

Structural and dynamic heterogeneity in the amorphous phase of Poly(L,L-lactide) confined at the nanoscale by co-extrusion process

Samira Fernandes Nassar¹, Sandra Domenek¹, Alain Guinault², Gregory Stoclet³, Nicolas Delpouve⁴, Cyrille Sollogoub^{2*}

1: UMR Ingénierie Procédés Aliments, AgroParisTech, INRA, Université Paris-Saclay, 1 avenue des Olympiades, F-91300 Massy, France

2: PIMM, Arts et Métiers-ParisTech/CNAM/CNRS UMR 8006, 151 bd de l'Hôpital, 75013 Paris, France

3: UMR CNRS 8207, Unité Matériaux et Transformations, Université Lille1 Sciences et Technologies, Bâtiment C6, Université de Lille Nord de France, 59655 Villeneuve d'Ascq, France

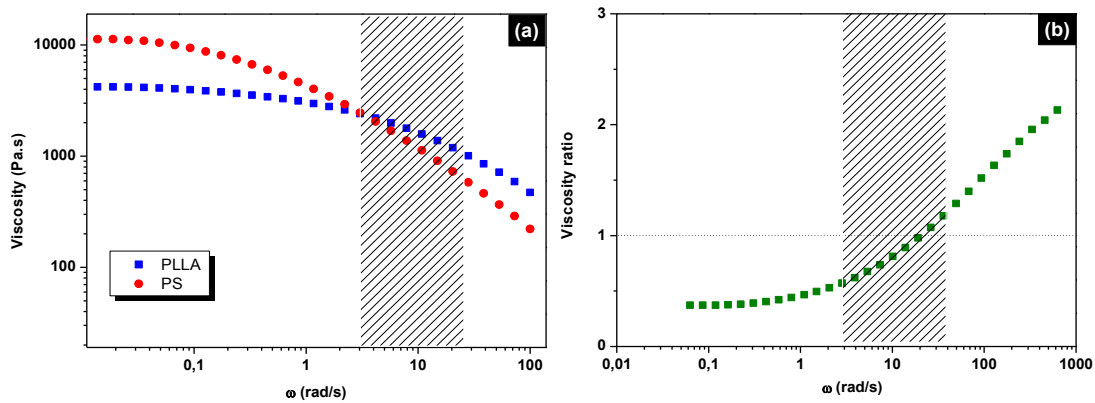
4: Normandie Univ, UNIROUEN Normandie, INSA Rouen, CNRS, GPM, 76000 Rouen, France

Corresponding author: cyrille.sollogoub@lecnam.net

Supporting information

SI 1. The extrusion conditions used to fabricate PLLA/PS films.

PLLA extruder (°C)	190/200/200/200
PS extruder (°C)	200/200/200/210
Pump + Feed block (°C)	200
Section with layer-multiplying elements (°C)	200
Flat die (°C)	200
PLLA screw speed (rpm)	22
PS screw speed (rpm)	57
PLLA throughput (g/h)	600
PS throughput (g/h)	1800



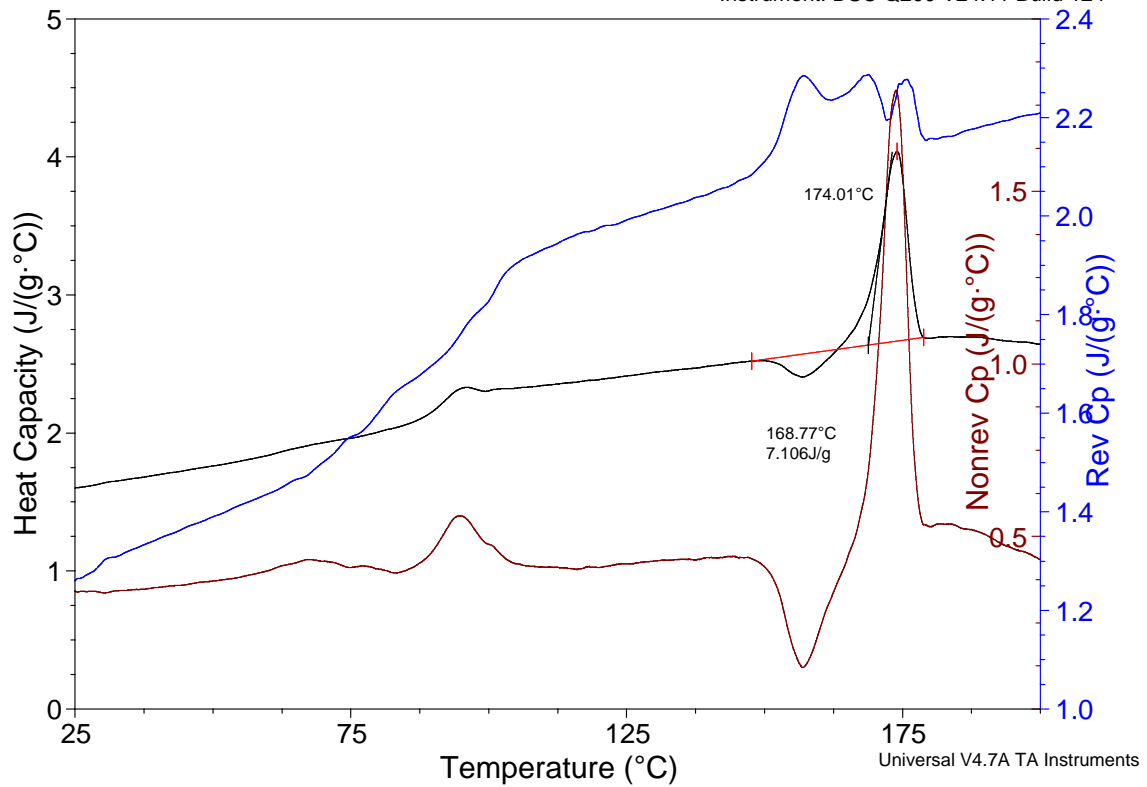
SI 2. (a) Viscosity curves of PLLA and PS (b) Viscosity ratio for PS/PLLA. The hatched zone corresponds to the typical shear rates reached in the co-extrusion process.

SI 3. DSC curves of films annealed at 85 °C during 3 hours.

Sample: PS PLLA echant 11_3couches_recul
Size: 9.3800 mg

DSC

File: PS PLLA echant 11_3 couches_recul 85
Operator: SN
Run Date: 07-Jul-2015 11:14
Instrument: DSC Q200 V24.11 Build 124

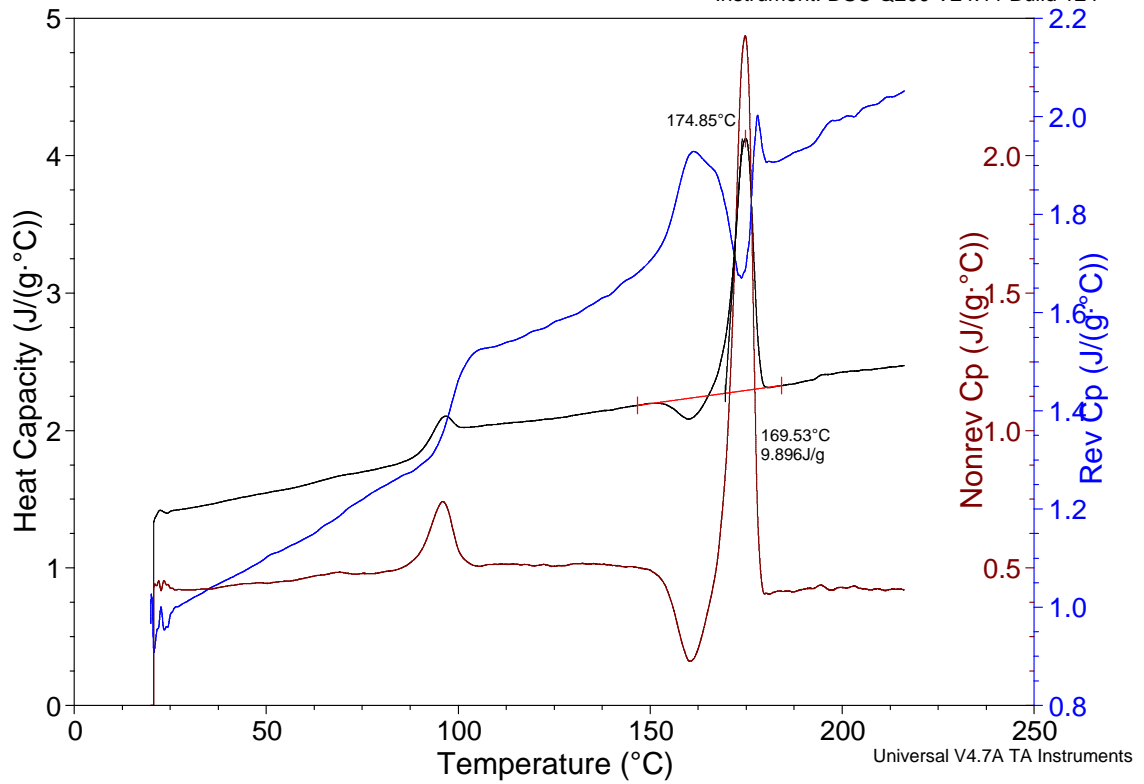


SI 3.1 Sample DSC raw data of 30000 nm PS/PLLA films after annealing at 85 °C for 180 min in the heating press. The melting enthalpy of PLLA (7.106 J/g corresponding to 25 % of the sample mass) equals a crystallinity degree of 30 %. This shows complete crystallization.

Sample: PS PLLA echant 70_8M_recuit
Size: 9.2500 mg

DSC

File: PS PLLA echant 70_8M_recuit 85°C 180
Operator: SN
Run Date: 06-Jul-2015 16:52
Instrument: DSC Q200 V24.11 Build 124

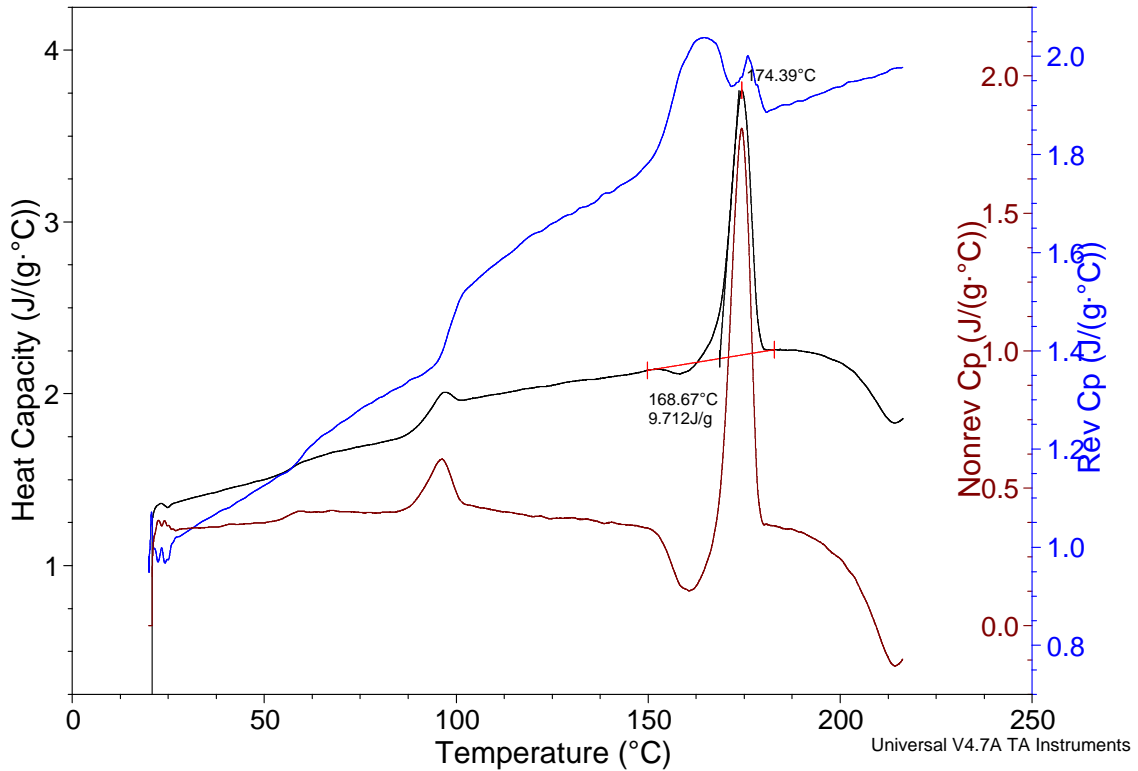


SI 3.2 Sample DSC raw data of 300 nm PS/PLLA films after annealing at 85 °C for 180 min in the heating press. The melting enthalpy of PLLA (9.896 J/g corresponding to 25 % of the sample mass) equals a crystallinity degree of 43 %. This shows complete crystallization.

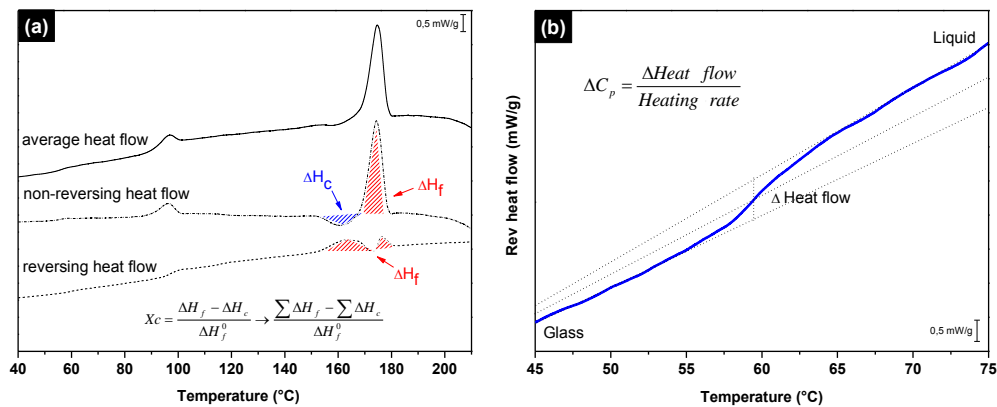
Sample: PS PLLA echant 73_10M_recuit
 Size: 7.7500 mg

DSC

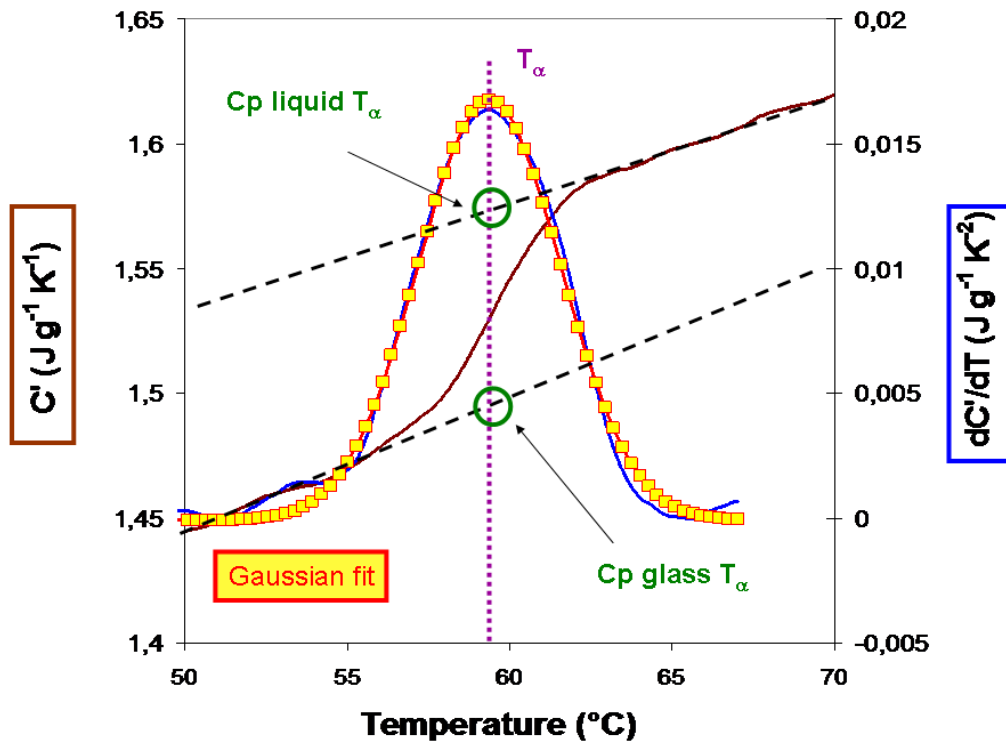
File: PS PLLA echant 73_10M_recuit 85°C 18
 Operator: SN
 Run Date: 07-Jul-2015 08:54
 Instrument: DSC Q200 V24.11 Build 124



SI 3.3 Sample DSC raw data of 20 nm PS/PLLA films after annealing at 85 °C for 180 min in the heating press. The melting enthalpy of PLLA (9.712 J/g corresponding to 25 % of the sample mass) equals a crystallinity degree of 42 %. This shows complete crystallization.



SI 4. (a) Protocol for the determination of the degree of crystallinity from MT-DSC curves obtained for the 20 nm annealed sample; Average heat flow (Solid line); reversing heat flow (dashed line); and non-reversing heat flow (dotted line) versus temperature (b) Reversing heat flow in the glass transition domain for the 20 nm annealed sample.



SI 5. Example of C' (T) and C'' (T) of confined amorphous PLLA at 20 nm of thickness obtained by TMDSC on PS/PLLA sample (2049 layers)