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Experiment Report Form

	Experiment title: Effect of bio-based nucleating agents on the crystallization kinetics of stereo-complex polylactic acid using micro focus X-ray scattering combind with fast chip calorimetry	**Experiment number**: **A26-2 948**
Beamline: BM26	**Date of experiment**: from: 04/11/2022 to: 08/11/2022	**Date of report**: 10/03/2023
Shifts: 9	**Local contact(s)**: Martin Rosenthal	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Moya Lopez-Pelaez, Carmen : Universite de Lorraine LMOPS 2 rue Edouard Belin FR - 57070 METZ

Hermida Merino, Daniel : DUBBLE CRG c/o ESRF 71 avenue des Martyrs CS40220 FR - 38043 GRENOBLE

Rosenthal, Martin : DUBBLE CRG c/o ESRF 71 avenue des Martyrs CS40220 FR - 38043 GRENOBLE

The experimental summary given below is just reporting on the preliminary data analysis of experiment A26-2 965 and was used in part for the PhD thesis:

« PLA stéréo-complexes à blocs : de la synthèse aux applications biomédicales »

by Carmen Moya Lopez Pelaez, sucessfully defended on 18/11/2022 in Metz

Thèses en préparation à l'Université de Lorraine, dans le cadre de C2MP - CHIMIE MECANIQUE MATERIAUX PHYSIQUE , en partenariat avec LMOPS - Laboratoire Matériaux Optiques, Photonique et Systèmes (laboratoire) depuis le 21-10-2019, La soutenance a été réalisée avec succès le 18/11/2022

PLA stereo-block copolymer: from synthesis to the biomedical application (extrait)

Due to the excellent physico-chemical properties and good stability of plastics, they are used on large scale in many applications. Most polymers come from petrochemical sources and this dependency has become an important social issue. Among the biopolymers, poly-lactic acid (PLA) has captured the attention of industry because of its biodegradability, transparency, stiffness and ease of application. PLA is specially used in 3D impression and also in biomedical applications thanks to its biocompatibility. PLA development and its use in certain applications as a replacement for petrol-based polymers depend therefore on the improvement of its working properties. There are two ways of amelioration: (i) to have a perfect control of the polymer microstructure during the synthesis and shaping in order to adjust the functional characteristics according to the application, (ii) to attach another biopolymer to PLA with the aim of compensating some limitations, for example, the lack of stability in a hygrothermical environment. The aim of the proposed thesis is to work on PLA and to exploit these two ways (i) and (ii) in order to

make biopolymers competitive for certain applications compared to polymers petrol-based. On the one hand, due to PLA chirality (PDLA or PLLA) it is possible to control PLA microstructure by creating a controlled block succession PDLA/PLLA. This blend co-crystallizes in a stereocomplex phase which has superior properties compared to homopolymer (melting temperature, mechanical properties, hydrolysis resistance, etc). The relationship between the shaping process and the physico-chemical properties isn't yet well stablished. On the second hand, the blend between PLA and other biopolymer, PA11, will be studied in order to improve PLA stability. PA11 is available commercially and the study will be carried out with different blend rates. The improvement of working properties of these materials consists on the control of the shaping process. Two processes will be studied: extrusion and electrospinning. One of the original aspects of this work is the spectroscopic in situ measures in order to follow in real time the microstructure and to optimize the shaping process parameters. Likewise, 3D impression tests will be developed.

One of the strategies to increase the crystallization rate of polymers and particularly of PLA consists of the addition of nucleating agents (NA) to reduce the energetic barrier to nucleate [1,2]. Likewise, the nucleation efficiency of three organic nucleating agents for the high molecular weight PLA- stereoblock coplymer (HMw PLA-SBC) was assessed to tackle one of the major disadvantages of PLA to substitute polyolefins at the industrial scale and in particular, with the advent of novel processing technologies such as 3D where the control of crystallization is key to tailor the properties of the final material. Besides, melt-soluble bio-organic NAs are generally preferred to conventional inorganic compounds as are designed to dissolve in the polymer melt and crystallize prior to the polymer on cooling, achieving higher nucleation efficiency due to the homogenous dispersion in the polymer matrix while preserving the biocompatibility of the afforded composites[3]. Likewise, the effect on the PLA-SBC crystallization of a series of low molecular weight NA featuring similar molecular groups with hydrogen bonding capability but differing on the structural rigidity and numbering of moieties was assessed. Therefore, the nucleation efficiency was assessed for *N,N'-Bis(2-hydroxyethyl) terephthalamide* [4] as well as *5,6,11,12-tetraoxo-4,7,10,13-tetraazahexadecane-1,16-dioate(OXA-2) and diethyl 5,6,13,14-tetraoxo-4,7,12,15-etraazaoctadecane-1,18-dioate (OXA-4)* [3] with a series of PLA-SBC derivatives featuring different molecular weight as well as an PLA-SBC derivative with an asymmetric block to evaluate structural parameters on the kinetics mechanism.

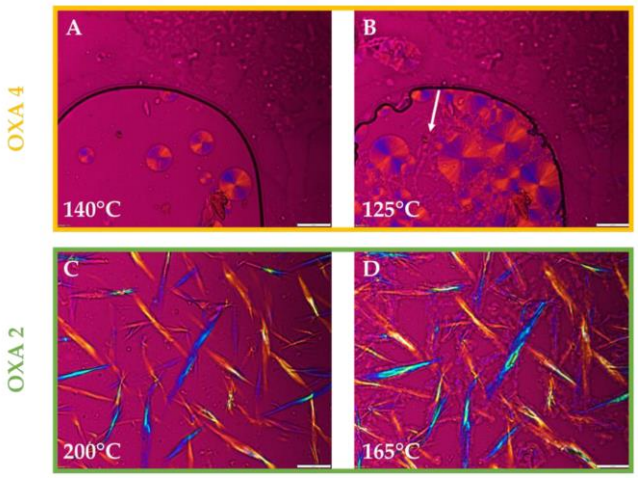

Figure 1. A-D) Polarized optical microscopy images of PLA film containing 2 wt % of OXA-4 (A,B) and OXA-2 (C,D).

Firstly, the nucleating capacity of the organic NA was assessed to identify the optimal conditions to then investigate the kinetics and morphology of crystallization in the different PLA-SBC derivatives at fixed nucleating agent concentration.

Films of PLA-SBC, MMw-HPm, were produced containing several concentrations (0.5, 1 and 2%) of two OBOCs, OXA-4 and OXA-2.The dissolution and crystallization of the NA in the PLA derivative matrix were clearly observed by optical microscopy (POM). The PLA-SBC containing OXA-4 crystallized above 140°C following homogeneous nucleation (**Figure 1A**), whilst the OXA-4 crystals appeared later than PLA spherulites, yielding also heterogeneous nucleation (**Figure 1B**, see arrow). In addition, OXA-2 crystals were formed above 200°C allowing the onset of the nucleation of PLA-SBC around 170°C (**Figure 1C-D**).

The difference between the OBOCs might be ascribed to the increase of the molecule flexibility by the increase of the number of methylene groups in-between oxalamide units. The higher flexibility increases the rotation freedom, increasing the energy to nucleate. Interestingly, an increase in both crystallinity and crystallization temperature was observed by DSC with increasing the content of OXA-2. Moreover, films

containing 1 and 2% of OXA-2 exhibited a double melting peak, which might be due to a competition between sterecomplexation and homoenatiomeric crystallization.

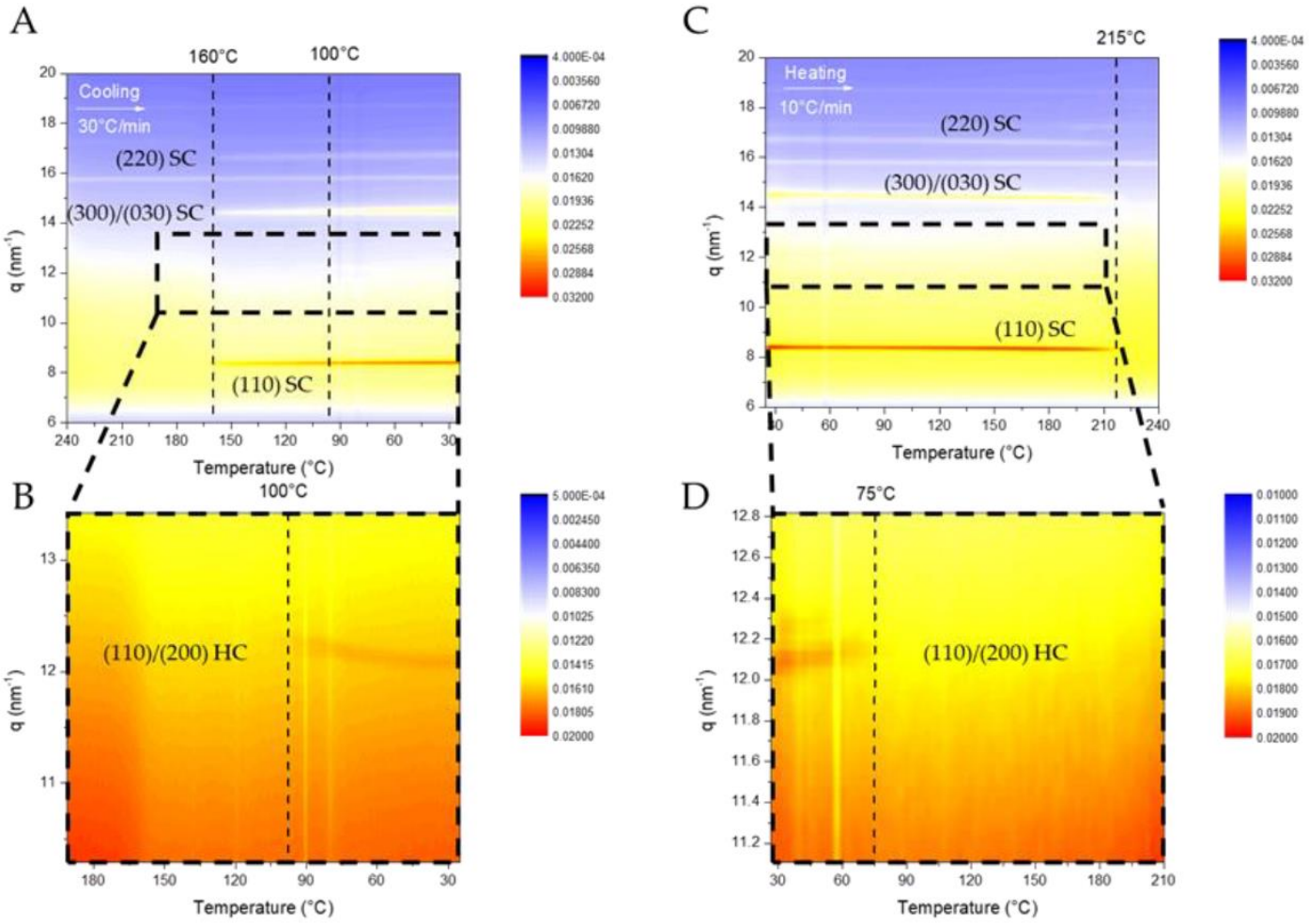

Figure 2: WAXS pattern of the L375:D375 film containing 2%wt of OXA-2 upon cooling (A) at 30°C/min and heating (C) at 10°C/min. (B) and (D) are zoom.

Likewise, the development of the α-phase upon cooling is in agreement with the double melting peak observed by DSC, however, it melts at 75°C (**Figure 2C-D**) which is in contradiction to the α-phase melting temperature (ca. 175°C). The nanostructure of the OXA-2 was analysed to discard the correspondence of the q(nm^{-1}) =12 signal to a diffraction peak of the NA, but the more intense peaks of the OXA-2 appeared at q higher than 13 nm^{-1}. Likewise, further analyses are required to understand the origin of diffraction reflection to the α-phase as well as its melting at 75°C.

References:

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