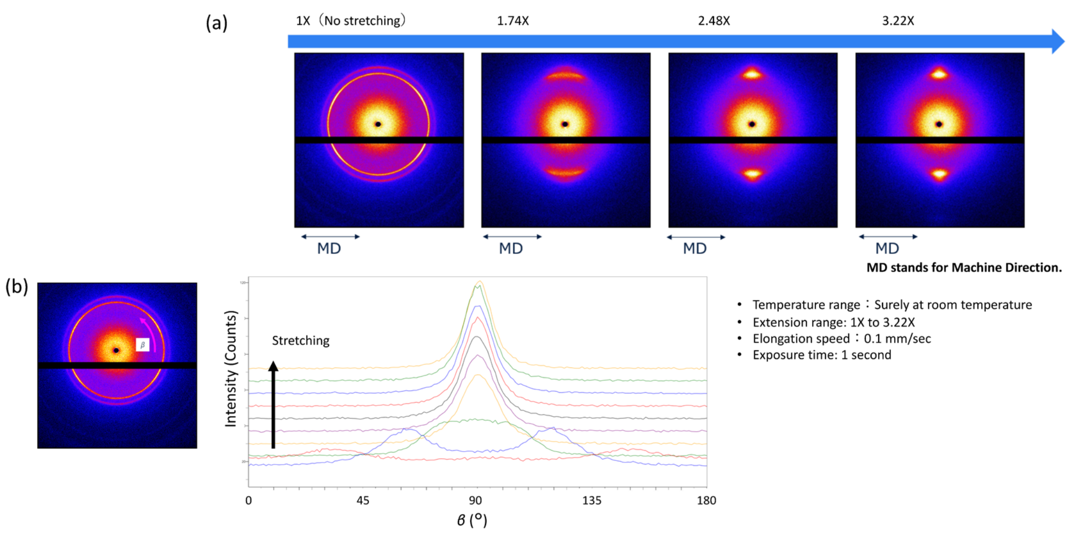

Fig. 9. High-speed time-resolved 2D diffraction measurement of PE film during isothermal stretching. (a) 2D data, (b) 1D profile after circular averaging (azimuthal (β direction)) (vertical axis is shifted)

important in polymer materials research. In particular, in-situ measurements under temperature and mechanical deformation, which can be used to reproduce the environment during the heating, cooling, and processing of polymer products, have traditionally been performed using synchrotron radiation. The combination of high-intensity X-rays and a high-speed, high-performance detector in NANOPIX-WE enables us to perform in-situ and operando measurements that have previously been possible only with synchrotron radiation.

The 2D-WAXS images of polyethylene terephthalate (PET) film were measured while heating the film from room temperature to 330°C at 20°C/min and converted to 1D scattering data, as shown in Fig. 8. The exposure time of these 2D-WAXS images was 1 second each, and they were measured repeatedly. The melting and recrystallization processes were clearly observed from the 2D diffraction images and the 1D scattering data, thus enabling fast time-resolved measurements in the laboratory.

The in-situ 2D-WAXS patterns from PE film during stretching process at different draw ratios are shown in the Fig. 9. The 2D-WAXS patterns of biaxial stretching PE film changes from biaxial orientation to uniaxial orientation depending on uniaxial drawing. The combination of NANOPIX-WE with a heating and stretching stage shows that in-situ structural evaluation of the stretching process can be performed in the laboratory.

4. Conclusion

NANOPIX-WE is a state-of-the-art wide-angle X-ray diffraction measurement system that combines Rigaku's latest X-ray generator, optic, and high-performance semiconductor detector technologies. Optimizing and combining these technologies with the optical system required for 2D-WAXS measurement makes NANOPIX-WE a 2D-WAXS measurement system for laboratory use with unprecedented performance, including sensitivity, speed, and spatial resolution close to that of synchrotron radiation.

NANOPIX-WE can be used in combination with a wide range of sample environment control attachments to perform in-situ or operando measurements on a wide range of materials, including not only functional polymers but also powders, powders and metallic materials, whether their structures are isotropic or anisotropic. NANOPIX-WE provides optimal structural analysis performance for sub-nanoscale structural evaluation of a wide range of materials, whether the structure is isotropic or non-isotropic, including not only functional polymer materials but also powders, powders, and metallic materials.