

Synthesis of polylactide/clay nanocomposites by *in situ* intercalative polymerization in supercritical carbon dioxide

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ABSTRACT

Poly(lactide) (PLA)/clay nanocomposites have been prepared by *in situ* ring-opening polymerization in supercritical carbon dioxide. Depending on the type of organoclay used, polylactide chains can be grafted onto the clay surface, leading to an exfoliated morphology. Nanocomposites with high clay contents (30-50 wt.%), called masterbatches, have also been successfully prepared and were recovered as fine powders thanks to the unique properties of the supercritical fluid. Dilution of these masterbatches into commercial L-poly(lactide) by melt blending has led to essentially exfoliated nanocomposites containing 3 wt.% of clay. The mechanical properties of these materials have been assessed by flexion and impact tests. Significant improvements of stiffness and toughness have been observed for the PLA/clay nanocomposites compared to the pure matrix, together with improved impact resistance.

Keywords: Nanocomposite, Poly(lactide), Montmorillonite, Supercritical CO₂

1. INTRODUCTION

During the last decade, an increasing attention has been paid to biodegradable polymers because of their sustainability. Poly(lactide) (PLA) is a well-known green polymer produced from renewable resources such as starch and is compostable, that draws a lot of attention in the polymer industry. These advantages make PLA an attractive alternative to classical commodity polymers, but several polylactide properties need to be improved in order to enlarge its range of applications, especially in packaging, since PLA is too much brittle and permeable to gases for some purposes. The introduction of a few percent of nanofillers, such as layered aluminosilicate clays, is known to enhance various polymer properties such as the stiffness/toughness balance, the fire resistance or the impermeability to gases. However, the highest property improvement can only be realized when the nanoparticles are fully and uniformly delaminated (exfoliated) in the polymer matrix. This is the main challenge for most polymers, as the direct melt blending of the clay usually leads to intercalated nanocomposites [1,2]. In this paper, the control of clay delamination has been achieved in PLA by *in situ* polymerization of D,L-lactide in supercritical CO₂ in the presence of an increasing clay content, from 3 up to 50 wt.%. The highest filled materials have been further used as masterbatches and redispersed into commercial PLA in order to achieve a final clay content of 3 wt.%.

Carbon dioxide has been chosen as a polymerization medium because it is environmentally friendly, non toxic, non flammable and inexpensive [3]. These advantages, combined with the easily attainable critical parameters ($T_c = 31.1\text{ }^\circ\text{C}$, $P_c = 73.8\text{ bar}$) makes CO₂ a solvent of choice for replacing less ecological organic solvents. Furthermore, this supercritical fluid has both gas-like diffusivities and liquid-like densities, and these properties can be continuously varied with small changes in temperature, making it a tunable solvent. Stassin et al. [4] first reported on the controlled ring-opening polymerization of ϵ -caprolactone in this medium, while Howdle was the first to undertake the suspension polymerization of L-lactide in scCO₂ [5].

The *in situ* polymerization of a monomer in the presence of clay has already been studied in detail by several authors [6,7]. In Paul's study [8], the ring-opening polymerization of lactide has been conducted in bulk with catalysts such as tin(II) octoate or triethylaluminum in the presence of organo-modified montmorillonite clays, with the organomodifier being an ammonium salt functionalized or not with hydroxyl groups. The monomer penetrates in the clay and then polymerizes inside the clay sheets, thus enhancing the delamination efficiency. The presence of hydroxyl groups has shown to be critical for the achievement of an efficient clay delamination, because these can act as initiators and lead to grafted polylactide chains onto the clay surface. The grafted chains push the lamellar sheets apart from each other and this allows the achievement of an excellent degree of clay exfoliation.

Some papers have quite recently described this type of polymer/clay synthesis in supercritical carbon dioxide (scCO₂) as the polymerization medium with methylmethacrylate (MMA) [9,10] or styrene [11-13] as the monomer and more recently our lab has investigated the ϵ -caprolactone *in situ* polymerization [14-16]. These works allow to prepare intercalated and exfoliated polymer/clay nanocomposites with a low clay content, whereas highly filled polymer/clay nanocomposites, with an inorganic content up to 50 wt.%, have been easily produced and recovered as fine powders in some cases [14-16], thanks to the scCO₂ properties.

Even if the *in situ* polymerization is the most efficient method for obtaining exfoliated clays into a polymer matrix, however, this is not the most practical technique from an industrial point of view. In fact, the melt intercalation technique (i.e., blending the clay with the molten polymer in a conventional kneader or extruder) is usually preferred for its easiness and because it uses already existing technologies. The efficiency of the *in situ* polymerization approach and the practicability of the melt intercalation technique can be combined by first synthesizing *in situ* a highly filled polymer/clay masterbatch in scCO₂ and then by dispersing it into the commercial polymer by melt blending. Indeed, the technical difficulties related to the high melt viscosity occurring when attempting to carry out *in situ* polymerization in bulk at silicate content above 20 wt.% are overcome by using scCO₂ as a polymerization medium. Moreover, it has to be noted that after depressurization, the masterbatch is usually obtained as a dry fine powder [15,16], avoiding the additional purification steps needed with more conventional media or synthesis conducted in bulk.

The masterbatch process has already been used by several workers [17-20], mostly with poly(ϵ -caprolactone) as the grafted polyester. More recently, Paul and coworkers have used this process for the dispersion of clay into commercial PLA. They obtained an excellent exfoliation degree of the clay after the melt redispersion of a PLA/MMT-clay masterbatch *in situ* synthesized in bulk.

In this paper, we describe the preparation of PLA/ MMT-clay masterbatches synthesized *in situ* in supercritical carbon dioxide and their dispersion into a commercial PLA. The resulting nanocomposites have been characterized in terms of composition, morphology and mechanical properties. D,L-LA has been chosen as the monomer with the aim to introduce an amorphous phase in the semicrystalline L-PLA. The amorphous phase, grafted to the nanoclay and homogeneously distributed throughout the matrix, is expected to enhance the material impact resistance.

2. EXPERIMENTAL

2.1. Materials

D,L-lactide (Purasorb DL) was provided by Purac Biochem (The Netherlands), and purified three times by recrystallization in dry toluene before use. Tin(II) octoate, from Sigma-Aldrich, was diluted in dry toluene and used as the catalyst, without further purification. CO₂ from Air Liquide Belgium (purity 99.995%) was used as received. Two different kinds of clays were provided by Southern Clay Products (Texas, USA). These montmorillonite clays are organo-modified either with dimethyl (dihydrogenated tallowalkyl) ammonium cation (Cloisite® 20A) or with bis-(2-(hydroxyethyl)methyl) (tallowalkyl) ammonium cation (Cloisite® 30B). The characteristics of these clays are presented in Table 1. They were dried under vacuum at 85 °C for one night in the reactor before use. Commercial L-poly lactide with a molecular weight of 130,000 g/mol (PDI = 2.1) has been kindly given by Natiss (Belgium).

2.2. Polymerization process

Polymerization was conducted in a 100 ml stainless steel high-pressure reactor equipped with a helical stirring system and an electrical heating mantle. Pressure, temperature, and stirring speed were monitored on a digital display control rack. The clay and monomer were dried in the reactor under vacuum at 40 °C for one night and then the catalyst was introduced under nitrogen flow. The desired temperature was set (usually 85 °C) and the desired CO₂ pressure was attained (240 bar) with a high-pressure syringe pump (ISCO corp.). At the end of the polymerization, the reactor was cooled down to room temperature and depressurized. The product was collected as a fine powder. Nanocomposites containing 3, 10, 35 and 50 wt.% of clay were produced, the two last ones being called masterbatches. The percentage of clay corresponds to the inorganic part of the nanocomposite.

The masterbatches have been dispersed into L-poly lactide by melt mixing in a counter-rotating twin-screw DSM microextruder at 200 °C for 5 min. Characterization of the nanocomposites morphology was done on 3mm-thick samples prepared by molding the compounded material in a hot press for 5 min at 200 °C

Rectangular bars (63 × 12 × 3.2 mm) have been prepared by injection molding at 200 °C for flexion and impact tests.

Table 1: Characteristics of the commercial clays used in this study.

Filler	Cation	Organic fraction (wt.%)	Interlayer spacing (nm)
Cloisite [®] 20A	(CH ₃) ₂ N ⁺ (C ₁₈ H ₃₇) ₂	29	2.4
Cloisite [®] 30B	(C ₂ H ₄ OH) ₂ N ⁺ (C ₁₈ H ₃₅)CH ₃	20	1.8

2.3. Characterization

Thermogravimetric analysis (TGA) has been conducted on a TA Instrument Q500 model in the Hi-Res dynamic mode, under N₂ flow, in order to determine the monomer conversion. In fact, the monomer degradation occurs between 100 and 180 °C whereas the polymer degrades in the 220-270 °C region. The formula $1 - [\text{wt.}\% \text{ monomer} / (\text{wt.}\% \text{ monomer} + \text{wt.}\% \text{ polymer})]$ gives the conversion degree.

XRD analysis was carried out with a powder diffractometer Siemens D5000 (Cu K_α radiation with $\lambda = 0.15406$ nm, 50 kV, 40 mA, Ni filter, $\theta/2\theta$ geometry) at room temperature for 2θ varying from 1.65° to 30° by 0.04 steps, in order to characterize nanocomposites morphology.

The degree of clay delamination into PLA was directly observed on compression-molded samples by transmission electron microscopy (TEM Philips CM100). Ultrathin sections (50-80 nm) were prepared with an Ultramicrotome Ultracut FC4e, Reichert-Jung. No staining was used since the aluminosilicate sheets are contrasting enough in the polymer matrix.

Flexural properties were measured on an Instron apparatus. The samples (51 × 12 × 3.2 mm) were subjected to a three point flexural test. The distance between the supports was 51.2 mm and the strain rate was 1.5 mm/min.

Charpy impact strength was measured with a Zwick pendulum impact tester at 20 °C according to the norm ISO 179-1. The size of the specimens was 51 × 12 × 3.2 mm, with a rectangular notch size of 2 mm deep and 1 mm large. The impact energy promoted by the hammer was 0.5 J. The impact strength values were evaluated on the average of five independent measurements.

Due to the huge difficulty to quantitatively extract the clay and the catalyst from the synthesized materials, even using LiCl-saturated THF solutions, it has not been possible to determine the molecular weight of the grafted PLA chains, neither by SEC nor NMR since montmorillonite contains paramagnetic metallic species that lead to excessive signal broadening.

3. RESULTS AND DISCUSSION

As reported in the literature, many monomers can be polymerized in scCO₂ [19]. Although this gas is a good solvent for many small molecules, most polymeric materials have a very low solubility in CO₂, except silicone- and fluorinated- based polymers. Depending on the monomer and polymer solubilities, different types of polymerization can therefore occur [20]: homogeneous polymerization, dispersion polymerization, emulsion/suspension polymerization, ... Looking at the diagram of lactide solubility in scCO₂ under variable conditions [21], it can be concluded that, upon the used experimental conditions ($T=85^{\circ}\text{C}$, $P = 240$ bar), the monomer is only partially soluble. As the polymer is completely insoluble in this medium, polylactide will precipitate during the polymerization.

In this study, we have prepared PLA/clay nanocomposites in scCO₂ by *in situ* ring-opening polymerization of D,L-lactide in the presence of two kinds of clays: Cloisite[®] 20A (CL20A) and Cloisite[®] 30B (CL30B). The major difference between these two clays is the functional hydroxyl groups borne by the ammonium cations of Cloisite[®] 30B. These groups are reactive towards the catalyst to form initiating species and therefore participate to the ring-opening polymerization of lactide, giving rise to polylactide chains grafted onto the clay surface [8].

The nanocomposites have been first prepared with a low clay content (3 and 10 wt.%, entries 2-5 of Table 2). With 3 wt.% of clay, the monomer conversion is complete after 30 h of polymerization, whereas at a higher clay content (10 wt.%), the conversion reaches 72% for PLA with 10 wt.% CL20A and 87% for PLA with 10 wt.% CL30B after 30 h. So, at a loading of 10 wt.%, the clay seems to decrease the D,L-lactide polymerization rate. This observation is further confirmed with a higher clay content, up to 50 wt.%, where the conversion slows down to 57% (entries 6 and 7, Table 2) after 30 h. This decrease in polymerization kinetics may be due to significant sterical hindrance of the clay at such high loadings. Anyway, an improved monomer conversion can be reached with increasing the polymerization time or temperature (entries 8, 9 of Table 2).

When comparing the polymerization kinetics of PLA-10 wt.% CL30B and PLA-10 wt.% CL20A, a slightly higher conversion can be observed for the first system. This is certainly due to the hydroxyl groups from Cloisite® 30B ammonium cations, which act as polymerization initiators, together with residual water impurities, thus increasing the initiator content.

The nanocomposites morphology was first determined by X-ray diffraction analysis (XRD) on the compression-molded samples. In Fig. 1 the XRD patterns of the organoclay CL20A and PLA-CL20A hybrids were compared. The primary silicate reflection at $2\theta = 2.53^\circ$ for the nanocomposite PLA-3 wt.% CL20A corresponds to an interlayer spacing of 3.8 nm according to Bragg's law, which is higher than the original clay (2.3 nm). This value is related to an intercalated nanocomposite. At 10 wt.% loading, the interlayer distance is slightly smaller (3.6 nm). The same analysis has been done on the PLA-CL30B system (Fig. 2). PLA-3 wt.% CL30B is characterized by the disappearance of the CL30B signal (1.8 nm) which is replaced by no other intercalation peak. This characteristic feature often characterizes exfoliation and is in fact proved by TEM analysis (see hereafter). The PLA-10 wt.% CL30B signal corresponds to a disordered system since the peak is broad and of low intensity. As the clay content is further increased, an intercalation peak appears and the mean interlayer distance progressively decreases, because of the physical hindrance that is too important to allow a complete separation of the clay layers.

Table 2: Influence of the type and content of clay on the polymer yield and clay interlayer spacing after 30 h of polymerization in *scCO*₂ (240 bar, 85 °C).

Entry	Sample	Type of clay	Initial clay content (wt.%)	Conversion ^a (%)	Interlayer spacing ^b (nm)
1	PLA	None	0	100	None
2	PLA-3 wt.% CL20A	20A	3	100	3.8
3	PLA-10 wt.% CL20A	20A	10	72	3.6
4	PLA-3 wt.% CL30B	30B	3	100	No signal
5	PLA-10 wt.% CL30B	30B	10	87	Broad distribution
6	PLA-35 wt.% CL30B	30B	35	72	3.6
7	PLA-50 wt.% CL30B-1	30B	50	57	3.3
8 ^c	PLA-50 wt.% CL30B-2	30B	50	69	3.3
9 ^d	PLA-50 wt.% CL30B-3	30B	50	69	3.4

^a Determined by Hi-Res thermogravimetric analysis.

^b Determined by XRD.

^c Experiment conducted at 90 °C instead of 85 °C.

^d Experiment conducted for 48 h instead of 30 h.

Nanocomposites containing a low clay content (3 wt.%) have been directly observed by transmission electron microscopy after compression molding (Fig. 3) The difference between the 20A and 30B nanocomposites is obvious, the first one being an intercalated nanocomposite (Fig. 3a), and the second one an exfoliated nanocomposite (Fig. 3b), with nearly every clay sheets independent from each other. These results confirm the conclusions made from the XRD analysis. From these observations, the beneficial effect of the PLA chains grafted onto the clay sheets is clearly put into evidence. These grafted chains enhance the affinity between the clay and the polymer and lead to an efficient delamination of the clay stacks. This conclusion is in accordance with Paul et al. [7] who have synthesized similar nanocomposites in bulk.

The highly filled PLA-CL30B nanocomposites, containing respectively 35 and 50 wt.% of inorganics, have been used as masterbatches to be dispersed by melt mixing into a commercial L-PLA. We must mention that as the

lactide polymerization was not quantitative in these masterbatches, some residual monomer is also introduced in the final composite. Anyway, as the amount of lactide introduced is low (1.4 wt.% maximum in the final material), it should have no significant influence on the clay dispersion nor on the nanocomposites mechanical properties. The XRD analysis of the nanocomposites resulting from the masterbatch dispersion is presented in (Fig. 4) The masterbatch diffraction peaks are broadened in the final nanocomposites and have a lower intensity. This kind of signal in the low angle region is characteristic of a mix of intercalated and exfoliated morphologies [22]. However, as can be seen on the TEM micrographies (Fig. 5), the clay is very well-delaminated, especially the sample PLA/ 3%(PLA-35 wt.% CL30B), with a lot of individual layers and also some remaining intercalated stackings composed of a few unseparated layers. These stacks must be the cause of the residual XRD signal.

Fig. 1: XRD data of (a) PLA, PLA-CL20A nanocomposites synthesized in $scCO_2$ with an inorganic clay content of (b) 3 wt.% and (c) 10 wt.%, and (d) original Cloisite[®] 20A.

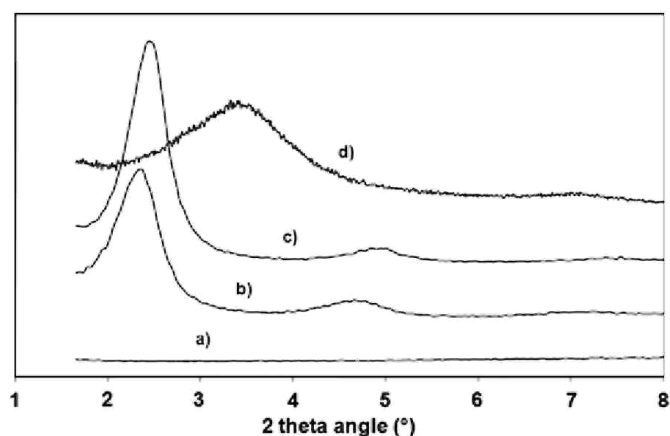


Fig. 2: XRD data of (a) PLA, PLA-CL30B nanocomposites synthesized in $scCO_2$ with an inorganic clay content of (b) 3 wt.%, (c) 10 wt.%, (d) 35 wt.%, (e) 50 wt.% (entry 8 of Table 2) and (f) Cloisite[®] 30B.

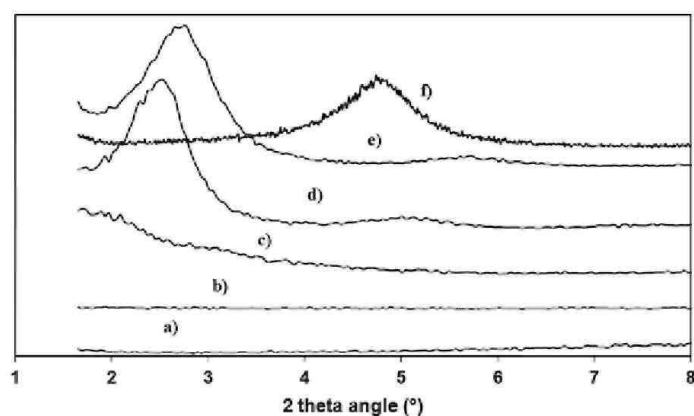


Fig. 3: TEM pictures of a PLA-3 wt.% clay nanocomposites based on (a) Cloisite® 20A and (b) Cloisite® 30B.

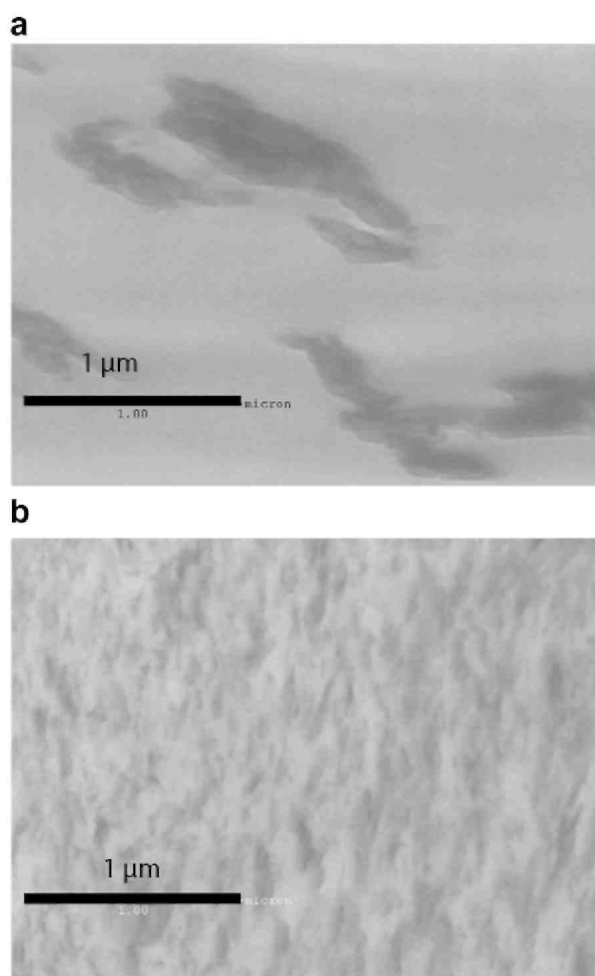


Fig. 4: XRD data of (a) commercial PLA, (b) PLA-35 wt.% CL30B masterbatch, (c) PLA-50 wt.% CL30B masterbatch, (d) PLA/3% (PLA-35 wt.% CL30B) nanocomposite and (e) PLA/3% (PLA-50 wt.% CL30B) nanocomposite.

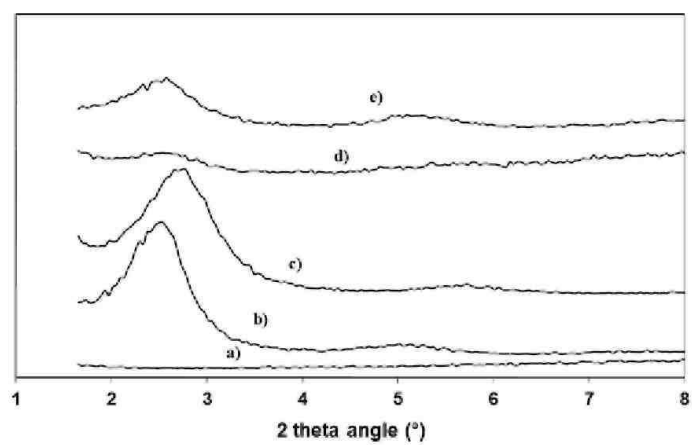
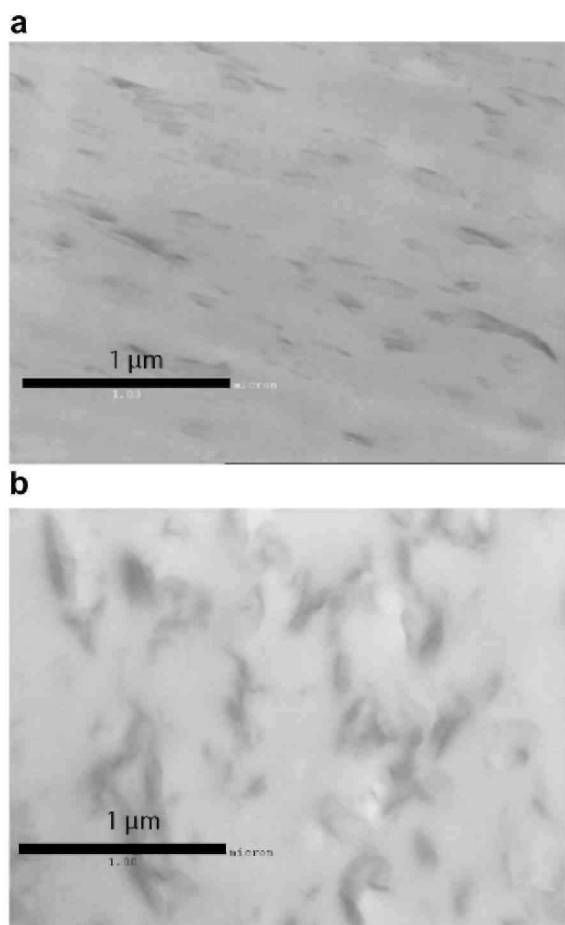


Fig. 5: TEM images of (a) PLA/3% (PLA-35 wt.% CL30B) and (b) PLA/3% (PLA-50 wt.% CL30B) nanocomposites.



We thus have shown that the use of masterbatches prepared in scCO_2 is efficient for the preparation of PLA nanocomposites with a large degree of exfoliation starting from a commercially available matrix.

PLA is known for its brittleness, so we have performed flexural tests in order to observe the influence of the clay on this property. In fact, it is well-known in the literature that a small amount of clay can improve significantly some polymer mechanical properties. Pure PLA samples have been prepared as well as PLA/3 wt.% clay nanocomposites coming from PLA/clay masterbatch dispersion. Three flexural tests have been performed on each sample and the average modulus and maximum constraint obtained are shown in Table 3. There is a significant increase in the nanocomposites modulus (up to 20%) compared to the pure polymer, and the maximum constraint is slightly increased, indicating that the incorporation of only 3 wt.% of clay has a beneficial effect on the mechanical properties of L-poly lactide.

Impact tests have also been performed on a filled polymer and a pure one for the sake of comparison.

The pure PLA impact resistance is enhanced from 5.1 to 6.0 kJ/m^2 with the addition of 3% of clay coming from the PLA/clay masterbatch containing 50% of inorganic clay. The filler increases thus slightly the material resistance, which is a very good result, since nanofiller addition into a polymer usually leads to a more brittle material. In these highly dispersed nanocomposites, the degree of clay dispersion thus allows to improve at the same time the stiffness (flexural modulus) and the toughness (impact resistance). This may be explained by the amorphous PLA grafted on the clay surface which coats the filler and may act as a choc absorber into the semicrystalline L-PLA.

Table 3: Flexural properties of PLA and PLA/3 wt.% clay nanocomposites.

Sample	Modulus (N/mm ²)	Max constraint (N/mm ²)
PLA	2958 ± 95	108.2 ± 2.9
PLA/3% (PLA-35 wt.% Cloisite [®] 30B)	3566 ± 87	107.7 ± 1.7
PLA/3% (PLA-50 wt.% Cloisite [®] 30B)	3348 ± 73	113.0 ± 3.1

4. CONCLUSIONS

Supercritical carbon dioxide has been successfully used as a polymerization medium for the *in situ* polymerization of D,L-lactide in the presence of organo-modified clays. Depending on the functional group borne by the organo-modifier, an intercalated or exfoliated nanocomposite has been obtained when a low clay level (3 wt.%) is reached. With increasing the amount of clay, a decrease in the polymerization kinetics is observed, which may be due to a significant sterical hindrance of the clay. Clay levels as high as 35 and 50 wt.% have been reached in these nanocomposites, which can then be used as masterbatches. The PLA-35 wt.% CL30B and PLA-50 wt.% CL30B masterbatches have been dispersed into a commercial PLA matrix by melt mixing to reach a final clay content of 3 wt.%. A good exfoliation degree has been observed with TEM and XRD analysis. These well-delaminated PLA/3 wt.% CL30B nanocomposites show significative improvement in both stiffness and toughness when compared with the unfilled matrix.

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