	Experiment title: Enhancing the nucleation efficiency of biopolymers with oxalamide-based nucleating agents (file nr 195.068.962)	**Experiment number**: 26-02-800
Beamline: BM26B	**Date of experiment**: from: 17-11-2016 to: 21-11-2016	**Date of report**: 23-1-2017
Shifts: 12	**Local contact(s)**: Daniel Hermida Merino <daniel.hermida_merino@esrf.fr>	*Received at ESRF:* *23-1-2017*

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Report:

In the allocated beamtime, we have tested the effect of three nucleating agents (Figure 1) on the crystallization of *i*PP (reference) and PLLA (biopolymer). All samples have been tested under quiescent conditions and after the subjection to shear. The application of shear was performed using both a Linkam-Shear shell, having a parralell plate-plate set-up, and a multi-pass rheometer Unfortunately, for the PLLA samples (Mw ~200 kg/mol), the viscosity of the samples was too low to identify any effect of shear on the crystallization behavior in both machines. In fact, only isotropic crystallization was observed for these samples, despite the application of high shear pulses. In contrast, for the iPP samples (Mw ~400kg/mol) a clear synergystic effect of the nucleating agent can be observed both after the application of high shear and under quiescent conditions (Figure 2). These results, obtained from the preliminary analysis, show the desired effects anticipated for the nucleating agents under shear conditions, thereby proving the concept we aimed to identify in this work. The results from this current proposal are expected to be published in at least one scientific publication.

In order to translate identify whether this synergistic effect of the developed NAs is also observed in biopolymers, future experiments will be conducted in collaboration with the group of professor Gerrit Peters (Eindhoven University of Technology). In this work we will design a new mold for the multi-pass rheometer. This mold, having a smaller diameter, allows us to probe the flow response of materials having a low melt-viscosity, for example, in currently used commercial PLLA samples. Once we successfully demonstrate to be able to work with such low viscous samples in this MPR mold, we will apply for new beamtime on this subject.

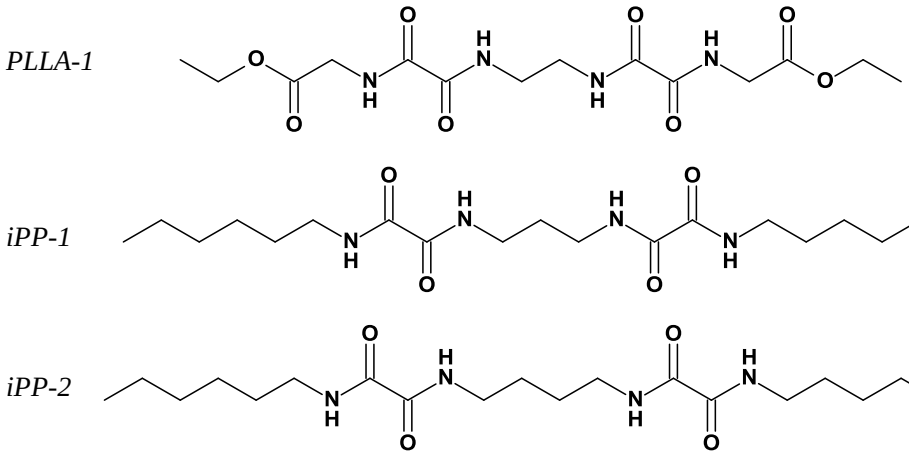

Figure 1. Chemical compositions of the three nucleating agents tested in this study.

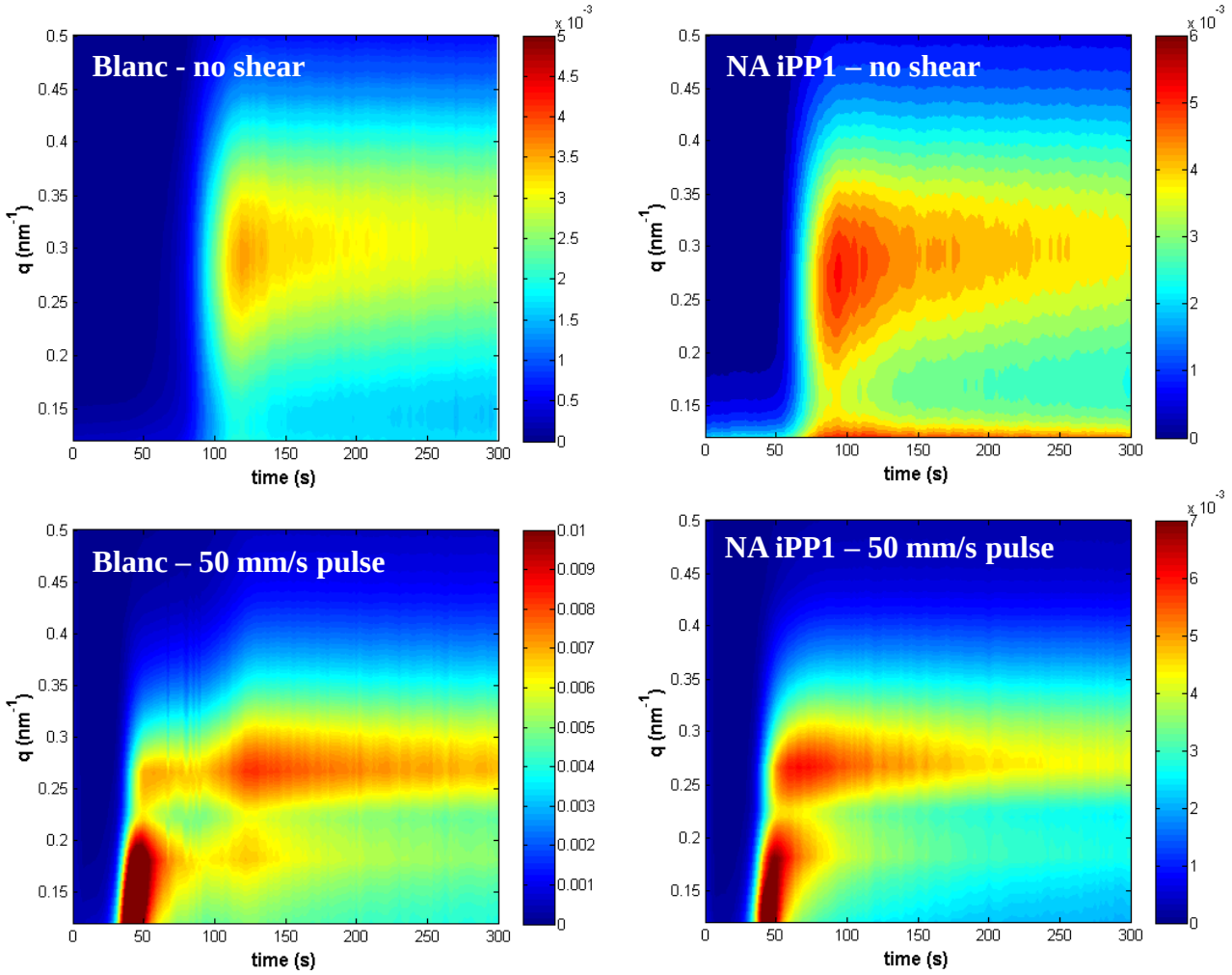

Figure 2. Time dependent changes in diffraction signals observed from small-angle x-ray diffraction studies. Experiments were performed at 170 °C, after which the samples were quenched to 100 °C using active cooling. From the data it can be seen that the onset of formation of crystal lamella is observed in iPP in the absence of shear after roughly 80 seconds of cooling (113 °C). Performing this experiment under the same conditions in the presence of NA iPP1, crystallization is observed already after 50 seconds of cooling (120 °C). The application of a shear pulse at 170 °C promotes the formation of a shish kebab morphology (formation observed in both samples around 30 seconds, 130 °C). However, this only occurs on the sheared part of the sample, which resides close to the wall of the MPR mold. The center of the sample is not affected by any shear-induced precursors, and crystallizes isotropically again around 110 °C. In contract, for the samples containing NA, the isotropic crystallization at the center of the samples occurs simultaneously with the generation of the shish-kebab morphology (~130 °C). The data confirms that the NA self-assembles upon the application of shear (even under low stress!), thereby exhibiting enhanced performace under processing conditions, thereby significantly decreasing processind times.