

Synchrotron X-ray scattering study on amorphous poly(ethylene furanoate) under uniaxial deformation

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ABSTRACT

Uniaxial deformation of amorphous poly(ethylene furanoate) (PEF) was studied using synchrotron-based simultaneous wide- and small-angle X-ray scattering (WAXS/SAXS) techniques, at four temperatures, namely, 90 °C, 100 °C, 110 °C, and 120 °C. Local ordering of the chains with a preferred orientation occurred before onset of strain-induced crystallization. The ordered domain in the amorphous phase displayed two characteristic length scales (~4 Å and ~2 Å), associated with the lateral inter-chain distance and staggering along the polymer chain direction, respectively. Fibrillar crystal morphology was induced, containing ~2–3 unit cells on average in the direction of each lattice primitive basis, due to crystallization from highly-oriented polymer chains in amorphous phase. Time-resolved *in situ* scattering studies have allowed direct correlations between structure and stress-strain behavior. In the early stage of deformation, stress increased slowly with strain, leading to a degree of orientation in the amorphous phase reaching ≈0.3 before strain-induced crystallization was first observed. The onset of strain-hardening occurred immediately after crystallization occurred, which could be explained by the reinforcement of material due to small amounts of crystals serving as physical cross-linking points.

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1. Introduction

Poly(ethylene furanoate) (PEF) has been attracting increasing attention from researchers in recent years, partly because the feedstocks for the monomer are completely based on renewable biomass, which has significant environmental advantages over traditional synthetic polymers based on petroleum sources [1]. The primary chain structure of PEF is similar to that of the widely used poly(ethylene terephthalate) (PET), except that the benzene group in PET is replaced by a furan group in PEF [2,3]. This seemingly minor change does however, have dramatic effects on the polymer properties, in particular the gas barrier properties, which are far

superior in PEF as compared to PET. Therefore, PEF is generating great interest to industrial communities involved in beverage/food packaging [4–9].

There are only a limited number of published studies on the physical properties of PEF, including its mechanical properties [2], classical quiescent crystallization behavior [10], and strain-induced crystallization [11]. Koros and co-workers have recently undertaken a series of studies on the absorption and transport properties of various gases and water, through PEF films [4–9]. Following a different line of research, we have carried out a series of synchrotron-based X-ray scattering studies, to explore structural aspects of PEF material. Recently using X-ray fiber diffraction a greatly refined crystal structure of PEF has been proposed, consisting of a monoclinic unit cell with $a = 5.784 \text{ \AA}$, $b = 6.780 \text{ \AA}$, $c = 20.296 \text{ \AA}$, and $\gamma = 103.3^\circ$ [3]. The space group was $P2_1$. The unit cell contained two PEF chains, with one located at the corner along the c -axis, and the other in the center of ab -plane.

In this paper, we report results from *in situ* experiments exploring the structural development during uniaxial deformation of PEF. Taking advantage of the high photon flux achievable at synchrotron X-ray scattering beamlines in addition to versatile sample environment equipment that can be used, a precise

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mapping of structural information to mechanical performance could be achieved. 2D detectors were used in these measurements (WAXS/SAXS), so that preferred orientation during uniaxial stretching could be examined in detail.

2. Experimental

2.1. Materials

The PEF was provided by Coca-Cola Company. The M_w and M_n values were previously determined to be 87,000 and 66,000 g/mol using multiangle light scattering (MALS) and 110,000 and 47,000 g/mol using refractive index (RI) techniques, respectively, calibrated using PMMA standards. The glass transition and melting temperature of raw PEF pellet as measured using Differential Scanning Calorimetry (DSC) were 83.6 °C (30 °C/min cooling from melt) and 219.2 °C (endothermic peak position, heating rate was 10 °C/min), respectively (see Fig. S1 in the Supporting Materials). Before making films, the PEF pellets were vacuum dried at 140 °C for 3 days to remove residual moisture.

2.2. Sample preparation

PEF films used for all uniaxial deformation experiments were prepared using hot-pressing method. The dried PEF pellets were first melted at 240 °C, and were then hot pressed into films with a uniform thickness of 0.8 mm. The film was held at 240 °C for 2 min, after which it was then taken off the press and allowed to naturally cool down to room temperature. The films were cut into 6 mm × 26 mm rectangular bars to be mounted on the Linkam TST350 tensile machine.

2.3. In situ WAXS/SAXS experiment

Simultaneous WAXS/SAXS experiments were performed at the DuPont-Northwestern-Dow Collaborative Access Team (DND-CAT) beamline located at Sector 5-ID of the Advanced Photon Source (APS), Argonne National Laboratory (ANL). Three Rayonix CCD cameras were installed successively to collect small- (SAXS), mid- (MAXS) and wide-angle (WAXS) X-scattering data simultaneously. Sample-to-detector distances (SDDs) for the three detectors were 197 mm, 1012 mm, and 7496 mm, respectively. The X-ray beam energy was set at 17 keV, corresponding to 0.7293 Å wavelength. Typical exposure time was 2 s.

The Linkam TST350 tensile, temperature controlled stage was mounted at the beam line so that the stretching direction was vertical, and the sample was perpendicular to the incident X-ray beam. The stretching speed of the samples in all experiments was 50 μm/s, thereby avoiding non-centered necking of the film. Scattering experiments were carried out at 90 °C, 100 °C, 110 °C, and 120 °C.

3. Results and discussion

3.1. Deformation in low to intermediate strains

The crystallization kinetics of PEF is known to be very slow [11]. Consequently, even though the PEF films were allowed to cool down naturally from its molten state (i.e., 240 °C) back down to room temperature, no crystallinity developed in the sample and it remained fully amorphous. This can be evidenced from the WAXS data, where no crystalline peaks were observed for films prepared using the above-mentioned protocol (see Fig. 1 for example). Although the *in situ* experiments were carried out at four different temperatures, in the following text, we discuss the detail of the

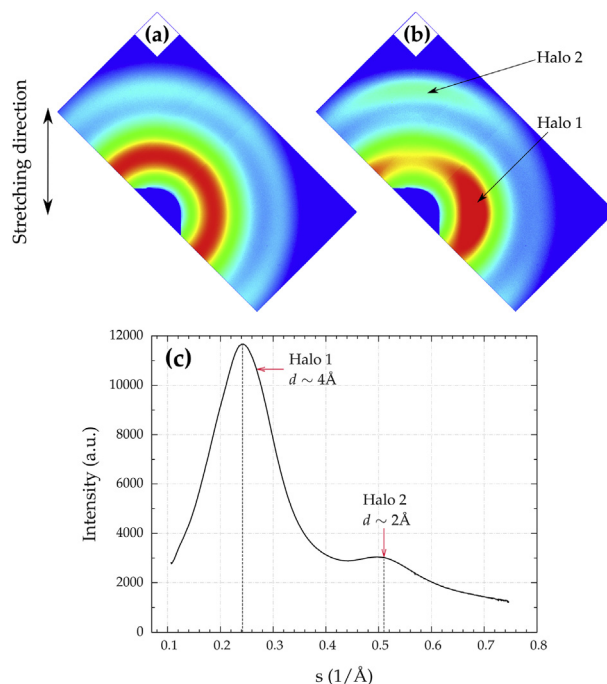


Fig. 1. 2D scattering patterns of amorphous PEF film uniaxially stretched at 90 °C at strain = 0 (a), and strain = 1.14 (b). The 1D integrated scattering intensity as a function of scattering vector from the unstretched PEF is shown in (c). 2D patterns are shown in logarithmic scale. Stretching direction is vertical.

analyses of the structural development of the sample measured at 90 °C, and then applying the same methodology to discuss the influence of temperature on structure and mechanical properties.

Fig. 1 shows WAXS data of a PEF film before undergoing deformation (Fig. 1a) compared to that collected in the strain region where crystallization was observed to take place (Fig. 1b). Before stretching, the WAXS pattern for the as made sample was isotropic, indicating the chains had no preferred orientation. The pattern consists of two obvious halos, where the positions of their maxima correspond to d -spacings of ~ 4 Å and ~ 2 Å, respectively (as shown in Fig. 1c). In the early stages of stretching, before development of a crystalline structure, the amorphous chains clearly orient, as indicated by the anisotropic scattering pattern shown in Fig. 1b. In these anisotropic patterns, halo 1, at the lowest scattering vector corresponding to length scale of ~ 4 Å becomes focused around the equator and is associated with an average lateral distance between the chains that are becoming closely packed. This inter-chain packing is a precursor for the strain-induced crystals that form, in which the inter-chain distance along the b -axis, namely, the distance between planes containing furan groups, is 3.39 Å (half of the unit cell dimension along b -axis) [3]. The lateral inter-chain distance in the pre-ordered amorphous phase is slightly larger than that in the resulting crystal, which is reasonable as polymer chains are close-packed in unit cells.

Interestingly, the second amorphous halo at a higher scattering vector, labeled halo 2, becomes localized in the meridian direction in the early stages of stretching, as shown in Fig. 1b. The position of this halo suggested a characteristic distance of ~ 2 Å along the chain direction, which will ultimately become the c -axis direction in the crystals that form. We have previously shown that in the crystalline state, the absence of the (006) plane in fiber diffraction pattern of PEF is associated with a chain-staggering of $c/12$, namely, a ~ 1.69 Å shifting between the corner-chain and central-chain along the c -axis direction [3]. Given the localization of amorphous halo 2 into the strain direction and its length scale we

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