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# Novel Hybrid Poly(L-lactic acid) from titanium oxo-cluster via reactive extrusion polymerization

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## Abstract:

This paper reports the synthesis of novel hybrid poly(lactic acid) by use of a titanium oxo-cluster, acting both as a catalyst and crosslinking agent of the polymer matrix. The already reported oxo-cluster  $\text{Ti}_{16}\text{O}_{16}(\text{OEt})_{32}$  ( $[\text{Ti}]_{16}$ ) was synthesized and screened at the lab-scale as catalyst for the bulk polymerization of L-lactide (L-LA).  $[\text{Ti}]_{16}$  was found to be highly active for this reaction as up to 90 % conversion in 30 min was obtained, affording PLLAs with  $M_n$  up to 65 000  $\text{g}\cdot\text{mol}^{-1}$  and relatively narrow dispersities (1.2 - 1.6). These polymerization reactions were further transposed to reactive extrusion process in which  $[\text{Ti}]_{16}$  oxo-cluster kept its high activity, affording hybrid-PLLA materials with  $M_n$  close to 58 000  $\text{g}\cdot\text{mol}^{-1}$  (some PLLAs could not be dissolved). Electronic microprobe analysis of the resulting hybrid materials confirmed that the titanium oxo-cluster was well dispersed all over the PLLA matrix. Finally, it was shown that the hybrid PLLA containing  $[\text{Ti}]_{16}$  display superior dimensional stability under heat than commercial PLLA of same molar mass.

**Key words:** Ring Opening Polymerization, Oxo-clusters, Hybrid poly(lactic acid) , Reactive extrusion.

## Introduction:

Nowadays, most of the raw materials used in the manufacture of polymer materials come from petrochemicals. The gradual replacement of petroleum-based materials with renewable resources ones is part of the society major concerns: national independence with regard to the supply of raw materials, preservation of the environment, reduction of greenhouse gas emissions. Among the different biobased materials available on the market, poly(lactic acid) (PLA) is becoming more and more competitive and accounts for about a quarter of biodegradable bioplastic production. Indeed, the industry has made many investments in this sector, leading to a reduction in its production and implementation costs. This biodegradable and biocompatible polyester is synthesized either by direct polycondensation of lactic acid, resulting from the fermentation of agrosources, or by Ring Opening Polymerization (ROP) of lactide, a cyclic ester derived from oligomerization-cyclization of lactic acid. Although the second synthetic route requires an additional step, it allows the formation of poly(lactic acid) of higher molar masses and is most commonly employed in industry [1]. The ROP requires the use of a catalyst which ring-opens the lactide and initiates its polymerization. Among ROP methods, coordination-insertion polymerization monitored by metal-based catalysts is a powerful and versatile technique, allowing access to well-defined high molar mass polymers. A wide range of metals are well-known to afford highly active catalytic systems for this reaction, such as tin [2], aluminium and group 13 metals [3], zinc and main group metals [4], group 4 [5], group 3 and lanthanides [6]. Among the commercial lactides, L-lactide (L-LA), resulting from the cyclization of the L- isomer of lactic acid, is particularly interesting since it leads, regardless of the type of polymerization initiator used, to 100 % isotactic poly(lactic acid) (PLLA). This semi-crystalline

material ( $T_m \approx 170$  °C) displays mechanical properties close to those of polyethylene terephthalate (PET) and its hydrolytic degradation is slower than that of amorphous poly(lactic acid)s. PLLA is a colorless polymer that can be stretched into thin films or fibers. It displays a glass transition temperature of about 60 °C along with a high elastic modulus (3-4 GPa) and a low elongation at break (2-6 %) at room temperature. PLLA is currently the most industrially produced poly(lactic acid) by the use of tin octoate as the catalyst. The latter has also been found to be highly active for the polymerization of L-lactide by reactive extrusion, a process allowing the continuous polymerization of a monomer without solvent [7]. However, PLA has a low glass transition temperature ( $\approx 60$  °C), which often makes it unsuitable as a substitute of everyday-life plastics as it can lose its dimensional stability under the effect of heat. In addition, the thermal degradations that can occur during industrial transformation processes may alter the structure of PLA and therefore its molecular weight, rheology and mechanical properties. As an example, current poly(lactic acid) fabrics display a very low thermo-mechanical strength during ironing, which makes it difficult to be used on the textile market [8]. However, it is possible to improve significantly the thermal properties of PLA by synthesizing stereocomplexed poly(lactic acid) from the homopolymers of the D- and L- isomers of lactide, however the mechanical properties remain low [9]. These latter, and in particular the elongation at break, can be improved by making composite materials or by mixing PLA with other polymers chosen in views with the targeted applications [10]. Another strategy consists in copolymerizing lactide monomer with other kind of cyclic esters, such as  $\epsilon$ -caprolactone [11]. However, these reactions are very challenging as they are conducted with oxophilic metal-based

complexes, and in most cases lactide monomer is preferentially inserted, leading either to pure poly(lactic acid), gradient or block copolymers with very few co-monomer inserted [12]. Recently, Hillmyer's group described the synthesis of poly(lactic acid) vitrimer from hydroxyl-terminated star-shaped poly((±)-lactide) which were cross-linked with methylenediphenyl diisocyanate, in the presence of tin octoate as the catalyst. The latter being trapped in the material at the end of the reaction, it was further used as a catalyst for transesterification reaction, allowing the thermo-stimulated healing of the material [13].

The present work focuses on the synthesis of hybrid poly(L-lactic acid), in one step synthesis from L-lactide monomer, by using a metal oxo-cluster acting both as a polymerization catalyst and crosslinking agent of the final material, with the aim to confer superior thermomechanical properties to PLLA and thus higher dimensional stability under heat. The strategy consists in using a polynuclear oxo-cluster able to act as a polymerization catalyst under reactive extrusion condition, allowing a good dispersion of the inorganic compound into the resulting PLLA matrix, giving rise to the hybrid material. Since the PLLA do not undergo any post-treatment at the extruder outlet, it is expected that the PLLA chains whose growth has been initiated from the Metal-OR groups of the cluster remain linked to the metal centers at the end of the polymerization, the Metal-O-PLLA alkoxide bonds formed being sufficiently stable to allow the material to be crosslinked. As mentioned above, the catalysts used for the industrial production of PLLA are tin-based catalysts, but due to REACH restrictions this metal might have to be replaced in a near future. In this context, we have focused our study on titanium-based compounds, a REACH-compliant metal, also known to give rise to complexes which can be highly active towards ROP of cyclic esters.<sup>5</sup> Moreover, the resulting [Ti]-O-PLLA bonds in the PLLA matrix should be stable enough to ensure the targeted crosslinking effect. In that context, we focus our study on polynuclear titanium oxo-cluster of the type  $[Ti_nO_m(OR)_{4n-2m}]$  (with OR = alkoxo ligand) able to act as ring opening polymerization catalyst of cyclic esters, and in particular of L-lactide, and thus bearing some Ti-OR active bonds able to ring-open this cyclic monomer. The titanium oxo-cluster  $Ti_{16}O_{16}(OEt)_{32}$  ( $[Ti]_{16}$ ), previously reported by the authors [14], was selected as it contains numerous [Ti]-OEt bonds able to ring-open L-lactide, but also because of its relative chemical and thermal stability among this class of clusters, and its accessibility in high yield. Moreover,  $[Ti]_{16}$  is already referenced as an efficient candidate to catalyse transesterification or transesterification reactions [15], and also to lead to hybrid materials as polymers nanocomposites [16], dendrimers [17], star shape polymers [18] or supramacromolecular architectures [19]. The oxo-cluster was screened as catalyst for the bulk (solvent-free in the melt) polymerization of L-lactide at small laboratory scale to evaluate its activity and the properties of the resulting polymers. Thereafter, the reactions displaying an activity compatible with the rates required for the reactive extrusion process were up-scaled in a twin-screw micro-extruder. Finally, the dimensional stability of these new PLLA hybrid materials under heat was herein qualitatively evaluated.

## Material and methods:

### 1. Reagents:

The oxo-cluster  $Ti_{16}O_{16}(OEt)_{32}$  ( $[Ti]_{16}$ ) used in this study was synthesized according to literature procedures [14a]. L-lactide (L-LA) supplied by Purac, was conditioned in small sealed bags

under vacuum, stored in a glove box ( $O_2 = 0$  ppm;  $H_2O = 2$  ppm) and used as received ( $H_2O$  content, measured by Karl-Fischer analysis, was found inferior to 5 ppm). The sealed bags were open just before mixing L-lactide with the catalyst in the glove box. Commercial poly(L-lactic acid) was supplied by NatureWorks LLC (Ref 4032D).  $CDCl_3$  was supplied by Aldrich (purity of 99.8 % of D). THF 99 +%, extra pure (stabilized with BHT) was supplied by Acros Organics.

### 2. Polymerization procedures

**Polymerization of L-Lactide at the lab-scale.** L-lactide (1 g,  $6.94 \times 10^{-3}$  mol) was introduced in a round bottom flask and mixed with the catalyst ( $1.39 \times 10^{-5}$  mol for  $[L-LA]/[Ti] = 500$ ) in a glove box. The reaction was conducted at 130 or 150 °C for a given time under stirring. At the end of the reaction, the highly viscous medium was dissolved in non-anhydrous chloroform. An aliquot of the obtained solution was taken and dried under vacuum to determine the conversion by  $^1H$  NMR in  $CDCl_3$ . The PLLA in solution in chloroform was then poured in ethanol. The isolated polymer was filtered and dried under vacuum.

### Polymerization of L-Lactide via reactive extrusion process.

L-lactide (20 g, 0,139 mol) and the titanium complex  $[Ti]_{16}$  (42 mg,  $2.77 \times 10^{-4}$  mol of Ti atom, for  $[L-LA]/[Ti] = 500$ ) were weighted and mixed together in a glass bottle in a glove box with a manual stirring, before feeding the extruder. The polymerization was performed in a co-rotating twin screw microextruder, from DSM (Geleen, the Netherlands) under nitrogen at 150°C with a screw speed of 100 rpm. The conversion of the reaction was determined by  $^1H$  NMR analysis of a sample of polymer in  $CDCl_3$ . The commercial PLLA used for dimensional stability tests was extruded in the same micro-extruder at 185°C for 5 min at 50 rpm.

### 3. Characterization techniques:

**Liquid  $^1H$  NMR.**  $^1H$  NMR spectra of poly(lactic acid)s were recorded on a Bruker Avance 300 MHz instrument at 300 K in  $CDCl_3$ . The chemical shifts were calibrated using the residual resonances of the solvent. The samples (about 5 to 15 mg) were dissolved in 0.5 mL of  $CDCl_3$  in a 5 mm diameter tube. The scan number was set to 32 and the delay (D1) between each scan was set at 4s. The conversion of the reaction was determined by integration of the CH signals of both the residual monomer and the polymer at 5.05 ppm and 5.15 ppm respectively.

**SEC measurements.** The number-average molar masses ( $M_n$ ) and dispersities ( $D = M_w/M_n$ ) of the poly(lactic acid)s were determined by size exclusion chromatography (SEC) in THF at 40 °C (1 mL/min) with a refractive index detector (Waters 2414). The SEC system was equipped with three Waters Styragel (HT1, HT3 and HT4) columns. Samples were prepared by dissolving the product (~10 mg) in 4 mL of THF. The solutions were then filtered with 0.45  $\mu m$  filters. Calibration was done with polystyrene standards and  $M_n$  values were corrected with Mark-Houwink factor 0.58 for PLLA.

**DSC analysis.** Thermal analyses were carried out using Differential Scanning Calorimetry (DSC) (TA Discovery instrument). All DSC experiments were performed under a nitrogen atmosphere. The apparatus was calibrated thanks to an indium sample of high purity according to standard procedures. The sample weight was in the range 5 - 10 mg and heating and

**Table 1.** Bulk polymerization of L-lactide with oxo-clusters [Ti]<sub>16</sub>.<sup>a</sup>

Run	Catalyst	T (°C)	[L-LA] / [Ti]	Time (min)	Conversion (%) <sup>b</sup>	M <sub>n</sub> th (g.mol <sup>-1</sup> ) <sup>c</sup>	M <sub>n</sub> SEC (g.mol <sup>-1</sup> ) <sup>d</sup>	<i>D</i> <sup>d</sup>	Eff (%) <sup>e</sup>
1	[Ti] <sub>16</sub>	130	500	120	59	21 260	65 130	1.29	33
2	[Ti] <sub>16</sub>	150	250	15	70	12 610	38 250	1.48	33
3	[Ti] <sub>16</sub>	150	500	30	90	32 430	44 770	1.65	72
4	[Ti] <sub>16</sub>	150	1000	40	27	19 460	31 100	1.22	63

<sup>a</sup> Experimental conditions: under argon in a glove box, m L-LA = 1 g, non-purified lactide, [L-LA] / [Ti] is given by titanium atom in the oxo-cluster. <sup>b</sup> determined by <sup>1</sup>H NMR in CDCl<sub>3</sub>. <sup>c</sup> Expected M<sub>n</sub> values for two growing chains per metal centre, M<sub>n</sub> = {[L-LA]<sub>0</sub> / [M]<sub>0</sub> × M(L-LA) × conversion} / (2). <sup>d</sup> determined by SEC in THF at 40°C, RI detection, PS standards, M<sub>n</sub> values corrected considering Mark–Houwink factor 0.58 for PLLA, *D* = M<sub>w</sub> / M<sub>n</sub>. <sup>e</sup> Efficiency = (M<sub>n(th)</sub> / M<sub>n(SEC)</sub>) × 100.

cooling rates were set at 10°C/min. Samples were first heated until 200°C in order to erase thermal history, then cooled down to room temperature before being reheated. Thermal characteristics were determined from the 2<sup>nd</sup> heating. Particularly the glass transition temperature (*T*<sub>g</sub>), is taken at the half of the heat capacity jump and the melting temperature (*T*<sub>m</sub>) at the maximum of the endothermic peak.

The degree of crystallinity has been calculated according to the following relation:

$$x_c = \frac{(\Delta H_m - \Delta H_{cc})}{\Delta H_m^0}$$

With  $\Delta H_m$ , the PLA melting enthalpy determined from the endothermic peak area,  $\Delta H_{cc}$ , the cold crystallization enthalpy determined from the exothermic peak,  $\Delta H_m^0$ , the standard melting enthalpy of PLA taken equal to 93 J/g [20].

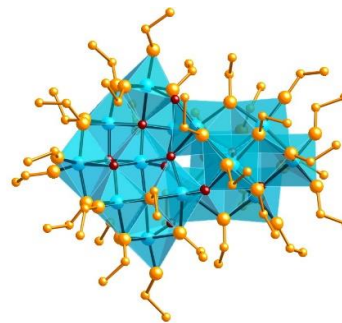
**TGA analysis.** Thermogravimetric analysis measurements were carried out on a Setaram TG92-16. Nitrogen was chosen to examine the decomposition of the materials with a flow rate of 100 mL/min. Samples of 8 ± 1 mg placed in silica crucibles were submitted to an isotherm at 50 °C for 20 minutes for thermal homogeneity then followed by a heating ramp up to 800 °C at 10°C per min. The onset temperature of degradation (T5%) corresponds to the temperature when 5 wt% weight loss is observed.

### Electronic micro-probe analysis.

Samples were embedded into epoxy resin, polished with SiC polishing sheets from grade 80 up to grade 4000 and carbon coated with a BalTec sputter coater to obtain a conductive surface. The polished cross-section of the samples was analyzed using a Cameca SX100 electron probe microanalyser (EPMA). Ti peak detection analyses were performed at 15kV, 20nA and Ti mappings were performed at 10kV, 40nA. A PET crystal was used to detect the Ti X-ray K $\alpha$ .

## Results and Discussion:

The activity of oxo-cluster Ti<sub>16</sub>O<sub>16</sub>(OEt)<sub>32</sub> ([Ti]<sub>16</sub>) [14a] (Figure 1) as polymerization catalyst of L-lactide in bulk conditions (melted medium without solvent) was first evaluated at small scale in round bottom flasks, prior to the upscale of the reactions in reactive extrusion, to get hybrid-PLLA material in high yield in order to conduct qualitative dimensional stability tests under heat on these materials. These lab-scale tests were conducted on 1 g of L-lactide in flasks that were filled with the monomer and catalyst in a glove box under argon where they were sealed. It is important to notice that the L-lactide used was not purified prior-use as the targeted catalyst is expected to be active with crude



**Figure 1.** Structure of oxo-cluster Ti<sub>16</sub>O<sub>16</sub>(OEt)<sub>32</sub> ([Ti]<sub>16</sub>) (red atoms: Ti; blue atoms: O; yellow atoms: OEt ligands)

monomer as the upscale in the extruder requires high quantities of starting materials, which does not allow the purification of such amounts. The results related to the polymerization of L-LA with [Ti]<sub>16</sub> as the catalyst at the lab-scale are presented in table 1. The temperature used for the polymerization tests was set up at 130 and 150°C, above the L-lactide melting point (about 110°C) and below the temperature of degradation of the cluster (196 °C, 5% weight loss, see Figure S11) which was determined by TGA. In these experimental conditions, the oxo-cluster was found to be highly active for this reaction. At a temperature of 130°C, 59 % conversion were reached after 2 h, affording PLLA with M<sub>n</sub> of 21 260 g.mol<sup>-1</sup> along with a dispersity of 1.29, what is relatively narrow for a polymerization conducted in bulk conditions (run 1). When the temperature was increased at 150°C the activity was significantly improved (runs 2 to 4). Indeed, with a low monomer loading of 250 equivalents of L-LA over titanium atom, 70 % conversion is reached over 15 min (run 1), with resulting PLLA displaying a molar mass of 38250 g.mol<sup>-1</sup> along with a dispersity of 1.48 (run 2). The monomer over catalyst ratio was then increased at 500 and 1000 equivalents of L-LA per metal centre (runs 3 and 4). The highest activity was observed for 500 equivalents of L-LA per titanium metal centre (run 3), with up to 90 % conversion in only 30 min along with M<sub>n</sub> up to 44 770 g.mol<sup>-1</sup> and relatively narrow dispersity (1.6). Regarding the efficiency of the catalyst, one can observe that the M<sub>n</sub> values of PLLAs synthesized with [Ti]<sub>16</sub> were observed to be higher than the calculated ones for two growing chains per titanium atom (presence of two OEt ligands per titanium centre in [Ti]<sub>16</sub>). This indicates that only a third to three quarters of the Ti-OEt bonds present on the oxo-cluster are initiating the polymerization reaction, depending on the experimental conditions (efficiency values from 33 to 72, table 1). This can be attributed to a faster propagation rate vs. initiation rate during the reaction.

The lab-scale polymerization reactions being successful and the activity of [Ti]<sub>16</sub> being compatible with polymerization rates

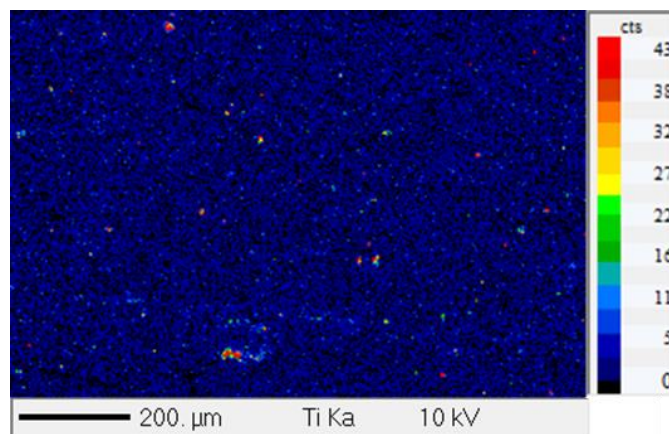
**Table 2.** Polymerization of L-lactide under reactive extrusion conditions with oxo-cluster [Ti]<sub>16</sub>.<sup>a</sup>

Run	[L-LA] / [Ti]	Time (min)	Conversion (%) <sup>b</sup>	M <sub>n</sub> theo (g.mol <sup>-1</sup> ) <sup>c</sup>	M <sub>n</sub> SEC (g.mol <sup>-1</sup> ) <sup>d</sup>	Đ <sup>d</sup>	Eff (%) <sup>e</sup>	T <sub>g</sub> (°C) <sup>f</sup>	T <sub>m</sub> (°C) <sup>f</sup>	X <sub>c</sub> (%) <sup>f</sup>
5	250	22	92	33 150	56 250	1.53	59	no	168	31
6	500	30	81	29 200	57 650	1.60	51	-	-	-
7	500	45	97	34 950	nd <sup>g</sup>	nd <sup>g</sup>	-	59	179	37

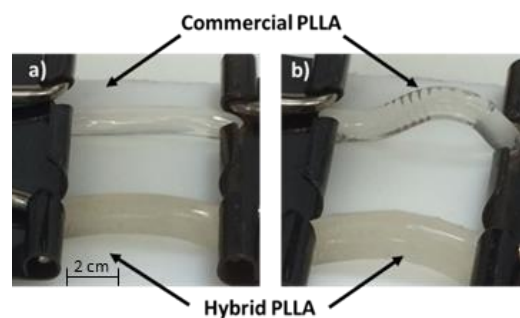
<sup>a</sup> Experimental conditions : reactions conducted in a DSM twin-screw micro-extruder, [Ti]<sub>16</sub> as the catalyst, m(L-LA) = 20 g, T = 150°C, rotation = 100 rpm under nitrogen, [L-LA] / [Ti] is given by titanium atom in the oxo-cluster. <sup>b</sup> Determined by <sup>1</sup>H NMR in CDCl<sub>3</sub>. <sup>c</sup> Expected M<sub>n</sub> values for two growing chains per metal centre, M<sub>n</sub> = {[L-LA]<sub>0</sub>/[Ti]<sub>0</sub> × M(L-LA) × conversion} / 2. <sup>d</sup> determined by SEC in THF at 40°C, RI detection, PS standards, M<sub>n</sub> values corrected considering Mark-Houwink factor 0.58 for PLLA, Đ = M<sub>w</sub> / M<sub>n</sub>. <sup>e</sup> Efficiency = (M<sub>n</sub>(th) / M<sub>n</sub>(SEC)) × 100. <sup>f</sup> determined by DSC from the 2nd heating, calculation of crystallinity degree: X<sub>c</sub> = [(ΔH<sub>m</sub> - ΔH<sub>c</sub>) / (ΔH<sub>m</sub><sup>0</sup> = 93)]. <sup>g</sup> not determined due to a lack of solubility in THF.

required for the reactive-extrusion process, we conducted transposition tests with this oxo-cluster on a DSM twin-screw micro-extruder with a capacity of 20 g (table 2). In opposition to the lab-scale experiments where the atmosphere is well controlled as the flasks are filled in a glove box under argon, the atmosphere in the micro-extruder is rendered inert via a simple nitrogen flow, what can have a high impact on the water and air concentrations and so on the activity of the catalyst. In the present case, one can observe that [Ti]<sub>16</sub> oxo-cluster is particularly stable as it displays activities similar to those observed for the small lab-scale experiments, as after 30 min of reaction 81% of conversion is reached under reactive extrusion conditions vs. 90 % when the reaction was conducted in sealed flasks (runs 6 vs. 3). Regarding the molar masses, the latter were also found to be higher than the calculated one with up to 57650 g.mol<sup>-1</sup>, as observed for the small-scale tests, indicating that only a half of the Ti-OEt bonds of the oxo-cluster are initiating the polymerization reaction, what is related to a faster propagation rate vs. initiation. Moreover, the experimental M<sub>n</sub> for PLLAs synthesized by reactive extrusion were found slightly higher than the ones from the reactions conducted in flasks (57 650 vs. 44 770 g.mol<sup>-1</sup> and 56 250 vs. 38 250 g.mol<sup>-1</sup> for runs 2 vs.5 and 6 vs.3), what can indicate that a small fraction of the catalyst can be degraded under these experimental conditions, giving rise to longer macromolecules as the conversion is overall the same. Concerning the dispersities, they are still in the same range, and the process does not seem to have any impact on this parameter. For a longer residence time of 45 min in the micro-extruder, complete conversion of the polymerization reaction could be reached (run 7), however the resulting polymer was found to be insoluble in THF which could occur for the obtaining of PLLA with high molar masses and/or high crystallinity and/or the crosslinking effect of the clusters on the macromolecular chains. The absence of epimerization during the polymerization reaction was highlighted by <sup>1</sup>H NMR and polarimetry analysis on the polymer samples (see Fig. S7 and S8 and Table S1 in supporting information), which both showed the absence of D-isomer. Finally, DSC analysis of the hybrid poly(lactic acids) indicated that these materials were semi-crystalline, as expected for a pure PLLA.

The reactive extrusion process is expected to allow a good dispersion of the inorganic component in the polymer matrix, to trap the catalytic species within the material at the end of the reaction and ultimately to obtain the targeted hybrid materials. The dispersion of the titanium oxo-cluster was studied by electron probe micro-analyzer (EPMA, Figure 2), which allows the obtaining of titanium mapping within the polymer. One can observe that, as expected, the titanium atoms (appearing as blue, yellow and red dots depending on the concentration) are present all over the polymer matrix, indicating a good dispersion of the oxo-cluster within the poly(lactic acid) via the reactive extrusion process. Once the first prototypes of hybrid poly(lactic acid)

**Figure 2.** EPMA X-Ray mapping of titanium (run 5).

canes were obtained from micro-extrusion, the qualitative study of the dimensional stability of these new hybrid materials was carried out. Actually, since the PLLA do not undergo any post-treatment at the extruder outlet, it is expected that the PLLA chains whose growth has been initiated from the Ti-OR groups of the cluster remain linked to the metal centers at the end of the polymerization, the Ti-O-PLLA alkoxide bonds formed being sufficiently stable to allow the material to be crosslinked. The behaviour of the hybrid PLLA synthesized by reactive extrusion and containing the highest concentration of oxo-cluster [Ti]<sub>16</sub> (run 5) was compared to that of a commercial PLLA of identical molar mass (≈ 60 000 g.mol<sup>-1</sup>) and having undergone the same thermal and mechanical treatment in the micro-extruder. The two canes of PLLA thus obtained were placed in supports and put in an oven at 150 °C for 10 h. One could observe that the commercial poly(lactic acid) was strongly deformed under heat, as expected for a thermoplastic material (Figure 3a). In contrast, the hybrid material has a shape almost similar to the initial one (Figure 3b). This clearly demonstrate the impact of the presence of the oxo-cluster [Ti]<sub>16</sub> in the polymer matrix and its role as crosslinking agent, allowing the material not to flow under thermal treatment.

**Figure 3.** (a) Commercial and hybrid PLLA rods at room temperature. (b) Commercial and hybrid PLLA rods after heating (150 °C, 10h): the dimensional stability for the hybrid PLLA is greatly improved.

## Conclusion

In this contribution we reported the synthesis of novel hybrid poly(L-lactic acid)s from titanium oxo-cluster  $[Ti]_{16}$  acting both as catalyst and crosslinker.  $[Ti]_{16}$  was shown to be an active catalyst toward the ring opening polymerization of L-lactide in bulk conditions, with up to 90 % of monomer converted within 30 min only, affording PLLAs with high  $M_n$  values up to 65 000  $g \cdot mol^{-1}$  and relatively narrow dispersities. These reactions were upscaled in a twin screw micro-extruder of a capacity of 20 g. The oxo-cluster kept a high activity in these experimental conditions, giving rise to hybrid poly(lactic acid)s of high  $M_n$  up to 57 700  $g \cdot mol^{-1}$  along with a good dispersion of the inorganic filler in the polymer matrix as shown by EPMA analysis. The impact of the presence of the oxo-cluster in the organic phase and its crosslinking effect were highlighted by dimensional stability tests under heat, showing a superior stability of the hybrid PLLA compared to commercial sample of same molar mass.

Some work is currently in progress to optimise the action of the oxo-cluster by varying its nature, nuclearity and concentration in the polymer matrix and to highlight its mechanism of action as crosslinking agent. The complete and quantitative study of the influence of the presence of the oxo-cluster within the polymer matrix on the thermo-mechanical properties of the final material is also in progress.

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