Polymer phase transformation

Simultaneous SAXS/WAXS measurements of a semi-crystalline polymer during thermal processing enables determination of route for phase transformation.

Introduction

It is well known that polymers undergo a large series of thermal transformations, from the synthesis in the reactor up to the final product shaping, i.e. during injection molding processing or film formation. Furthermore, quenching is sometimes part of the processing, for instance to retain a given nanostructure orientation or an out-of-equilibrium phase. Since polymers may self-organize over a wide hierarchical range, from the atomic scale up to several tenth of nanometers, simultaneous Small-Angle/Wide-Angle X-ray Scattering (SAXS/WAXS) is the ideal technique to study such samples.

Simultaneous data collection is of particular interest during thermal processing as it enables dynamic *in-situ* multi-scale investigation of both the crystalline phase and nanostructure to define the phase transformation route.

Measurements & results

A single layer of a 20 µm solvent cast thick film of fluoropolymer was measured in simultaneous SAXS/WAXS mode on the Xeuss 2.0 SAXS/WAXS system. The system was heated from room temperature up to 130°C at a heating rate of 1°C/min using an integrated temperature control stage (Linkam HFSX350). This thermal process was the first heating of the sample.

Detection was performed both in SAXS and in WAXS with a dual detector set-up.

During the thermal process, this fluoropolymer is known to undergo a ferroelectric to paraelectric transition called the Curie transition. This transition is also known to be reversible only once the sample is "stabilized".

Figure 1 represents the resulting SAXS and WAXS 1D curves as a function of temperature. These results provide information on both the crystalline phase and on the lamellar phase nanostructure evolution as a function of temperature.

The WAXS data shows clearly the reversibility of the transition as crystalline peaks remain at the same positions. However, SAXS data show that the long period is being shifted from 14 nm up to 32 nm after this first thermal treatment crossing the Curie temperature.

Subsequent thermal cycles (not shown) do not show any further shift of the long period. This indicates that stabilization was obtained after the first thermal cycle. From there, reversibility is achieved.

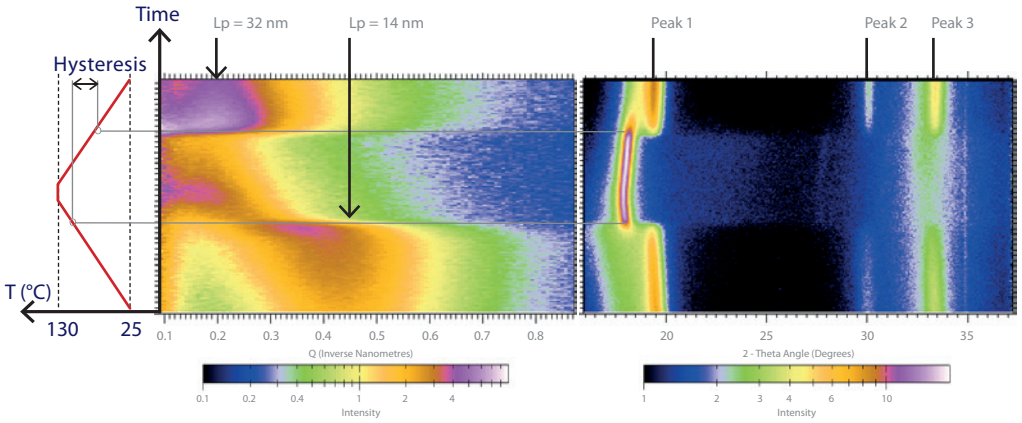

Figure 1. - Simultaneous SAXS (left) and WAXS (right) study of a fluoropolymer film during first heating and cooling. Ramp at 1°C/min (far left). 2D representation of SAXS and WAXS 1D curves as a function of temperature. Each horizontal pixel line corresponds to a 1D curve [Intensity = f(q) or f(2θ)] of 1 min exposure time.

To go further

In-situ experiments of polymer films as a function of thermal treatments, before only performed on synchrotron beamlines[1,2], are now possible in the lab using the Xeuss 2.0 or the Nano-inXider SAXS/WAXS systems.

Xenocs SAXS/WAXS systems enable a wide range of kinetic and dynamic *in-situ* multi-scale studies, using dedicated environmental control stages such as a stretching cell or a humidity control stage.

[1] P. Panine et al., Polymer, 2008, 49, 676-680
[2] Wang et al., Macromolecules, 2000, 33, 978-989

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