

An in-situ synchrotron X-ray view on the crystallization of synthetic polymers for 3D printing under Fast Scanning Calorimetry conditions

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Nowadays fast scanning chip calorimeters (FSC) are commercially available, allowing to study the thermal behavior of sub microgram samples at heating rates up to 40000 °Cs⁻¹ and cooling rates up to 5000 °Cs⁻¹ [1-2]. In fact, for maintaining thermal control, minute sample amounts are mandatory rather than optional. Besides downscaling in sample mass, the availability of fast rates opens the possibility to create and study metastable structures that otherwise remain inaccessible. However, although the thermal behavior reveals the presence of such structures, the calorimeter on its own cannot identify their nature or morphology. Moreover, some of these phases are short living or only existing at temperatures other than room temperature by which morphological investigations of the material conditioned on the chip – after having been detached from the calorimeter - are not possible. There is therefore a need for methodologies that provide morphological information at the scanning rates comparable to those of such chip calorimeters.

We recently modified an existing Mettler Flash DSC 1 in such a way that the chip can be controlled outside the machine. The chip in action can therefore be presented in front of an X-ray beam.

Experiments were conducted at DUBBLE, the Dutch Belgian Beam Line at the ESRF. The setup and the measuring protocol (stroboscopic data acquisition) were optimized by using high-density polyethylene (HDPE). WAXD patterns at every degree during the crystallization and melting at FSC typical scanning rates from 20 up to 200 °C s⁻¹ were analyzed in terms of the temperature and scanning rate dependent material crystallinities and crystal densities. Interestingly, the combined approach revealed FSC thermal lag issues, for which can be corrected [3].

In a second set of experiments the high-rate crystallization and melting behavior of polyamide 12 (PA12) and polyamide 11 (PA11) was considered. These polymers are used in 3D printing via the selective laser

sintering (SLS) of 50 µm grains. High rate crystallization and melting is inherent to this sintering process. The isothermal crystallization of PA11 and PA12 were studied over the entire temperature range between the glass transition temperature and the melting temperature. Using cooling rates of 1000 °Cs⁻¹ allowed bypassing crystallization on cooling which enabled studying the isothermal crystallization at large supercooling. Similar to other polymers reported in literature [4], a bimodal crystallization rate dependence on temperature is observed for PA11 and PA12 (Figure 1).

Isothermal solidification at high supercooling yields a mesomorphic phase in less than a second, whereas at very low supercooling crystals are obtained. At intermediate supercooling, mixtures of mesomorphic and crystalline material are generated at a ratio proportional to the supercooling. This ratio is constant over the isothermal solidification time [3]. The obtained data lead to the hypothesis that the two maxima in the crystallization rate are due to a crystallization retardation at the minimum in the crystallization rate curve. This retardation results from the competition between mesomorphic and crystalline phase formation and is referred to as 'self-poisoning'.

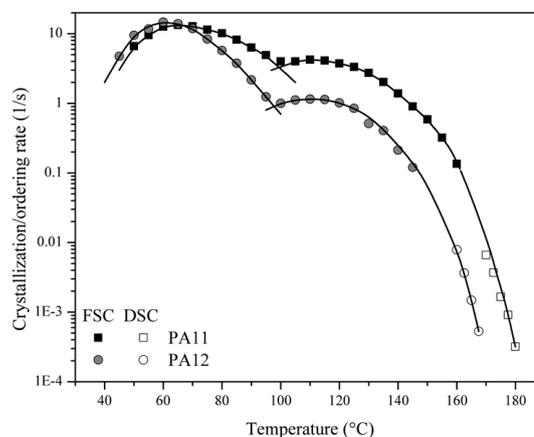


Figure 1. FSC-based crystallization rate of PA11 and PA12.

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