



## Experiment Report Form

<b>Experiment title:</b>	Shear enhanced relaxation in thermotropic polyesters: Identifying the role of pressure, stress and shear rates on molecular orientation and relaxation.		<b>Experiment number:</b> 26-02 890
<b>Beamline:</b> BM26B	<b>Date of experiment:</b> from: 26/09/2018                      to: 01/10/2018		<b>Date of report:</b> 30/1/2019
<b>Shifts: 12</b>	<b>Local contact(s):</b> Daniel Hermida Merino	<i>Received at ESRF:</i>	
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### Report:

Thermotropic polyesters (LCP) are well known for their high performance properties after processing into fibers or tapes. Their performance can be attributed to the high molecular orientation in the processed products, originating from the combination between high chains stiffness and low melt viscosities. In previous work, our research group has developed various renewable liquid crystal polymers (BioLCP). These materials have shown to exhibit good mechanical performance, making them excellent candidates as fillers for the development of fully renewable polymer blends. In fact, these BioLCPs display an efficient nucleating ability for crystallization of other polyesters, as confirmed by SAXS experiments performed at BM26. In order for the LCPs to be excellent fillers, they should exhibit high molecular orientation after processing. Taking injection-moulding as example; the LCP component should orient during injection but should be quenched before relaxation of the LCP phase occurs in order to exhibit the desired mechanical performance. Unfortunately, both literature and our experimental findings (Figure 1) indicate that LCPs relax faster when being subjected to higher stresses.

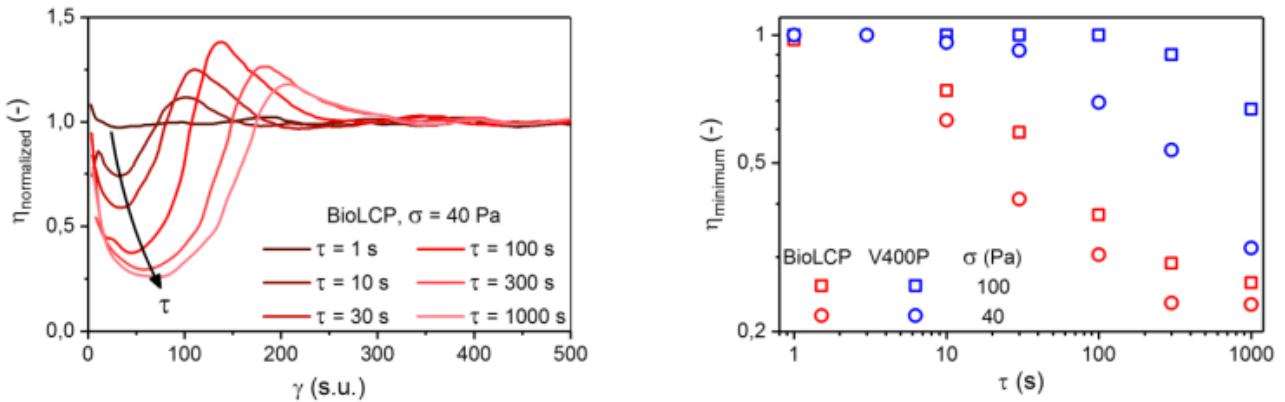


Figure 1: Left) Characteristic change in viscosity of BioLCP during start-up of shear observed after allowing the system to relax ( $\tau$ ) after continuous shear with a stress of 40 Pa. The decreasing well observed with increasing relaxation time is correlated the morphology of the LCP: The deeper the well, the closer the material is to being in a fully relaxed state. Right) Overview of well-depth ( $\eta_{\text{minimum}}$ ) normalized to the steady state viscosity during continuous shear for various LCPs at various stresses. Overall it is observed that an increase in stress during shear results in a decrease of the relaxation time. In other words, relaxation of thermotropic polyesters is enhanced with increasing stresses during processing.

Therefore, in the allocated beamtime we have assessed the effect of shear on blends of 1) LCP and 2) LCP dispersed in a PLA matrix. The experiments were performed in a multi-pass rheometer (MPR), providing excellent control over shear and shear rate on the samples. The MPR experiments suggested that the LCP relaxation is directly related to the viscosity of the surrounding matrix. In other words, relaxation of pure LCP is determined by its own viscosity (thus, the higher the LCP molecular weight, the higher its viscosity, and the longer its relaxation time!) and when blended in a entangled polymer melt, the relaxation of the LCP is determined by the viscosity of the polymer melt. In fact, when shear pulses are applied for LCP dispersed in a PLA matrix, the relaxation process happens within several seconds. Unfortunately, the framerate of our experiments (being 2 seconds to ensure a well-resolved inter-chain LCP diffraction signal), prevents us to accurately monitor the LCP relaxation process.

For this reason, after two days of MPR experiments, the experimental set-up was switched to the Linkam Shear-cell. For this purpose, we have heated different samples with preoriented LCP fibrils to a specific temperature with a known viscosity of the PLA matrix. Beside the growth of oriented PLA crystals upon heating (Figure 2), these experiments allowed us to confirm the previously outlined hypothesis: The lower the viscosity of the surrounding matrix, the faster the relaxation of the LCP. In general, once can observe from Figure 3 that the LCP relaxation in the semi-crystalline L130 PLA grade proceeds dramatically once exceeding the melting temperature of PLA (L130, 185 °C). However, when monitoring the relaxation of the LCP at decreasing temperatures of 180 °C and 175 °C (hence, the PLA matrix remains semi-crystalline), the orientation parameter relaxes slower and levels off at higher values. Furthermore, when using an amorphous PLA grade (6302D grade), the relaxation is even faster, originating from the fact that there are no PLA crystals preventing the relaxation of the LCP, thus allowing the relaxation to proceed already at lowered temperatures. Overall these findings will be taken up in two scientific publications where one focuses on the orientation and relaxation behavior of the pure LCP materials and the other on the orientation and relaxation behavior of the LCP blends in PLA.

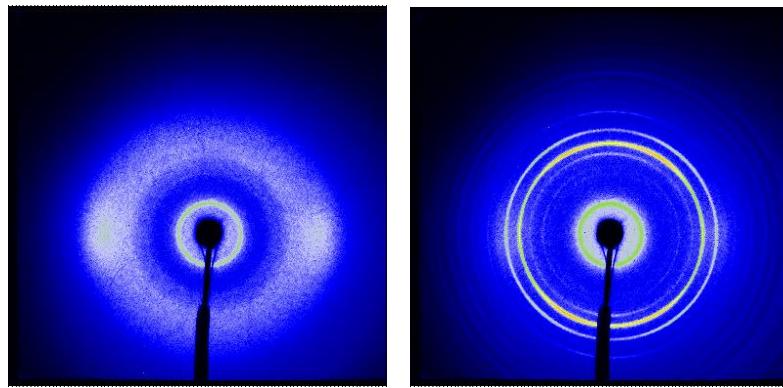


Figure 2. Left, WAXD pattern taken at room temperature showing an oriented tape with 30% LCP and PLA residing in the amorphous phase. Right, WAXD pattern of the same sample, after heating to 100 °C depicting the presence of oriented PLA crystallites induced by the LCP fibrils.

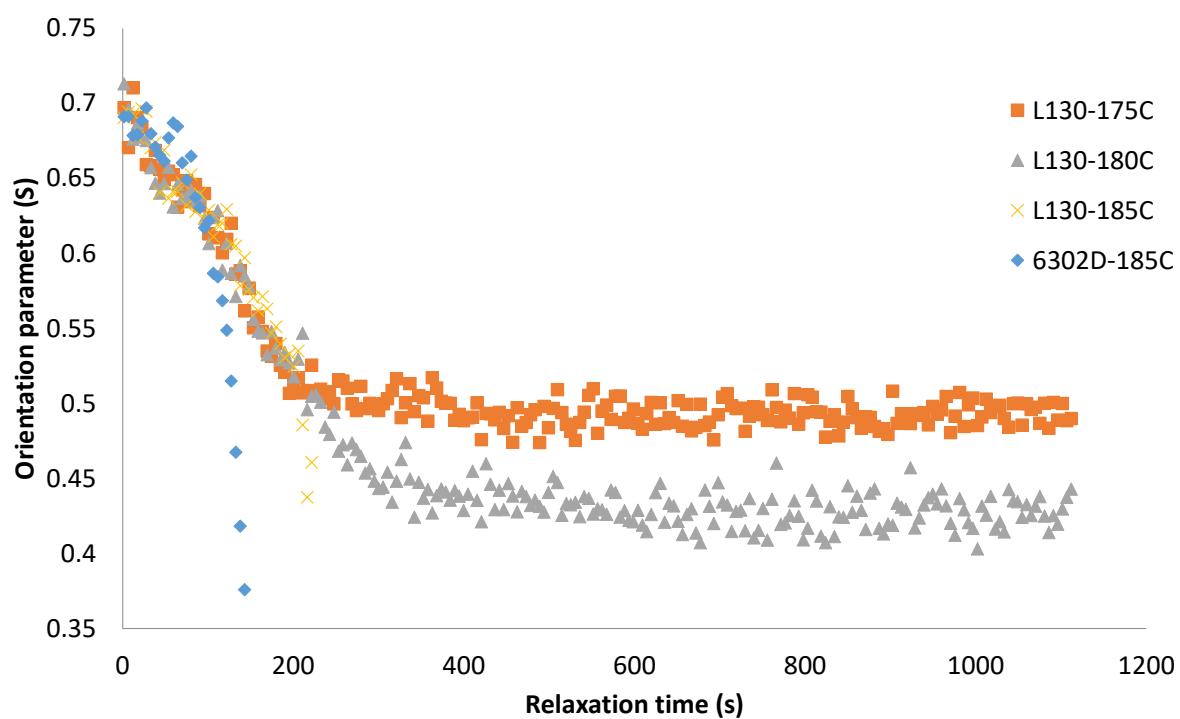


Figure 3. LCP relaxation as detected by the change in orientation parameter calculated from the LCP inter-chain diffraction signal in different PLA grades and after exposure to different temperatures.