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New nanocomposite materials based on plasticized poly(L-lactide) and organo-modified montmorillonites: thermal and morphological study

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Abstract

Plasticized poly(L-lactide) (PLA) based nanocomposites were prepared by melt blending of the matrix with 20 wt% of poly(ethyleneglycol) 1000 (PEG 1000) and different amounts of montmorillonite, organo-modified or not. The intercalation of the polymer chains between the aluminosilicates layers and morphological structure of the filled PLAs were analysed by wide-angle X-ray scattering (WAXS). Thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC) were performed to study the thermal behaviour of the prepared composites. At constant filler level, it appears that from all the clays studied, the montmorillonite organo-modified by bis-(2-hydroxyethyl)methyl (hydrogenated tallowalkyl) ammonium cations brings the greater effect in terms of thermal stability. Increasing the amount of clay allows to delay the onset of thermal degradation of the plasticized polymer matrix. It was also pointed out, by WAXS and DSC analyses, that it exists a real competition between PEG 1000 and PLA for the intercalation into the interlayer spacing of the clay.

Keywords: Polylactide; Melt intercalation; Nanocomposites

1. Introduction

Aliphatic polyesters such as polylactides encounter nowadays various applications due to their biodegradable and/or biocompatible character. They are involved in the preparation of medical devices (bone surgery, suture, chemotherapy, etc.) and are intensively studied as an alternative solution to partially solve the ecological problem of plastic waste accumulation [1,2], with a special focus on packaging. Poly(L-lactide) (PLA) is produced from L-lactic acid, that is derived itself from the fermentation of corn or sugar beet. PLA, thanks to its biodegradation ability, presents the major advantage to enter in the natural cycle implying its return to the biomass. PLA, with a glass transition temperature around 55 °C, is a relatively stiff and brittle polymer with low deformation at break. Furthermore, PLA synthesized from optically active L-lactic acid by a stereocontrolled polymerization process, is semi-crystalline. Its melting temperature can be as high as 175 °C, depending on the optical purity of the polyester chains, i.e. the content in L-lactic acid units. In order to render PLA able to compete with more flexible and ductile commodity polymer such as polyethylene or polypropylene, there is a need to plasticize this polyester matrix. As a biodegradable plasticizer, poly(ethylene glycol) has proved its efficiency to strongly increase the elongation at break and the impact resistance of poly(L-lactide) [3]. However, other properties including thermal stability and gas barrier properties of the resulting PLA-based materials still need to be improved to fulfil for instance the requirements for food packaging applications. For several years now, the field of polymer nanocomposites [4,5] based on layered silicates, such as montmorillonite or hectorite, has given rise to a steadily increasing interest from scientists and industrials, as the nanoscale distribution of such high aspect ratio fillers brings up some large improvements to the polymer matrix in term of mechanical, fire retardant, rheological, gas barrier and optical properties, especially at low clay content (as tiny as 1 wt%) in comparison with more conventional microcomposites (>30 wt% of microfiller). In order to reach this nanoscale distribution, it is often needed to render the naturally hydrophilic clay filler more compatible with the organic

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polymer matrix. To do so, the hydrated Na^+ or Li^+ cations located between the aluminosilicate platelets constituting the clay can be replaced by more hydrophobic ammonium cations bearing long alkyl chains. The properties enhancement that is recorded when dispersing these organo-modified clays in a polymer matrix can be attributed to the morphology of the so-obtained nanocomposites. As layered silicates are basically constituted of stacks of platelets with a high aspect ratio (with a ca. 1 nm thickness and lateral dimensions varying from 100 nm to 1 μm), depending on the relative distribution/dispersion of those platelets in the polymer matrix, two extreme morphologies can be described: an intercalated structure if a regular stacking of polymer monolayers and silicate layers is generated or an exfoliated morphology if the silicate platelets are totally and homogeneously delaminated and dispersed in the polymer matrix. Most often, an intermediate morphology is observed where both intercalation and exfoliation co-exist to some extent. The balance between intercalation and exfoliation strongly depends on the nature of the matrix, the (organo-)clay and the preparative route followed to obtain the nanocomposite. Mainly two pathways can lead to the preparation of nanocomposites: either the polymerization of monomers intercalated within the interlayer spacings or the intercalation of the polymer chains in the molten state.

One of the first involvements of nanofillers in the area of biodegradable or renewable materials has lead to natural composites based on thermoplastic starch and alumino-silicates clays such as montmorillonite [6]. Concerning synthetic polymers, improving the properties of flexible biodegradable polyesters matrix such as plasticized PLA through the preparation of layered silicate-based nanocomposites could lead to the development of a field like film packaging with enhanced properties, especially in term of mechanical, thermal and gas barrier behaviour. It is interesting to point out that PLA-based montmorillonite composites were first prepared by solvent-casting using chloroform as co-solvent [7]. However, this preparation route did not lead to the formation of a nanocomposite, only a geometrical structure in tactoïds (microcomposites) was detected by X-ray diffraction. The melt extrusion technique was first used by Giannelis research group [8] to disperse organo-modified silicates into neat PLA matrix in order to improve its thermal and mechanical properties. Very recently, biodegradable aliphatic polyesters, synthesized from diols and carboxylic acids, were involved in the preparation of layered silicates nanocomposites by melt blending [9] or solvent casting [10] using various clays organo-modified by dimethyl (2-ethylhexyl) hydrogenated tallow ammoniums, bis(2-hydroxyethyl) methyl hydrogenated tallow ammoniums or dimethyl benzyl hydrogenated tallow ammoniums. In both cases, at least intercalation occurred as evidenced by XRD and TEM analyses. As expected from this kind of morphology, an increase in thermal stability and melt viscosity of the polyester matrix was achieved with increasing the clay content. On another hand, PLA/layered silicate nanocomposites were also prepared by melt extrusion of PLA and montmorillonite organically modified by octadecylammonium cations [11], using poly(ε-caprolactone)-oligomers (o-PCL) as compatibilizers. The addition of o-PCL leads to better parallel stacking of the silicate layers and also much stronger flocculation due to the hydroxylated edge–edge interaction of the silicate layers. Furthermore, the PLA/layered silicate nanocomposites exhibited remarkable improvement of materials properties in both solid and melt states compared to the matrix without clay. Some of us have also shown that PLA nanocomposites could be obtained by the melt blending preparative pathway. Intercalated nanocomposites were obtained by melt blending neat poly(L-lactide) with a montmorillonite organo-modified by dimethyl 2-ethyl hexyl (hydrogenated tallowalkyl) ammonium cations [12]. To the best of our knowledge, no study on the possibility to form nanocomposites from flexible plasticized PLA has been reported yet.

This paper aims at reporting on the preparation and properties of nanocomposites obtained by direct melt blending of plasticized poly(L-lactide) filled with different types of montmorillonites organo-modified or not. PLA plasticization with poly(ethyleneglycol) was performed along with the (organo-)clay filling/dispersion by mechanical kneading in an internal mixer. The resulting materials were analysed by wide-angle X-ray scattering (WAXS) to determine their morphological structure. Some thermogravimetric analyses (TGA) and differential scanning calorimetry measurements (DSC) were also performed to investigate the thermal and crystallization behaviour of these compositions, in relation to the nature and relative content of the organo-modified (or not) clays.

2. Experimental part

2.1. Materials

Poly(L-lactide) with 100% of L-lactide unity (PLA) kindly supplied by Galactic S.A. ($M_n = 81{,}800$, $I = 1.9$) was used as the polyester matrix. Poly(ethyleneglycol) 1000 (PEG, M.W. = 1000) used as plasticizer for PLA, was purchased from Sigma-Aldrich (Fluka div.). Four different clays were used and were provided from Southern Clay Products (Texas, USA). The unmodified montmorillonite-Na (Cloisite®Na^+) has a cation exchange capacity of 92 meq/100 g. The three other clays are organo-modified montmorillonites. Cloisite®25A is modified with dimethyl 2-ethylhexyl (hydrogenated tallowalkyl) ammonium cations, Cloisite®20A with dimethyl di(hydrogenated tallowalkyl) ammonium cations and Cloisite®30B with bis-(2-hydroxyethyl)methyl (hydrogenated tallowalkyl) ammonium cations. The level of organic materials contained in the

organo-modified clays was determined by thermogravimetric analysis (Table 1).

2.2. Sample preparation

Before processing, PLA was dried over night at 60 °C under reduced pressure and stored under vacuum in the presence of a humidity absorbent. The clays were also dried at 40 °C under reduced pressure during 4 h. Blending of PLA with clay particles and PEG 1000 (5, 10 or 20 wt%) was conducted in the presence of 0.3 wt% of Ultranox® 626 stabilizer on a Brabender counter-rotating mixer with a rotation speed of 20 rpm for 4 min, then at 60 rpm for 3 min. Throughout this paper, the filler content is expressed as the amount of inorganics in the resulting composites, independently of the amount of possible clay surface organic modifier. The processing temperature was set at 180 °C but it increased to 190 °C upon mixing. 3 mm thick plates were then shaped by compression molding at 180 °C. The material was pressed under 150 bars for 120 s, followed by a cycle where the pressure was kept successively at 20, 80, 140 bars for 5 s and then released for 1 s after each pressure molding increase (in order to get rid of any bubbles), and finally under 30 bars for 240 s. The samples were then cooled down by compressing at 15 °C under 30 bars for 5 min.

2.3. Characterization

TGA were performed using a Hi-Res TGA 2950 thermogravimetric analyzer from TA instrument with a heating ramp of 20 K/min under air flow (74 cm^3/min) from room temperature to 600 °C.

Thermal behaviour was measured with a DSC 2920 from TA instruments, with a heating and cooling ramp of 10 K/min from −50 to 200 °C under nitrogen flow and the values were recorded during the second heating scan. The morphological analysis by X-ray diffraction was performed on a Siemens D5000 diffractometer using Cu K_α radiation (wavelength, 1.5406 Å) at room temperature in the range of $2\theta = 1.5–30°$ with a scanning rate of 2°/min. Molecular weight determination of poly(L-lactide) was carried out after eliminating the clay by filtration of samples dissolved in chloroform. The catalyst residues were removed by liquid–liquid extraction with a 0.1 M HCl aqueous solution and PLA was recovered by precipitation from cold methanol, in which PEG 1000 was soluble. Size exclusion chromatography measurements were performed in THF at 35 °C using a Polymer Laboratory (PL) liquid chromatograph equipped with a PL-DG802 degazer, an isocractic HPLC pump LC1120 (flow rate: 1 ml/min), a Basic-Marathon autosampler, a PL-RI refractive index detector and four columns: a guard column PLgel 10 μm (50×7.5 mm^2) and three columns PLgel 10 μm mixed-B (300×7.5 mm^2). Molecular weights and molecular distributions were calculated by reference to a universal calibration curve relative to PS standard, and using the Kuhn–Mark–Houwink equation for PLA in THF: $M_n(\mathrm{PLA}) = 0.4055 \times M_n(\mathrm{PS})^{1.0486}$.

3. Results and discussion

Poly(L-lactide) (PLA) matrix alone leads to highly stiff materials preventing their use in applications such as flexible food packaging. Accordingly 20 wt% of poly (ethyleneglycol) 1000 (PEG 1000) was systematically incorporated as plasticizer [3]. PLA has been melt blended at 190 °C with the plasticizer and a known amount of clay in an internal mixer (Section 2). Four different (organo)-clays have been dispersed within the plasticized PLA matrix and the influence of the interlayer cations on the morphological and thermal properties of the composites has been studied while keeping constant the level of inorganics (3 wt% layered aluminosilicate). Furthermore, the relative content in organo-clay has been varied from 1 to 10 wt% as well as the PEG 1000 content (from 5 to 20 wt%) in order to study their implication in the obtained morphologies and thermal properties.

3.1. Influence of the clay organo-modifier

In order to get some insight in the composite morphology, WAXS analysis has been performed on compositions filled with 3 wt% of the four studied montmorillonites. Table 1 presents the clay interlayer spacings (corresponding to the $d_{(0,0,1)}$ diffraction peak) observed in each composite and compared to the values registered for the respective clays alone. It is interesting to note that X-ray diffraction analysis shows that all of the studied montmorillonites lead

Table 1
Interlayer spacing as determined by WAXS analysis

Code	Filler	Ammonium cation (organic fraction in wt%)		Interlayer spacing (Å)	
				In clay	In PLA/PEG composite (3 wt% of filler)
1	Cloisite®Na^+	Na^+	(–)	12.1	17.7
2	Cloisite®30B	$(C_{18}H_{37})–N^+(C_2H_4OH)_2CH_3$	(20.1)	18.4	38.0
3	Cloisite®25A	$(C_{18}–H_{37})–N^+–(CH_3)_2–CH_2–CH(C_2H_5)–C_3H_8$	(26.9)	20.4	32.4
4	Cloisite®20A	$(CH_3)_2N^+(C_{18}H_{37})_2$	(29.2)	23.6	36.5

to the formation of intercalated nanocomposites, even for the unmodified Cloisite®Na^+. Most often, melt blending polymer matrices with montmorillonite-Na results in the formation of a microcomposite, as most of the polymers are too highly hydrophobic to migrate into the hydrated Na^+ interlayer space. However, Vaia et al. [13] have reported on the intercalation of poly(ethylene oxide) between the aluminosilicate layers of unmodified montmorillonite-Na. This intercalation leads to an increase of the interlayer distance from 12.4 Å for the pristine clay to 17.7 Å in the composite. We have also observed such an increase in the basal spacing of the clay in the plasticized PLA/Cloisite®Na^+ composite, as the interlayer distance increases from 12.1 to 17.7 Å (Table 1). Obviously, in the presence of Cloisite®Na^+, PEG 1000 intercalates preferentially the interlayer spacings of the clay. This selective PEG intercalation is further confirmed by the impossibility to form a nanocomposite by melt blending non-plasticized PLA with Cloisite®Na^+. Indeed, some of us have previously reported that only microcomposites were recovered by melt blending neat PLA (non-plasticized) and montmorillonite-Na [12]. As far as the organo-modified clays are concerned, a competition between the plasticizer and the polymer matrix for the clay interlayer intercalation cannot be excluded since organo-clay such Cloisite®25A and neat PLA can form intercalated nanostructure [12]. In order to shed some light about the nature of the organic material that intercalates effectively within the clay interlayers, the X-ray diffraction patterns obtained for Cloisite®30B, PLA/Cloisite®30B blend, simple blend of Cloisite®30B and PEG 1000, (plasticized) PLA alone and its melt blend with Cloisite®30B have been compared in Fig. 1. Even if it appears that PEG 1000 mainly intercalates between the layers, the intercalation of PLA chains, even partial, cannot be totally precluded. Moreover, a puzzling characteristic feature in all X-ray diffractograms of the plasticized PLA unfilled or filled with the organo-modified clays, is the presence of a small diffraction peak in the range of 18.6 Å, i.e. at 4.9° as 2θ angle. In case of plasticized PLA/Cloisite®30B composites, this small peak overlays the $d_{(0,0,1)}$ peak characteristic of the organo-modified clay interlayer distance, rendering difficult the interpretation in terms of intercalation. The examination of the WAXS profile of a nanocomposite prepared with 3 wt% of Cloisite®25A brings a first evidence that the peak located at ca. 18.6 Å is due to a superstructure displayed by the PEG-plasticized PLA (Fig. 2). Indeed, the diffraction peaks (in curve (e)) at 16.7 and 32.4 Å correspond, respectively, to the interlayer clay distances $d_{(0,0,2)}$ and $d_{(0,0,1)}$, from the intercalation of the polymer chains into the clay interlayer spacings. The peak at 18.6 Å can only be attributed to the plasticized PLA matrix, as it was confirmed by XRD (curve (c) in Fig. 2).

DSC analyses have shown that the nature of the clay does not affect the glass transition temperature or the melting temperature of the PLA matrix (Table 2), excepted for the Cloisite®Na^+ based composite where a slight decrease in both T_g and T_m can be detected. This temperature decrease will be discussed in more details in Section 3.2 since it is significantly enhanced at higher Cloisite®Na^+ content.

The TGA performed on the resulting blends, where the weight lost due to the volatilization of degradation by-products

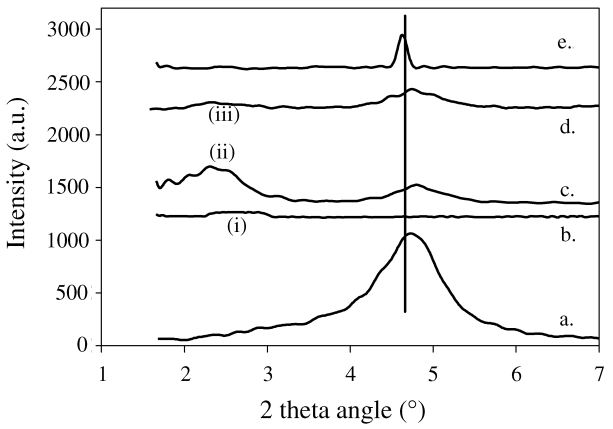

Fig. 1. WAXS diffractograms (shown here for 2θ from 1 to 7°) of Cloisite®30B alone (curve a), PLA/Cloisite®30B nanocomposition (curve b), PEG 1000/Cloisite®30B blend (curve c), plasticized PLA/3 wt% Cloisite®30B nanocomposition (curve d) and plasticized PLA alone (p.PLA) (curve e). The straight line corresponds to a diffraction angle of 4.9°, which itself corresponds to an interlayer distance of 18.6 Å. (i) as noted for interlayer distance of 38.6 Å; (ii) as noted for interlayer distance of 37.8 Å; (iii) as noted for interlayer distance of 38.0 Å. For curve (e), the intensity scale has been amplified for sake of clarity.

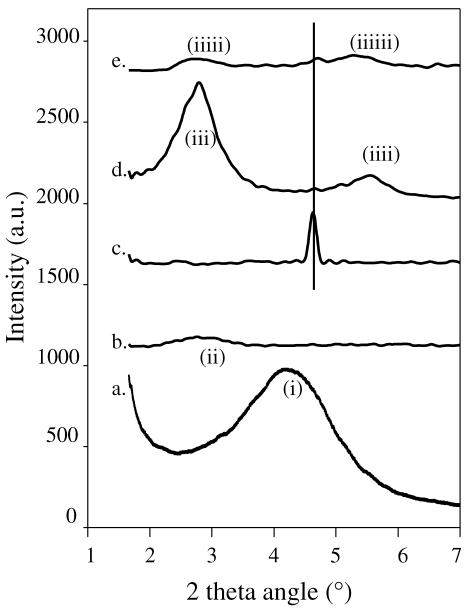

Fig. 2. WAXS diffractograms of Cloisite®25A alone (curve a), PLA/Cloisite®25A nanocomposition (curve b), plasticized PLA alone (p.PLA) (curve c), PEG 1000/Cloisite®25A blend (curve d) and plasticized PLA/3 wt% Cloisite®25A nanocomposition (curve e): (i) as noted for interlayer distance of 20.4 Å; (ii) as noted for interlayer distance of 32.4 Å; (iii) as noted for interlayer distance of 31.6 Å; (iiii) as noted for interlayer distance of 15.9 Å; (iiiii) as noted for interlayer distance of 32.4 Å; (iiiiii) as noted for interlayer distance of 16.7 Å.

Table 2
DSC of PLA, plasticized PLA with 20 wt% PEG 1000 (p.PLA) and the p.PLA (organo-clay) composites with 3 wt% inorganics. Experiments carried out under nitrogen flow with a heating ramp of 10 K/min from − 50 to 200 °C

Code	Samples type	T_g (°C)	T_m (°C)
A	PLA	55	167
B	p.PLA	15	170
1	p.PLA/Cloisite®Na^+	14	168
2	p.PLA/Cloisite®30B	16	171
3	p.PLA/Cloisite®25A	16	171
4	p.PLA/Cloisite®20A	16	170

is monitored as a function of temperature increase, show an increase of the thermal stability of the polymer matrix when filled with a small amount of nanoclay as low as 3 wt% in inorganics (Fig. 3). Depending on the nature of the alkyl-ammomium cations (length of the alkyl chain or functionality attached onto the ammonium cation), this effect is more or less pronounced, the greater thermal stability improvement is triggered by Cloisite®30B where the main process of degradation is shifted towards higher temperature by 40 °C. Such behaviour may be related to the structure of the nanocomposite and has already been reported for other layered silicate nanocomposites based on matrices such as nylon-6 [14], polystyrene [15], ethylene–vinyl acetate copolymers [16] or poly(ε-caprolactone) [17] filled with various types of organo-modified montmorillonites. In fact, the layers of organo-modified phyllosilicates are thought to increase the diffusion pathway of the combustion by-products, as they are impermeable to such components [18]. To give an idea of the burning behaviour of the composites, some visual tests of combustion have been performed. Compared with the unfilled plasticized PLA matrix, the nanocomposites based on organo-modified clays did not produce any burning droplets anymore. Rather, these PLA nanocomposites were characterized by a marked char formation. This charring has been reported to be partially

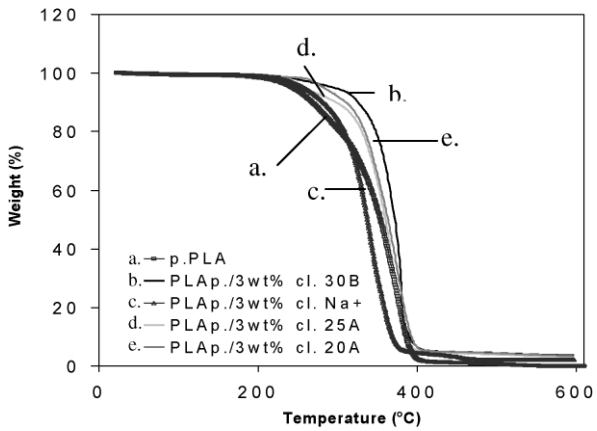

Fig. 3. Thermogravimetric analysis of PLA plasticized with PEG 1000 and filled with 3 wt% of (organo-modified)-montmorillonite. Cl. stands for Cloisite® and p.PLA for plasticized PLA. (Experiments carried out under air flow with a heating ramp of 20 K/min from 25 to 600 °C).

responsible for the limited diffusion of the combustion gases and could be at the origin of the fire retardant properties of polymer layered silicate nanocomposites [19]. Interestingly, the plasticized PLA composition prepared from Cloisite®Na^+ (thus characterized by selective PEG 1000 intercalation) burns in producing burning droplets (without any charring effect) very similarly to the unfilled polyester matrix, which seems to indicate that the sole intercalation of PEG 1000 into the interlayer spacing of the clay is not sufficient to promote fire retardant properties. Quantitative characterization of the flame-retardant properties of the plasticized PLA/clay nanocomposites is under current investigation and will be the subject of another communication.

3.2. Influence of the clay content

The relative content of (organo)-clay within the plasticized PLA matrix has been varied as well. Particularly, different compositions have been prepared by incorporating 1, 3, 5 and 10 wt% of either Cloisite®30B or Cloisite®Na^+, and characterized by WAXS. Interlayer distances do not vary significantly as the filler content increases. This is demonstrated for Cloisite®30B-based composites in Fig. 4. For Cloisite®Na^+ based compositions, the interlayer distance stands close to 17.7 Å while increasing the level of clay from 1 to 10 wt%. This observation can be considered as an additional evidence for the selective PEG 1000 intercalation in the interlayer space of the unmodified montmorillonite-Na. As far as compositions filled with Cloisite®30B are concerned, the ratio between intercalation and exfoliation seems to increase with the filler content, as shown by a slight ascent of the diffraction profile baseline at

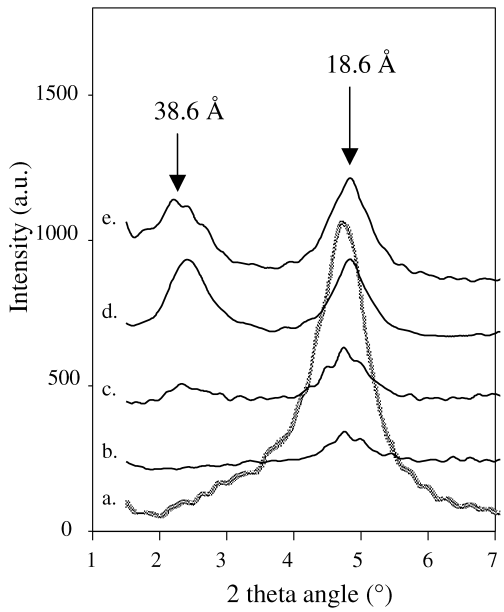

Fig. 4. WAXS diffractograms of Cloisite®30B (curve a) and plasticized PLA (p.PLA)/Cloisite®30B nanocomposition with different contents of clay (1 (curve b), 3 (curve c), 5 (curve d) and 10 wt% (curve e) inorganics).

very low angle for the highest loading (Fig. 4). Analysis of the diffractograms cannot allow to assert definitively which species from PLA or PEG chains intercalates as both polymers, when investigated as the sole intercalating agent, give intercalation peaks with very similar interlayer spacing values, i.e. $d_{(0,0,1)}$ at ca. 38 Å. Some further morphological analyses by transmission electronic microscopy (TEM) have been carried out to determine the extent of clay exfoliation along with the organo-clay content. However, the electron beam destroyed the samples before any picture could be taken into account for interpretation of the nanocomposites morphology. Such sensitivity to the electron beam may be due to the lowering of the molar masses of PLA during processing.

An increase in thermal stability with the clay content is observed by TGA, with a maximum obtained for a loading of 5 wt% in clay (Fig. 5). When further increasing the filler content, a decrease in thermal stability is however noticed. A very similar thermal behaviour has already been reported for EVA-based nanocomposites [10], for which optimal thermal stabilization was obtained at a filler content around 3 wt%. Such behaviour was explained by the relative extent of exfoliation/delamination in function of the amount of organo-clay. Indeed at low filler content, exfoliation dominates but the amount of exfoliated silicate layers is not sufficient to promote any significant improvement of the thermal stability. Increasing the filler content leads to relatively more exfoliated individual particles, and increases the thermal stability of the nanocomposites. However, at filling content above ca. 5 wt%, complete exfoliation of such high aspect ratio silicate layers gets more and more hindered because of geometrical constraints within the limited space remaining available in the polyester matrix and no more increase in thermal stability (even some decrease) is detected.

In contrast to Cloisite®30B based composites TGA curves recorded for plasticized PLA filled with Cloisite®Na^+ show that increasing the filler content triggers a substantial continuous decrease in thermal stability. As the unmodified montmorillonite level varies from 1 to 10 wt%, the maximum of d-TGA curves (derivatives from TGA curves) has been shifted from 371 °C down to 325 °C, which could denote the formation of shorter PLA chains as the clay content increase. To explain this behaviour, it must be reminded that the Na^+ cations present in the interlayer spaces are highly hydrated cations. At high temperature, some water release could be responsible for the PLA chain degradation by hydrolysis. Therefore, at higher montmorillonite-Na content, chain cleavage by ester hydrolysis reaction will be more pronounced, leading to the formation of much shorter PLA chains, known to degrade at lower temperature. This degradation of PLA chains upon melt blending with Cloisite®Na^+ has been confirmed by SEC. The number average molecular weight of the chains decreases from 33,200 to 8900 as the filler content increases from 1 to 10 wt%. Undoubtedly the most interesting data are provided by the differential scanning analysis recorded on both composites issued from Cloisite®Na^+ and Cloisite®30B (Table 3). Indeed, while the filler content does not influence greatly the glass transition temperature (T_g) and the melting temperature (T_m) of the polymer in composites based on plasticized PLA and Cloisite®30B, these temperatures are noticeably modified by the presence of unmodified montmorillonite-Na, especially at higher filler content (10 wt% Cloisite®Na^+). These analyses tend to confirm the preferential intercalation of PEG 1000 in Cloisite®Na^+, which renders it less available to plasticize the PLA matrix. It results an increase of the glass transition temperature, particularly remarkable at 10 wt% of loading. At lower content in Cloisite®Na^+, the proportion of plasticizer intercalated into the interlayer space of the clay remains insufficient to really have an effect on the T_g of the PLA matrix. For the Cloisite®30B based nanocomposites, the T_g value stays close to 16 °C, showing that PEG 1000 keeps its plasticizer role for the PLA matrix. It implies that PEG 1000 is not preferentially intercalated into the

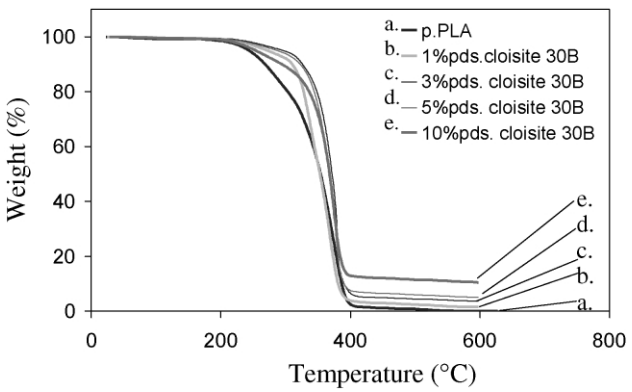

Fig. 5. Thermogravimetric analysis of PLA plasticized with PEG 1000 (p.PLA) and filled with various amounts of Cloisite®30B. (Experiments carried out under air flow with a heating ramp of 20 K/min from 25 to 600 °C).

Table 3
Thermal transition of neat PLA, PLA plasticized with 20 wt% PEG 1000 (noted p.PLA) and p.PLA filled with increasing amounts of Cloisite®Na^+ and Cloisite®30B, as measured by DSC. Experiments carried out under nitrogen flow with a heating ramp of 10 K/min from −50 to 200 °C

Code	Samples type	T_g (°C)	T_m (°C)
A	PLA	55	167
B	p.PLA	15	170
5	p.PLA/1 wt% Cloisite®Na^+	15	170
6	p.PLA/3 wt% Cloisite®Na^+	14	168
7	p.PLA/5 wt% Cloisite®Na^+	13	163
8	p.PLA/10 wt% Cloisite®Na^+	21	161
9	p.PLA/1 wt% Cloisite®30B	16	170
10	p.PLA/3 wt% Cloisite®30B	16	171
11	p.PLA/5 wt% Cloisite®30B	15	170
12	p.PLA/10 wt% Cloisite®30B	16	170

Table 4
Effect of the relative content in PEG 1000 plasticizer on the thermal transitions and melting enthalpy of plasticized PLA filled with 3 wt% of Cloisite®30B, as determined by DSC. Experiments carried out under nitrogen flow with a heating ramp of 10 K/min from −50 to 200 °C.

Code	PEG 1000 (wt%)	T_g (°C)	T_m (°C)	ΔH_m (J/g)	ΔH_c (J/g)[a]
13	5	32	173	44.7	39.6
14	10	25	172	47.3	41.6
15	20	16	171	58.4	52.7

[a] As determined from the controlled cooling ramp (10 K/min from 200 to −50 °C, under nitrogen flow) which directly follows the heating ramp.

interlayer space of the clay compared to the polyester, or at least that the affinity between the silicate layers surface and PEG 1000 is not sufficient to force the majority of the plasticizer to intercalate into the clay. This is probably due to a more significant hydrophilicity difference between PEG 1000 and Cloisite®30B than between PEG 1000 and Cloisite®Na^+. The concomitant decrease of the melting temperature is more likely due to the chains cleavage by hydrolysis of the polyester chains as already aforementioned.

3.3. Influence of the plasticizer content

The effect of the PEG 1000 relative content on the morphology and thermal behaviour of Cloisite®30B based nanocomposites has been also studied in order to shed some light on the actual role of the plasticizer. The amount of clay was fixed at 3 wt% while the PEG 1000 was incorporated at the level of 5, 10 and 20 wt%. Noting that the best results in term of thermal stabilization were obtained for the Cloisite®30B based plasticized PLA nanocomposites, it was decided to study the influence of the plasticizer content on compositions containing 3 wt% of this organo-clay.

It should be noted again from the WAXS analysis the presence of a diffraction peak at 18.6 Å for all the samples, which has been assigned to the plasticized matrix as discussed before. Moreover, the X-ray diffractograms reveal that increasing the plasticizer level does not lead to significant morphological evolution in the intercalation of plasticized PLA chains, as the clay interlayer distance remains almost unchanged ($d_{(0,0,1)}$ at ca. 32.6 and 33.1 Å for a PEG 1000 level of 5 and 10 wt%, respectively). This observation tends to confirm that the intercalation is not entirely due to the PEG chains, but that PLA also can crawl into the interlayer space of the filler. As expected for a plasticizer, PEG 1000 increases the molecular motions of the polyester chains (lower T_g at larger PEG content), and therefore induces a higher PLA crystallinity, as shown by the increase of the melting and crystallinity enthalpy values (Table 4). Thermogravimetric analysis has shown that increasing the plasticizer content in the nanocomposition from 5 to 20 wt% do not affect the thermal stability of the materials, as the maximum of degradation temperature was kept near 378 °C.

4. Conclusions

Plasticized poly(L-lactide) (organo-)clay nanocomposites have been prepared by direct melt blending. X-ray diffraction has pointed out that all the studied clays, including montmorillonite-Na, lead to intercalated nanostructures. In the latter case, owing the polarity difference between the PLA matrix and this type of clay, the intercalation is essentially provoked by the interlayer migration of poly(ethyleneglycol) 1000 plasticizer. DSC performed on composites containing increasing levels of filler confirms this hypothesis since the T_g of PLA matrix increases at high montmorillonite-Na content (10 wt%), attesting for the PEG trapping within the clay interlayers. Morphological analyses carried out onto the organo-modified montmorillonites-based composites have shown the possible competition between the polymer matrix and the plasticizer for the intercalation between the alumino-silicates layers. From the TGA, it was found that the more efficient organo-modified clay to form intercalated and possibly partially exfoliated nanocomposites is the montmorillonite surface treated with bis-(2-hydroxyethyl)methyl (hydrogenated tallowalkyl) ammonium cations.

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