



Contents lists available at ScienceDirect

European Polymer Journal

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

Probing structure and orientation in polymers using synchrotron small- and wide-angle X-ray scattering techniques

Yimin Mao*, Ying Su, Benjamin S. Hsiao*

Department of Chemistry, Stony Brook University, Stony Brook, New York 11794-3400, United States

ARTICLE INFO

Article history:

Received 17 December 2015

Accepted 19 January 2016

Available online xxxx

Keywords:

WAXS

SAXS

Fiber

Orientation

Cellulose

Deformation

ABSTRACT

Synchrotron small- and wide-angle X-ray scattering (SAXS/WAXS) techniques are frequently used to study hierarchical structure and preferred orientation in polymers and biopolymers. In this article, two examples based on materials showing preferred orientation at different length scales are given. In the first example, cellulose fibers/nanofibers were investigated from the perspectives of crystal polymorphism, preferred orientation and nanoscale morphology. In the second example, a time-resolved SAXS/WAXS study was carried out to investigate the melting and recrystallization processes of a pre-stretched random co-polymer, poly(propylene-*ran*-1-butylene) (PB).

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Polymers and biopolymers can often exhibit hierarchical structures due to complex molecular and supermolecular interactions, which are very well suited for X-ray scattering studies. X-ray, as a short-wavelength electromagnetic radiation that interacts with electrons in the matter, is sensitive to the density variation of the system. Therefore, the structural information, as manifested in density fluctuations in real space, can be understood in reciprocal space by examining the Fourier transformation of the scattering data. The relationship between the real and reciprocal spaces, bridged by the Fourier transformation, can be described by the Fraunhofer diffraction theory, which is a good approximation to simplify data interpretation for both small-angle X-ray scattering (SAXS) or wide-angle X-ray diffraction (WAXD) studies [1,2].

There are only minor differences between the scattering/diffraction studies using synchrotron X-rays and laboratory X-rays, in terms of the experimental protocol and data analysis. In some cases, such as the crystallographic study of small-molecule single crystals, the laboratory X-ray source is being utilized in a routine manner. However, synchrotron X-ray scattering facilities can offer several unique advantages over the laboratory X-ray sources, thus are of particular interest to material scientists working on the kinetics, dynamics and processing of soft matter. First, the high intensity of synchrotron X-rays can allow a great deal of experiments to be completed in a very short period of time, enabling *in situ* or real-time studies. Second, synchrotron radiations can produce a wide spectrum of wavelengths that empowers new types of scattering experiments, such as resonance scattering. Third, hard X-rays can be used to measure complex fluids, where the attenuation issue due to solvent may be mitigated.

* Corresponding authors. Current addresses: Department of Materials Science and Engineering, University of Maryland, College Park, MD 20742, United States. NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899, United States (Y. Mao).

E-mail addresses: yimin.mao@nist.gov (Y. Mao), benjamin.hsiao@stonybrook.edu (B.S. Hsiao).

As synchrotron X-ray beamlines are usually much more flexible for hosting different experimental chambers than the laboratory facilities, a large variety of different sample environments can be introduced, including flow cells [3–5], high pressure apparatuses [6–10], vapor chambers [11,12], mechanical deformation devices [13–18], simulated and real-life processing equipment (e.g. fiber spinning and film extrusion) [19], in *in situ* X-ray studies. The combined characterization techniques involving synchrotron X-rays and other analytical probes, such as light scattering [20], Raman and IR spectroscopy [21–23], are also feasible to cover a broad range of structural and functional information.

In this article, we use two examples to illustrate how one can use synchrotron SAXS/WAXS techniques to characterize the structure and orientation information in polymer and biopolymer systems at different length-scales. In the first example, the structures of disperse nanocelluloses and corresponding crystal aggregates in natural woods were investigated. In the second example, stretching-induced structure and preferred orientation of a random copolymer, poly(propylene-*ran*-1-butylene) (PB), was examined in a time-resolved matter. The demonstrated methodology can be applied to more general cases, such as studying the fibrillation process of cellulose biomass (wood and non-wood) in real time using synchrotron X-ray scattering/diffraction techniques, which is of increasing interest in exploring new material discovery from natural resources.

2. Theory

2.1. General treatment

Theoretical formulations for the analysis of scattering and diffraction data are essentially derived from the same geometric consideration. When X-ray interacts with matter, part of the incident beam is scattered elastically, meaning there is no energy (and consequently wavelength) change during the process. In the Fraunhofer diffraction regime, the scattered wave is a Fourier transform of a spatial density fluctuation in real space, $\rho(\mathbf{r})$, written as $F(\mathbf{s})$. \mathbf{r} and \mathbf{s} represent points of interest in real space, and in reciprocal space, respectively. \mathbf{s} is often termed the scattering vector, with its modules written as $s = (2/\lambda) \sin \theta$, where λ is the wavelength of the X-ray beam and 2θ is the scattering angle. Different coordinate systems can be used to describe the scattered wave function, depending on the mathematical convenience. In X-ray crystallography, due to the 3D translational orders in crystals, three basis vectors, in coincidence with \mathbf{a} -, \mathbf{b} -, and \mathbf{c} -axis of a unit cell are often used to describe the spatial arrangement of the motif in real space. Correspondingly, in reciprocal space, \mathbf{a}^* , \mathbf{b}^* , and \mathbf{c}^* can be used to define a reciprocal lattice.

In practice, $\rho(\mathbf{r})$ is a real function, but $F(\mathbf{s})$ is a complex-valued function, not a quantity that can be directly measured in a scattering experiment. The scattered intensity $I(\mathbf{s})$ is the square of the modulus of $F(\mathbf{s})$, registered on a detector. Hence, all the phase information is lost by the transformation between real and reciprocal spaces. As a result, the major task of the data interpretation is to derive $\rho(\mathbf{r})$, based on the known intensity distribution, which can be approximately written as:

$$I(\mathbf{s}) = |F(\mathbf{s})|^2 S(\mathbf{s}) \quad (1)$$

$F(\mathbf{s})$ is often termed as the structure factor and $S(\mathbf{s})$ as the lattice factor in the crystallography community. However, in the SAXS community, the former is termed the form factor and the latter the structure factor. In spite of the nomenclature difference, $F(\mathbf{s})$ is originated from the *smallest* scattering unit in the probing range, while $S(\mathbf{s})$ indicates how these units are intercorrelated. The complete formulation of the scattered intensity $I(\mathbf{s})$ can be quite complex, and sometime is a formidable task to achieve. However, one can carefully design a scattering measurement to simplify the problem experimentally. For example, if the particle/molecular geometry is of interest, a dilute solution can be prepared, so that the lattice/structure factor can be safely treated as a unity. On the other hand, in crystallography, atomic scattering factors are often known. Thus, the task is to map out their spatial arrangement.

Samples used in a scattering experiment can be oriented or isotropic. Consequently, various detection schemes need to be used to deal with the different scenario. In the case of single crystals having 3D translational order, scattering vectors along all three basis vectors need to be recorded in order to fully define the crystal lattice. Often, the crystal sample is rotated and/or oscillated in the experiment, so that the scattered intensity distribution in 3D reciprocal space can be registered. In polymer and biopolymer systems, an important category of samples possess fiber symmetry with preferred orientation in a given direction, where the scattered intensity at given $s = |\mathbf{s}|$ is a constant around the fiber axis. In this case, the sample orientation can be determined by an area detector. In the last case, if the scattering unit in the sample is randomly oriented with no preferred orientation, the scattered intensity is only a function of scalar s , where all information about the preferred orientation is averaged out. Both powder diffraction and solution-SAXS experiment are examples of this case.

2.2. Preferred orientation for system with fiber symmetry

With X-ray diffraction technique, the crystal structure of polymer/biopolymer is often determined by using the sample with fiber symmetry. This is because it is often difficult for polymers to grow into a large single crystal form, but it is relatively easy to shape the sample into a fiber form. This technique is termed the fiber diffraction approach, which is also used in structure determination of fibrillar biopolymers and viruses. In some scenario, the structure of the system is known, but the degree of orientation is not. This is the case for polymer processing, where the structure development is a function of time and external filed parameters (e.g. shear or elongational force). This information is essential for the manipulation of

Download English Version:

<https://daneshyari.com/en/article/7804344>

Download Persian Version:

<https://daneshyari.com/article/7804344>

[Daneshyari.com](https://daneshyari.com)