Structure Development in Polymer Materials Additively Manufactured by Fused Filament Fabrication (FFF) as Revealed by X-Ray Scattering with Synchrotron Light

T. A. Ezquerra[1]
A. Nogales[1], E. Gutiérrez-Fernández[1], M.C. García-Gutiérrez[1], E. Rebollar[2], I. Šics[3], M. Malfois[3], S. Gaidukovs[4], E. Gēcis[5], K. Celms[5], G. Bakradze[6].

[1]Instituto de Estructura de la Materia (IEM-CSIC), Serrano 121, 28006, Madrid, Spain . [2]Instituto de Química Física Rocasolano (IQFR-CSIC), Serrano 119, 28006, Madrid, Spain. [3]ALBA Synchrotron, Carrer de la Llum 2-26,08290 Cerdanyola del Vallès, Barcelona, Spain. [4] Faculty of Materials Science and Applied Chemistry, Institute of Polymer Materials, Riga Technical University, Riga, Latvia. [5]Purpose AM Systems Ltd, Riga, Latvia. [6]FabControl Ltd, Riga, Latvia.
t.ezquerra@csic.es

Abstract
In recent years various methods of Additive Manufacturing (AM), popularly referred to as 3D printing, have emerged allowing to process not only polymers but also ceramics, metals, glass and composites1. Fused Filament Fabrication (FFF) is one of the polymer AM methods which is based on the continuous layer-by-layer deposition of a polymer melt produced by hot extrusion [1-2]. Upon deposition the polymer melt cools down and solidifies. If a semicrystalline polymer is employed, the solidification process of the extruded polymer may crystallize eventually resulting in warping of the 3D-printed parts. Inherent to FFF is the creation of welds between adjacent layers whose quality is crucial for the mechanical performance of the finished product [2].
In this study, microstructure formation in individual layers during Fused Filament Fabrication (FFF) in polymer sample was studied by simultaneous measurement of small- (SAXS) and wide-angle X-ray Scattering WAXS) methods employing synchrotron light. Individual layers as well as welding zone between individual layers were investigated in isotactic polypropylene (iPP). The lines were deposited by an FFF 3D printer which was custom-built to fit into the synchrotron beamline (Fig.1). The polymer microstructure was characterized in terms of crystallinity and long-spacings. Avrami analysis indicates that the crystallization behavior of iPP in thin layers is rather similar to that observed in quiescent crystallization of bulk iPP, suggesting similar nucleation and growth mechanisms. Our results revealed that the polymer is more crystalline in the bulk of the layer and less crystalline in the vicinity of the interfaces. This effect can be advantageous to facilitate the welding between the layers, i.e. to improve the overall mechanical performance of the 3D printed object.

Figures

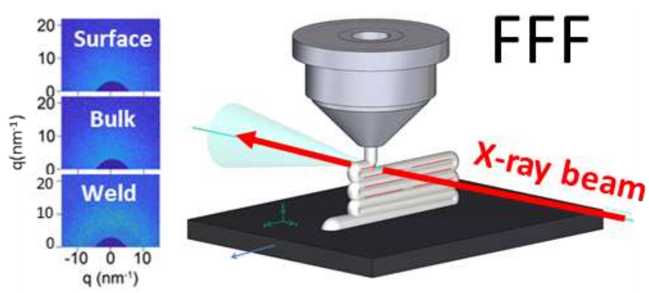

Figure 1: Conceptual view of the experimental approach followed to investigate in real time structure development during Fused Filament Formation (FFF) [3].

References
[1] Vaezi, M. et al. *Journal of Advanced Manufacturing Technology* 67 (5-8), **2013,** 1721-1754.
[2] Nogales A. et al. Macromolecules, 52(24) **2019**, 9715-9723