Structure Development in Polymers during Fused Filament Fabrication (FFF): An in-situ Small and Wide Angle X-ray Scattering Study using Synchrotron Radiation

Aurora Nogales*, Edgar Gutiérrez-Fernández, Mari-Cruz García-Gutiérrez, Tiberio. A. Ezquerra*

Instituto de Estructura de la Materia (IEM-CSIC), Serrano 121, 28006, Madrid, Spain.

Esther Rebollar

Instituto de Química Física Rocasolano (IQFR-CSIC), Serrano 119, 28006, Madrid, Spain.

Igors Šics, Marc Malfois

ALBA Synchrotron,Carrer de la Llum 2-26,08290 Cerdanyola del Vallès, Barcelona, Spain

Sergejs Gaidukovs

Faculty of Materials Science and Applied Chemistry, Institute of Polymer Materials, Riga Technical University, Riga, Latvia.

Egils Gēcis, Kristofers Celms

Purpose AM Systems Ltd, Riga, Latvia.

Georgijs Bakradze

FabControl Ltd, Riga, Latvia.

*Corresponding Authors: Aurora Nogales (aurora.nogales@csic.es), Tiberio A. Ezquerra (t.ezquerra@csic.es). Instituto de Estructura de la Materia (IEM-CSIC), Serrano 121, 28006, Madrid, Spain

Supporting information

Movie SI1: SI1_3D_Printing_1.wlmp (Movie of a 3D printing experiment, the movie has been fast-forwarded)

Experimental procedure

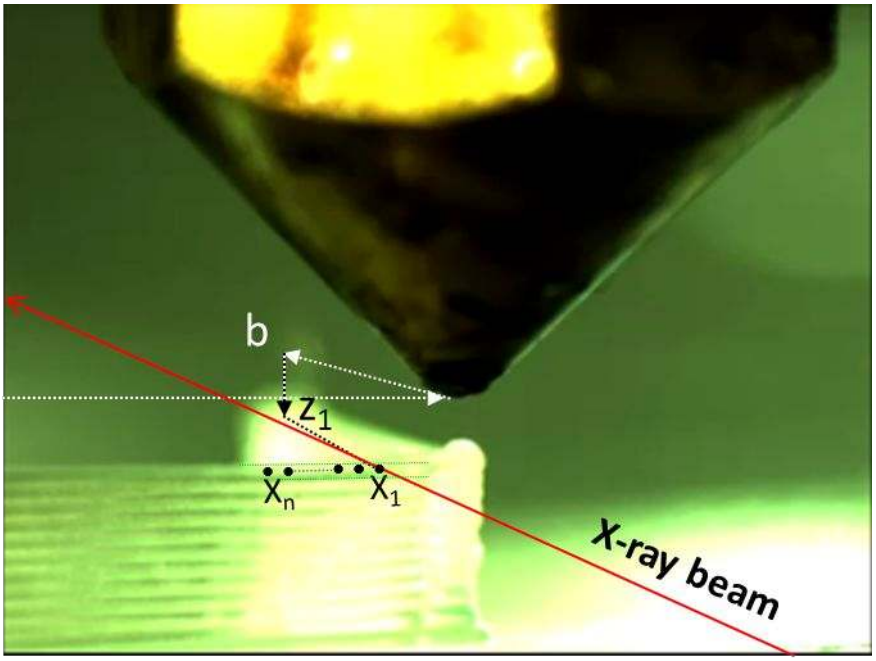

Figure SI_1. Scheme of the experimental procedure. For every measurement, a Π-shaped five-layer single-walled sample was 3D printed under fixed conditions which were optimized in a series of ex-situ studies to produce samples with an adequate mechanical stability. After printing a Π-shaped five-layer single-walled sample (long side 5.92 cm, short side 0.5 cm), i.e. when the printing head reached the position b, the nozzle stopped extrusion, the filament was retracted, the substrate moved down Z_1 = 0.050 cm and the build platform moved with a travel speed of 14 cm/s to the selected measurement position, X_i. Once the selected measurement position has been reached the data acquisition was triggered and SAXS and WAXS data were acquired as a function of time.

Calculation of the crystallinity degree from the WAXS patterns.

The crystallinity was calculated by means of a fit parameter study proposed by Blundell and Osborn[26, 28]. Figure SI_2a shows the azimuthally integrated scattered intensity as a function of the modulus of the scattering vector q as-calculated from the corresponding WAXS patterns obtained from the first frames (when polymer has not crystallized, A(blue pattern)) and final frames (when polymer has crystallized, B(red pattern)) in a given experiment.

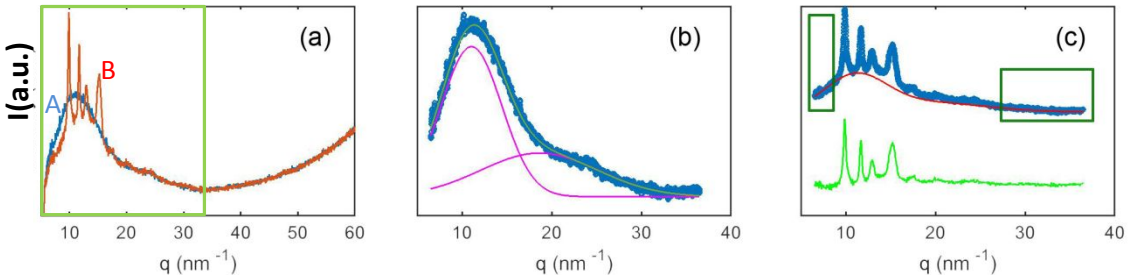

Figure SI_2*. (a) An example of the azimuthally integrated scattered intensity as a function of the modulus of the scattering vector q as-calculated from the corresponding WAXS patterns for an initially amorphous polymer, A(blue pattern), and eventually semicrystalline, (B, red pattern), sample. (b) An example of an amorphous halo fitted by two Gaussian functions. (c) An example of an intermediate state where the contribution of the amorphous halo can be deconvoluted from the contribution of the Bragg peaks. The green rectangles in (c) indicate the q-region where both amorphous halo and measured data should coincide.*

The green rectangle in Fig. SI_2a indicates the data range we used for the calculation. After the background correction the intensity was fitted by two Gaussian functions (Figure SI_2b). In general, every frame was considered to be composed of: (i) the amorphous halo (multiplied by a scaling factor lower than unity), (ii) the amorphous

phase, (iii) the crystalline phase (Figure SI_2c). To calculate the scaling factor for the contribution of the amorphous halo we used the low and high q regions which are highlighted by the green rectangles in Figure SI_2c, where the Bragg peaks have the least contribution. The crystalline contribution is considered to be the difference between the calculated halo and the total signal (see the bottom curve in Figure SI_2c). The fit parameter study was performed using a self-written code implemented in Matlab®.

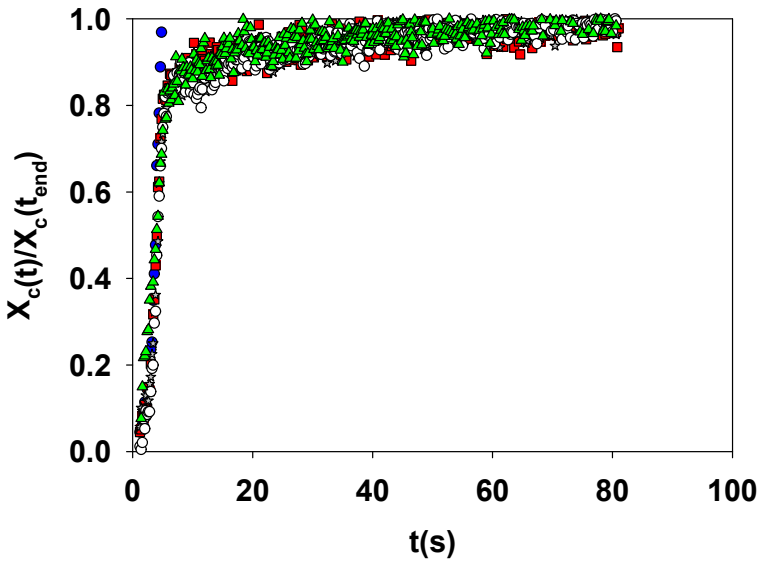

Figure SI_3*. Degree of transformation as derived from crystallinity data across the layer of Fig. 5a normalized by the final crystallinity value. The measurements were performed in different Z positions across the top layer in a five-layer sample: on the free surface (●); 0.005 cm (■), 0.010 cm, (★), 0.015 cm (○), 0.020 cm (▲).*

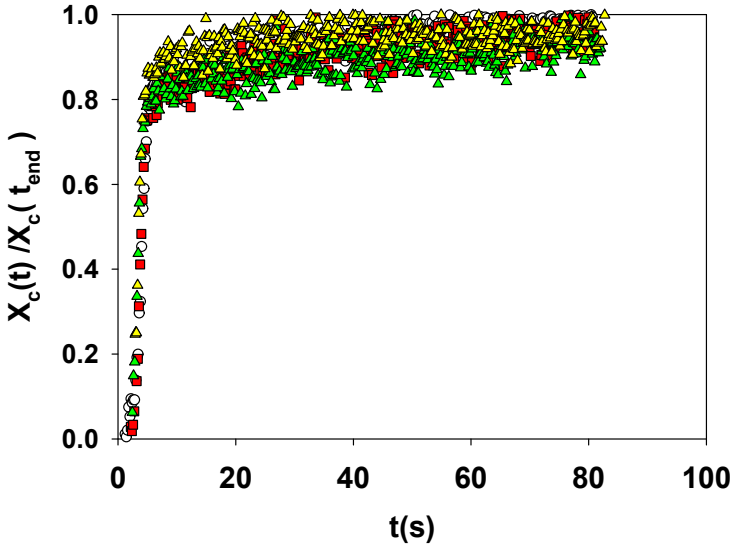

Figure SI_4. *Degree of transformation as derived from crystallinity data along the layer of Fig. 7a normalized by the final crystallinity value. The measurements were performed in four different positions along the top layer in a five-layer sample: 0.10 cm* (○)*, 0.90 cm* (■)*, 1.40 cm* (▼)*, and 1.90 cm* (▲) *from to the edge of the Π-sample, respectively.*