

## **THE EFFECT OF DIFFERENT CLAYS ON THE STRUCTURE, MORPHOLOGY AND DEGRADATION BEHAVIOR OF POLY (LACTIC ACID)**

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## **Abstract**

In this work, polylactic acid (PLA)-based composites filled with different kinds of clay were prepared and their structure, morphology and degradation behavior were compared. A similar degree of dispersion was achieved in the case of cationic and anionic clays. However, these two types of fillers had different effects on the structure and morphology. The anionic perkalite clay induced higher crystallinity, a faster crystallization rate and also a modification of the crystallization mechanism. Moreover, when perkalite clay was used, the lamellar framework of PLA was preserved. Cationic clays, on the other hand, were detrimental for a regular crystallization of the PLA matrix, producing very disordered lamellar stacks. The effects of anionic and cationic clays were different also on the degradation behavior, with the perkalite-containing composite degrading much faster than either the matrix or the montmorillonite-reinforced materials. This comparison shows that a rational choice of the chemical nature of the nanofiller allows to tune both the degradation rate of PLA, and its structure, and as a consequence also the mechanical properties of the composite.

## 1. Introduction

Modern society produces ever-increasing quantities of waste materials, which are causing environmental concerns. Many objects produced from polymers that derive from fossil sources, once they are consumed and discarded into the environment, finally end up as un-degradable wastes and therefore contribute greatly to global pollution. Increasing environmental awareness and inconsistency in petroleum pricing opened a way to develop eco friendly materials and to replace plastics which are mainly causing environmental problems. Research mainly focused on materials from renewable resources like agricultural products and thus polymeric materials from agro based products are not only gaining interest for environmental concerns but also for political reasons.

The development of innovative biopolymer materials has been underway for a number of years, and continues to be an area of interest for many scientists. Among the most popular and important biodegradable polymers are aliphatic polyesters, such as poly(lactic acid) (PLA). PLA is linear thermoplastic polyester produced by the ring opening polymerization of lactide (Ray and Ramontjia, 2009). Lactide is a cyclic dimer which is obtained from the fermentation of sugar feedstocks, corn, etc. PLA has attracted considerable attention due to its renewable sources, biodegradation, biocompatibility, superior thermal properties, and the transparency of the processed materials (Urayama et al., 2002; Tsuji and Suzuyoshi, 2002). However, there are properties such as flexural properties, gas permeability, impact strength, etc. that are to be improved for widening the end use applications of this polymer. (Feijoo et al., 2005; Ray and Okamoto, 2003).

A wealth of investigations was carried out on PLA, to improve material performance, and recently the strategy for achieving this aim was focused on the preparation of nanocomposites (Ray et al., 2002, 2003a, 2003b; Maiti et al., 2002b; Hasook et al., 2006, Ogata et al., 1997, Jollands and Gupta, 2010, Huang et al., 2010; Das et al., 2010; Tabatabaei and Ajjii, 2011; Li et al., 2009). Most of the authors observed interesting increases in tensile and functional properties as a consequence of the addition of clay, however until now nanocomposites did not fulfill all the expectations, because the improvement in mechanical properties was not substantial in comparison to conventional microcomposites (Kontou et al., 2011).

The most widely used clay is montmorillonite, because of its large cation exchange capacity (Ray et al., 2002, 2003a, 2003b; Maiti et al., 2002b; Hasook et al., 2006, Ogata et al., 1997, Jollands and Gupta, 2010, Huang et al., 2010; Das et al., 2010; Tabatabaei and Ajjii, 2011; Li et al., 2009).

Other types of layered filler, such as layered double hydroxides are less represented in the scientific literature (Katiyar et al., 2010; Dagnon et al., 2009; Pan et al., 2008). Layered double hydroxides (LDHs), known as anionic clays, consist of a stacking of positive hydroxylated layers  $[M_{1-x}^{2+} M_x^{3+} (OH)_2]^{x+}$  separated by interlayer anionic species and water molecules  $[A_{x/q}^{q-} \cdot nH_2O]$ , where  $M^{2+}$  is a

divalent metal ion (such as  $Mg^{2+}$ ,  $Zn^{2+}$ ),  $M^{3+}$  is a trivalent metal ion (such as  $Al^{3+}$ ,  $Cr^{3+}$ ), and A is an anion with valency q (such as  $CO_3^{2-}$ ,  $Cl^-$ ,  $NO_3^-$ ). (Leroux and Taviot-Gueho, 2005) Because of their highly tunable properties and unique anion exchange properties, LDHs are considered an emerging class of layered materials for the preparation of polymeric nanocomposites. (Kohjiya et al., 2007) Pan et al. prepared by melt mixing PLA based composites containing dodecyl sulfate-modified LDH, and observed a good dispersion of the filler within the matrix (Pan et al., 2008). These authors mainly focused on the crystallization behavior of the polymer, which experienced a nucleating effect due to LDH (Pan et al., 2008). Dagnon and colleagues prepared nanocomposites with a PLA matrix filled with ibuprofen-modified LDHs with the aim of balancing the mechanical properties and the cell proliferation on these materials (Dagnon et al., 2009). They obtained an increase in modulus and ultimate strength, while at the same time reducing cell proliferation thanks to ibuprofen release (Dagnon et al., 2009). Katiyar and coworkers recently compared the performance of PLA-based nanocomposites containing a combination of LDH and cationic clay with analogous materials just filled with cationic clay. The presence of LDH was found to be detrimental for gas barrier properties, to modify the crystallization behavior of the matrix and to increase the tendency to filler agglomeration (Katiyar et al., 2010).

Most LDH layers disperse homogeneously in a PLA matrix in the nanometer scale yielding intercalated or exfoliated structures. Incorporation of organically modified LDH brings considerable increase in the crystallization rate of PLA, because of the heterogeneous nucleating effect. With the presence of LDH, the nucleation density increases and the spherulite size reduces. Besides, it was found the incorporation of LDH has little or no discernable effect on the crystalline structure as well as that melting behavior of PLA. As a consequence, it is considered that LDHs could possibly be a kind of promising fillers for reinforcing the biodegradable polyesters to produce biocompatible nanocomposite materials (Pan et al., 2008).

Despite the relevant amount of work done on PLA-based nanocomposites, there are two aspects still underrepresented, which are the motivation of this paper. Firstly, few authors compared the performance at equal preparation conditions of anionic and cationic clays for the property improvement of PLA. Secondly, most reports focus on the investigation of the effect of clay on mechanical performance, but just a few highlight the relationship between the presence of clay, the crystallization behavior of the matrix and the degradation rate of the material.

## **2. Materials**

PLA, with D content of 1.1-1.7% was obtained from Unitika Co. Ltd. According to the supplier, it had a weight average molecular weight  $M_w = 200$  kg/mol, density = 1.25 g/cm<sup>3</sup> (ASTM 1238). Two different cationic clays i.e. Dellite HPS (deriving from a naturally occurring especially purified montmorillonite) and Dellite 43B (montmorillonite modified with a quaternary ammonium salt, i.e. dimethylhydrogenated tallow ammonium) were kindly donated from Laviosa Chimica Mineraria s.p.a., Italy. Perkalite is an organically modified layered double hydroxide (kindly donated by Akzo Nobel Polymer Chemicals, Netherlands). All materials were dried at 50°C prior to use.

All composites were prepared with 3% of clay (W/W) in melt mixing in a camera mix (Barbender) at 190°C. Mixing conditions were set at 80 rpm for 7 minutes, which were the parameters reported by Jollands and Gupta as optimal for maximum mechanical property improvement (Jollands and Gupta, 2010).

The obtained lumps were sliced into small pellets and then melt pressed in a hot press at a temperature of 190°C in order to obtain films for further analysis. To obtain a crystalline material, all samples were annealed at 100°C for 4 hours. Only annealed samples were used for all further analysis. Filler level was kept constant in all cases, because it is reported that filler levels above 5% results in reduction of mechanical properties (Jollands and Gupta, 2010; Kontou et al., 2011).

The samples were coded according to the type of clay used for the preparation of PLA nanocomposites. For example, the composite prepared with perkalite, was given the code PLA-PERK.

## 2.1 Wide Angle X-ray Diffraction (WAXD)

WAXD transmission patterns were recorded in the diffraction angular range 1.5-30° 2 $\theta$  by a Philips X'Pert PRO diffractometer, working in the reflection geometry and equipped with a graphite monochromator on the diffracted beam (CuK $\alpha$  radiation). The application of the least-squares fit procedure elaborated by Hindeleh and Johnson (Hindeleh and Johnson, 1971) gave the degree of crystallinity by weight which was then transformed in degree of crystallinity by volume ( $\phi_{WAXD}$ ).

## 2.2 Small Angle X-ray Scattering (SAXS)

The SAXS patterns of the samples were recorded by an MBraun system, using a CuK $\alpha$  radiation from a Philips PW 1830 X-ray generator. The data were collected by a position sensitive detector and were successively corrected for blank scattering, desmeared and Lorentz-corrected.

Finally, the Lorentz correction was applied:  $I_1(s) = 4\pi s^2 I(s)$ , where  $I_1(s)$  is the one-dimensional scattering function and  $I(s)$  the desmeared intensity function, being  $s = (2/\lambda) \sin\theta$ .

### 2.3 Differential Scanning Calorimetry (DSC)

All the measurements were carried out with a TA Instruments mod. 2920 calorimeter operating under N<sub>2</sub> atmosphere. Polymer samples weighing about 5 mg closed in aluminum pans were used throughout the experiments. Indium and tin of high purity were used for calibrating the DSC temperature and enthalpy scales. The kinetics of crystallization was studied by subjecting each sample to the following thermal cycle: after erasure of previous thermal history by keeping the polymer at 200°C for 5 min, it was cooled at the maximum rate to the crystallization temperature ( $T_c$ ). The heat evolved during the transition was monitored as a function of time during an isothermal at  $T_c$  of suitable length. The fraction  $X$  of material crystallized after the time  $t$  was estimated from the relation:

$$X = \frac{\int_0^t \left( \frac{dH}{dt} \right) dt}{\int_0^{\infty} \left( \frac{dH}{dt} \right) dt}$$

Where the numerator is the heat generated at time  $t$  and the denominator is the total heat of crystallization. The Avrami equation (Avrami, 1941) was used to correlate  $X$  with time:

$$X = 1 - \exp[-K(t - t_0)^n]$$

$K$  is the kinetic constant of crystallization,  $n$  is a coefficient linked to the time dependence and the dimensions of growth of crystallites.

### 2.4 Transmission Electron Microscopy (TEM)

For TEM, 80 nm ultra-thin sections were prepared by an ultramicrotome (Ultracut E, Reichert-Jung) with a 35° Diamond knife (Diatome, Switzerland) at room temperature. TEM pictures were obtained by a TEM LEO 912 (Zeiss, Germany) at an accelerating voltage of 120 kV. The PLA samples are very unstable in the TEM. That means they move themselves and cavitation occurs by the use of the electron beam. These cavities expand and the section is destroyed. Therefore a very low current was used, which was smaller than 1  $\mu$ A.

### 2.5 Degradation studies

Degradation studies were performed on all prepared samples in phosphate buffer solution (PBS) at pH 7.4. Samples were taken out from the media at different time intervals, washed thoroughly with distilled water and dried at room temperature for 24 hours, weighed and returned to the media.

### 3. Results and discussions

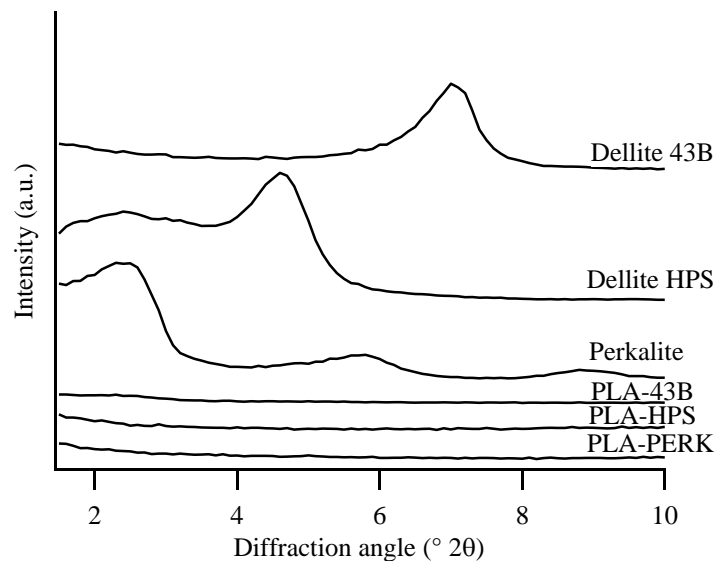


Fig.1 WAXD diffractograms for different clays and composites at lower angles

The dispersion of clay in the prepared composites was analyzed by WAXD. Peaks related to the pristine clays and of dispersed clay particles in the matrix polymer are shown in fig.1. Basal peaks were recognized at  $2\theta \sim 2.4^\circ$ ,  $4.6^\circ$  and  $7.0^\circ$  for pristine perkalite, dellite HPS and dellite 43B respectively. These basal peaks disappeared when clays were mixed within the PLA matrix; it indicates that a very good dispersion was attained in the composite. It is often reported in the literature that when the basal signal disappears, this is a sign that exfoliation occurred. Considerable attention should be exercised in taking this conclusion, though, because WAXD alone is not sufficient to prove exfoliation (Benetti et al., 2005; Causin et al., 2005; Costa et al., 2005; Vaia and Liu, 2002).

In order to correctly assess the degree of interaction between polymer and clay, WAXD and SAXS must be used complementarily. Extensive intercalation could in fact separate clay layers to such an extent to be undetectable by WAXD but that can still be determined by SAXS [(Causin, 2010) and references therein].

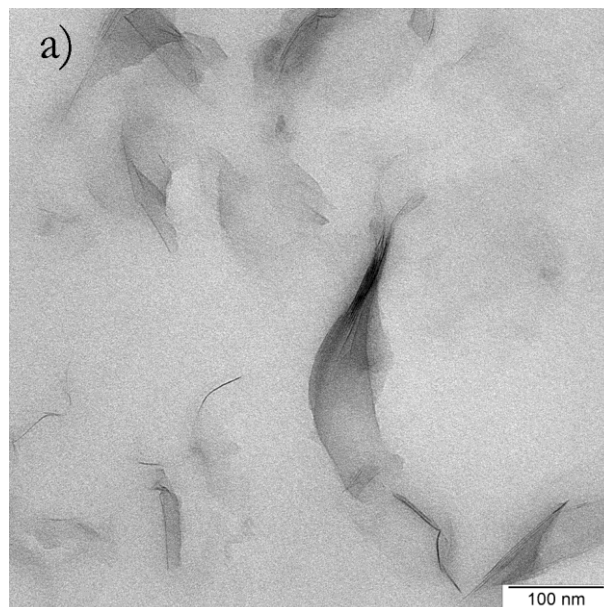
Only the disappearance of SAXS signals and Transmission Electron Microscopy (TEM) observations can confirm that exfoliation has occurred. Moreover a number of possible factors, such as the small sample size, when very low clay loadings are used, or orientation issues, could

determine the disappearance or at least a dramatical weakening of the basal signal that could be misinterpreted as exfoliation.

Very interesting comparisons of WAXD and TEM data, showed moreover that the WAXD signal can disappear even if some intercalation is present. The lack of Bragg scattering can suggest that a wide range of basal layer spacings is present within the tactoids. This variation in persistence lengths (which correspond to regions that have a constant value in the  $d$ -spacing) can result from a number of different reasons: incomplete exchange of the cations present in the pristine clay galleries with the organomodifier, uneven polymer intercalation, single clay layers organized in tactoids with large interlayer spacing and not regularly ordered, variable composition within a tactoid which affects clay surface charge, and small tactoid effects [(Causin, 2010)and references therein]. This latter situation, i.e. reduction of the size of tactoids to just two or three layers (Zhang et al., 2005), can be considered practically equivalent, as far as properties are concerned, to exfoliation (Mehta et al., 2004; Fasulo et al., 2004; Causin et al., 2006, 2008)

SAXS traces in the periodicity region typical of clay were featureless (not shown), corroborating the WAXD observation that a significant disordering of clay tactoids was achieved in the composites.

We performed TEM analysis in order to confirm the degree of dispersion of clay in our prepared composites. Figure 2, [shows](#) TEM micrographs of the composites prepared using different clays.





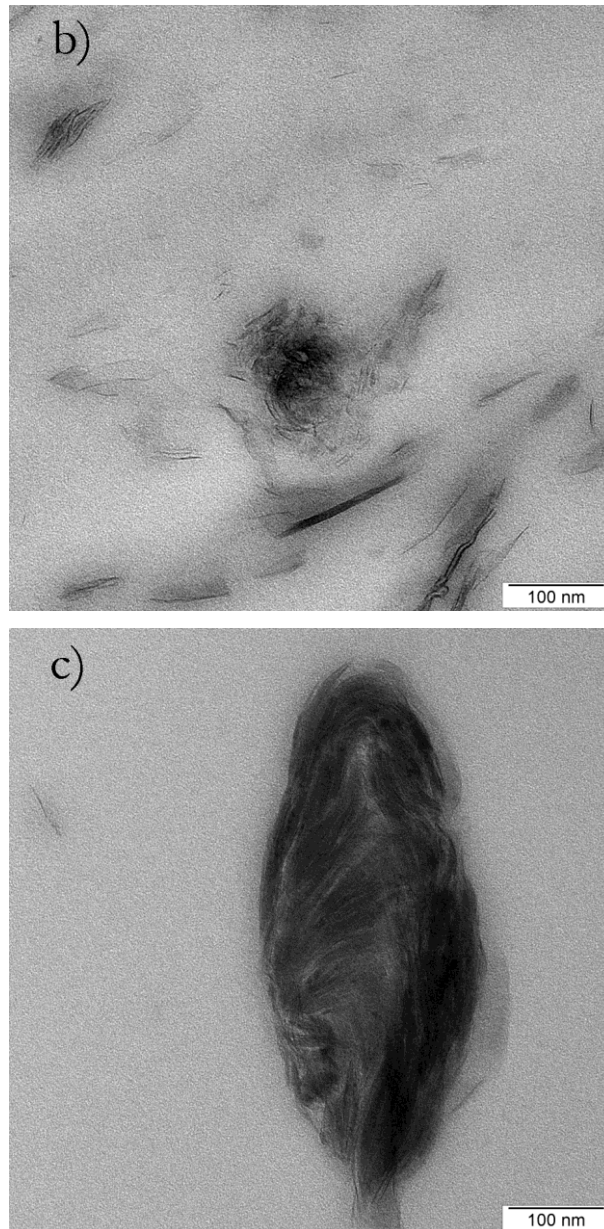


Fig.2. TEM images of PLA43B (a); PLAPERK (b); and PLAHPS (c)

It is evident from TEM micrographs that all the nanocomposites prepared show the presence of delaminated clay layers, in accord with the very weak basal signals. We also observed, though, intercalated and agglomerated structures along with the delaminated platelets, especially in PLAPERK (fig 2b) and PLAHPS (fig 2c). Hence, the absence of peaks in WAXD is not the confirmation of exfoliation or complete delamination of clay layers. The morphology of clay dispersion is rather consistent with a dispersion of small intercalated tactoids, similarly to what was reported by Jollands and Gupta (Jollands and Gupta, 2010) in similar preparation conditions, and by other authors by in-situ polymerization (Katiyar et al., 2010) and by solution mixing (Huang et al., 2010).

The WAXD patterns of the samples are those typically found for PLA (fig. 3) (Pan et al., 2008). Macroscopically no effect of any clay was observed on the structure of matrix polymer. WAXD traces were fitted to calculate the degree of crystallinity ( $\phi_{\text{WAXD}}$ ) by deconvoluting the contribution of the crystalline and amorphous domains to the diffraction pattern and corresponding results are reported in table 1. In all compositions, addition of clays brought about an increase in  $\phi_{\text{WAXD}}$ , especially in the case of the composite with perkalite.

Several authors have reported that clay brings about an increase in the degree of crystallization of PLA (Li et al., 2009; Das et al., 2010; Fukushima et al., 2011). Anionic clays appear to be more effective in increasing the fraction of crystallized polymer in the composites.

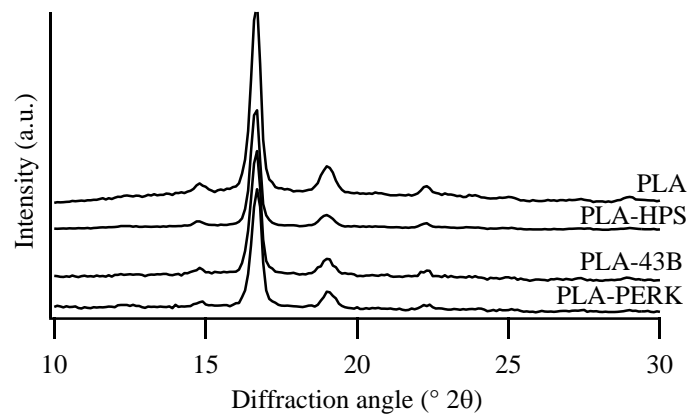


Figure 3. WAXD diffractograms of PLA and of its composites at higher angles

Table 1: Degree of crystallinity of all prepared samples measured by fitting WAXD traces

sample	Degree of crystallinity ( $\phi_{\text{WAXD}}$ ) (%)
PLA	54
PLA-HPS	72
PLA-43B	79
PLA-PERK	84

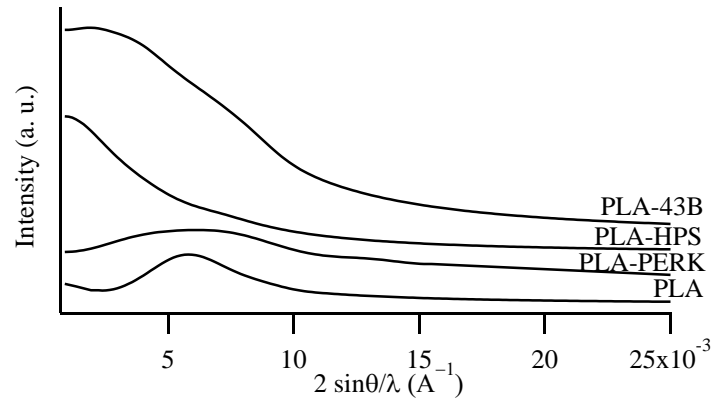


Fig. 3 Lorentz-corrected SAXS patterns of pure PLA matrix polymer and of its composites

The morphology of the polymer at lamellar level was studied by SAXS. Resulting SAXS patterns are reported in Fig. 3. In the pure matrix polymer, a sharp peak appeared, indicative of very well ordered crystalline lamellae. In the composites, on the other hand, the SAXS peaks were much less neat. The composite with perkalite retained the same long period of neat PLA, but with a significant broadening of the SAXS signal. This indicates that lamellar stacks are less homogeneous in size and morphology (Causin et al., 2008, 2009; Marega et al., 2009). In the case of the materials with cationic clays, the SAXS signal disappears. SAXS data are coherent with a disruption of the order of the lamellar stacks due to an intimate contact between matrix and filler. This is maybe because clay particles are dispersed in the matrix polymer, and thus they function like obstacles for the free motion of polymer chains when crystalline lamellae were forming. This is not surprising because it is reported that nanofillers influence the shaping of the structure at a crystalline cell level, but it has its most significant effects on polymer lamellae.(Causin et al., 2008, 2009; Marega et al., 2009; Lincoln et al., 2004; Maiti et al., 2002a; Homminga et al., 2005)

A similar, apparently conflicting behavior of clay was reported earlier (Li et al., 2009) On one hand, it increases the degree of crystallinity, i.e. the fraction of polymer which attains crystalline order in the solid state, on the other hand clay hinders the mobility of the macromolecules, favoring a less ordered semicrystalline framework.

Table 2. Isothermal crystallization kinetic studies at different temperatures

Sample	at 100°C		at 110°C		at 120°C	
	n	ln (k)	n	ln (k)	n	ln (k)
PLA	1.9	-6.1	1.9	-6.0	1.7	-2.4
PLA-HPS	1.9	-4.7	1.9	-4.2	1.7	-3.8

<b>PLA-43B</b>	1.7	-4.2	1.6	-3.9	1.6	-3.2
<b>PLA-PERK</b>	2.8	-3.4	2.0	-2.3	1.7	-4.4

Structural and morphological data are consistent with an effect of clay on the crystallization rate. The influence of clay on the crystallization of PLA is still controversial. Some authors maintain that primary nucleation happens in the bulk, not on the intercalated clay platelets and spherulites grow normally until they encounter an organoclay platelet (Li et al., 2009; Strawhecker and Manias, 2003). Other researchers, however, reported a significant nucleation activity of clay platelets (Li et al., 2009; Kontou et al., 2011; Picard et al., 2007; Jiang et al., 2011).

In order to better understand the influence of the different clays on the crystallization behavior of PLA, the crystallization kinetics was studied. Isothermal measurements at three different crystallization temperatures,  $T_c$ , (100, 110 and 120°C) were performed to establish the nucleating effect of clays on PLA matrix, and the obtained results were interpreted according to the Avrami equation (Avrami, 1941). Such data treatment allows to obtain two parameters describing the crystallization kinetics:  $\ln K$ , which is a kinetic constant, and  $n$ , which is a parameter related to the mechanism of nucleation and to the dimensionality of growth in the crystallization. It has been already reported that clay particles increase the crystallization rate and thus increase the number of spherulites formed in nanocomposites compared to pure PLA matrix. (Li et al., 2009; Ray and Okamoto, 2003; Day et al., 2006; Huang et al., 2010). Day et al (Day et al., 2006) reported that when the materials were crystallized in the temperature range from 120–130°C the crystallization rate for the composite material was approximately 15 to 20 times faster than that for the neat PLA. In our study, we observed multiple effects of clays on the crystallization behavior of PLA. At low temperatures, i.e. at 100 and 110°C,  $K$  is larger in composites compared to neat PLA, meaning that clays are showing nucleating effect on PLA matrix. On the other hand, when materials were studied at 120°C, neat PLA had larger  $K$  values than composites. This is not surprising because sometimes clays act as inhibiting agents rather than as nucleating agents. In a work by some of us (Neppalli et al., 2011), Cloisite 15A showed an inhibiting effect on PCL rather than acting as nucleating agent as it has been reported. This could be due to the subtle interplay between enhanced nucleation due to clay and the obstacle to the growth of the crystal. At low temperature, when nucleation dominates the crystallization process, clay increases the crystallization rate, whereas when the temperature increases, crystal growth gains importance, and the hindering role of clay becomes predominant.  $n$  remained approximately constant in all samples (~1.9) except in PLAPERK at 100°C, where it increased to 2.8 from 1.9 which corresponds to neat PLA. This indicates that no significant changes in the crystallization mechanism were brought about by clay except with perkalite. It is especially

interesting to note the crystallization behavior of the samples at 100 °C, which is the temperature at which they were annealed in the present work. K increases in the same order as  $\phi_{WAXD}$ , i.e. perkalite has the largest crystallinity and the fastest crystallization; on the contrary neat PLA is the least crystalline sample and crystallizes slowly. Moreover, a sharp difference in crystallization mechanism could be seen between composites, with cationic clays which have the same n of PLA, and that of PLA-PERK, in which the change in n is indicative of a change in crystallization mechanism. This difference in crystallization mechanism is reflected by SAXS data: PLA-PERK maintains a rather ordered lamellar morphology, whereas PLA-HPS and PLA-43B displayed a dramatic disordering of the lamellar stacks, which brought to featureless SAXS traces.

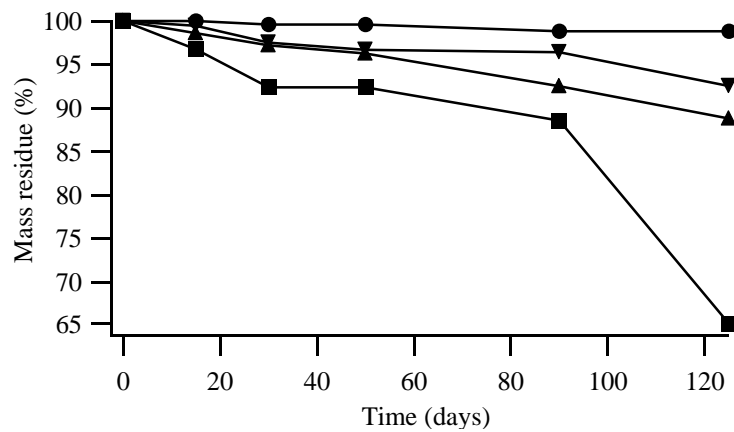


Figure 5. Mass loss of pure PLA matrix and of its composites in PBS solution. ●: PLA; ■: PLA-PERK; ▲: PLA-HPS; ▼: PLA-43B

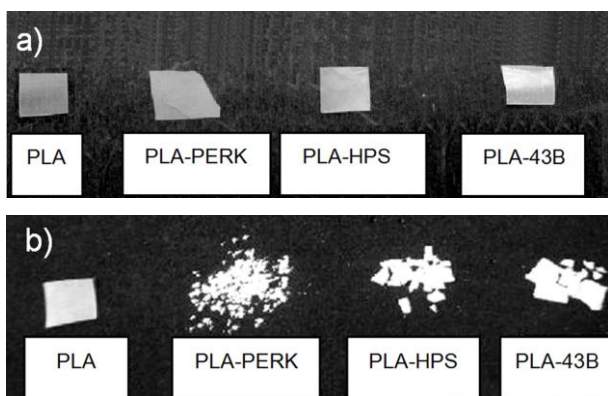


Fig.6. Samples (a) and (b) after degradation studies

Studies were performed to investigate the effect of clay on the rate of degradation (Figs. 5 and 6). Figure 5 shows the results after 125 days in PBS. PLA showed a negligible weight loss. On the other hand, the composites with cationic clays lost about 10% of their initial weight, whereas almost 40% of sample PLA-PERK degraded after 125 days in PBS. Differently from cationic clays, perkalite initiates degradation early in the first days of exposure to PBS. The composites containing Dellites started losing mass after 15 days. Armentano and coworkers (Armentano et al., 2010) recently reviewed the effect of nanofillers on the degradation of biodegradable-polymer-based nanocomposites, and highlighted the role of nanofillers in favoring the exchange of water within the composites, thereby increasing the rate of hydrolysis-based degradation mechanisms. Fukuhima and coworkers (Fukushima et al., 2011) reported that addition of modified montmorillonite and sepiolite delays the degradation of PLA because of its inducing PLA crystallization effect. On these grounds, it seems surprising that PLA-PERK, the most crystalline composite, is also the fastest-degrading sample. However, a number of reports observed that clay-containing nanocomposites had a higher degradation rate (Ray et al., 2003b; Zhou and Xanthos, 2008; Paul et al., 2005) because such samples exhibited a high volume of polymer matrix in contact with the nanoclay edges and surface, resulting in easier water attack of the polymer chains as compared to the unfilled polymer (Zhou and Xanthos, 2008). It was argued that the acceleration of degradation of clay-containing nanocomposites could be due to the presence of terminal hydroxylated edge groups on silicate layers, which favor alcoholysis reactions (Nieddu et al., 2009; Fukushima et al., 2009). The faster degradation rate of PLA-PERK is thus probably linked to the chemical nature of perkalite, which may allow a better interaction with the incoming water. The high hydrophilicity of clays has been indicated as the reason of their catalytic effect on the degradation of PLA [(Fukushima et al., 2011) and references therein]. PLA-PERK is also the composite displaying the best filler dispersion. A thorough dispersion of the filler layers within the matrix increases the barrier effect (Kontou et al., 2011; Picard et al., 2007), so slowing down the penetration of water in the material. This allows a longer contact time between polymer and water, thus favoring the hydrolysis reaction. S. S. Ray et al. (Ray et al., 2002) reported the rate of degradation of neat PLA and of its composites with montmorillonite in compost environment. They reported that addition of clay to PLA promoted the rate of degradation in compost and it took only two months of time for complete degradation of the composite in compost.

## **Conclusions**

The structure, morphology and degradation behavior of PLA-based composites filled with different kinds of clay were compared.

Even though a similar degree of dispersion could be achieved in cationic and anionic clays, these two kinds of fillers exerted different effects on the structure and morphology. The anionic perkalite clay induced higher crystallinity, a faster crystallization rate and also a modification of the crystallization mechanism. Moreover, when perkalite clay was used, the lamellar framework of PLA was preserved. These differences were reflected in the degradation behavior of the materials. This shows the potential of the addition of nanofillers for tuning the degradation rate of PLA, in order to widen the application range of this promising polymer.

## References

- Armentano, I., Dottori, M., Fortunati, E., Mattioli, S., Kenny, J.M., 2010. Biodegradable polymer matrix nanocomposites for tissue engineering: A review. *Polym. Degrad. Stab.* 95, 2126-2146.
- Avrami, M., 1941. Kinetics of phase change III. Granulation, phase change, and micro-structure. *J. Chem. Phys.* 9, 177-184 and references therein.
- Benetti, E.M., Causin, V., Marega, C., Marigo, A., Ferrara, G., Ferraro, A., Consalvi, M., Fantinel, F., 2005. Morphological and structural characterization of polypropylene based nanocomposites. *Polymer* 46, 8275-8285.
- Causin, V., 2010. Wide-angle X-ray diffraction and small-angle X-ray scattering studies of rubber nanocomposites, in: Thomas, S., Stephens, R. (Eds.), *Rubber Nanocomposites. Preparation, Properties and Applications*. Wiley, Singapore.
- Causin, V., Marega, C., Marigo, A., Ferrara, G., 2005. *Polymer* 46, 9533-9537.
- Causin, V., Marega, C., Marigo, A., Ferrara, G., Ferraro, A., Selleri, R., 2008. Structure-Property Relationships in Isotactic Poly(propylene)/Ethylene Propylene Rubber/Montmorillonite Nanocomposites. *J. Nanosci. Nanotech.* 8, 1823-1834.
- Causin, V., Marega, C., Marigo, A., Ferrara, G., Idiyatullina, G., Fantinel, F., 2006. Morphology, Structure and Properties of a Poly(1-butene)/Montmorillonite Nanocomposite. *Polymer* 47, 4773-4780.
- Causin, V., Yang, B.X., Marega, C., Goh, S.H., Marigo, A., 2009. Nucleation, structure and lamellar morphology of isotactic polypropylene filled with polypropylene-grafted multiwalled carbon nanotubes. *Eur. Polym. J.* 45, 2155-2163.
- Causin, V., Carraro, M.L., Marega, C., Saini, R., Campestrini, S., Marigo, A., 2008. Structure and morphology of solution blended poly(vinylidene fluoride)/montmorillonite nanocomposites. *J Appl Polym Sci* 109, 2354-2361.

Costa, F.R., Abdel-Goad, M., Wagenknecht, U., Heinrich, G., 2005. Nanocomposites based on polyethylene and Mg-Al layered double hydroxide. I. Synthesis and characterization. *Polymer* 46, 4447-4453.

Dagnon, K.L., Ambadapadi, S., Shaito, A., Ogbomo, S.M., DeLeon, V., Golden, T.D., Rahimi, M., Nguyen, K., Braterman, P.S., D'Souza, N.A., 2009. Poly(L-lactic acid) Nanocomposites with Layered Double Hydroxides Functionalized with Ibuprofen. *Journal of Applied Polymer Science* 113, 1905.

Das, K., Ray, D., Banerjee, I., Bandyopadhyay, N.R., Sengupta, S., Mohanty, A.K., Misra, M., 2010. Crystalline Morphology of PLA/Clay Nanocomposite Films and Its Correlation with Other Properties. *J. Appl. Polym. Sci.* 118, 143-151.

Day, M., Nawaby, A.V., Liao, X., 2006. A DSC study of the crystallization behaviour of polylactic acid and its nanocomposites. *J. Therm. Anal. Calorimetry* 86, 623-629.

Fasulo, P.D., Rodgers, W.R., Ottaviani, R.A., Hunter, D.L., 2004. Extrusion processing of TPO nanocomposites. *Polym. Eng. Sci.* 44, 1036-1045.

Feijoo, J.L., Cabedo, L., Gimenez, E., Lagaron, J.M., Saura, J.J., 2005. Development of amorphous PLA-montmorillonite nanocomposites. *J Mater Sci* 40, 1785-1788.

Fukushima, K., Abbate, C., Tabuani, D., Gennari, M., Camino, G., 2009. Biodegradation of poly(lactic acid) and its nanocomposites. *Polym. Degrad. Stab.* 94, 1646-1655.

Fukushima, K., Tabuani, D., Dottori, M., Armentano, I., Kenny, J.M., Camino, G., 2011. Effect of temperature and nanoparticle type on hydrolytic degradation of poly(lactic acid) nanocomposites. *Polym. Degrad. Stability* 96, 2120-2129.

Hasook, A., Tanoue, S., Iemoto, Y., Unryu, T., 2006. Characterization and mechanical properties of poly(lactic acid)/poly(epsilon-caprolactone)/organoclay nanocomposites prepared by melt compounding. *Polym. Eng. Sci.* 46, 1001-1007.

Hindeleh, A.M., Johnson, D.J., 1971. The resolution of multipeak data in fiber science. *J. Phys. D: Appl. Phys.* 4, 259-263.

Homminga, D., Goderis, B., Dolbnya, I., Reynaers, H., Groeninckx, G., 2005. Crystallization behavior of polymer/montmorillonite nanocomposites. Part I. Intercalated poly(ethylene oxide). *Polymer* 46, 11359-11365.

Huang, S.M., Hwang, J.J., Liu, H.J., Lin, L.H., 2010. Crystallization Behavior of Poly(L-lactic acid)/Montmorillonite Nanocomposites. *J. Appl. Polym. Sci.* 117, 434-442.

Jiang, G., Huang, H.X., Chen, Z.K., 2011. Microstructure and thermal behavior of polylactide/clay nanocomposites melt compounded under supercritical CO<sub>2</sub>. *Adv. Polym. Tech.* 30, 174-182.



Jollands, M., Gupta, R.K., 2010. Effect of Mixing Conditions on Mechanical Properties of Polylactide/Montmorillonite Clay Nanocomposites. *J. Appl. Polym. Sci.* 118, 1489-1493.

Katiyar, V., Gerds, N., Koch, C.B., Risbo, J., Hansen, H.C.B., Plackett, D., 2010. Poly L-lactide-layered double hydroxide nanocomposites via in situ polymerization of L-lactide. *Polym. Degrad. Stability* 95, 2563-2573.

Kohjiya, S., Tosaka, M., Furutani, M., Ikeda, Y., Toki, S., Hsiao, B.S., 2007. Role of stearic acid in the strain-induced crystallization of crosslinked natural rubber and synthetic cis-1,4-polyisoprene. *Polymer* 48, 3801-3808.

Kontou, E., Niaounakis, M., Georgiopoulos, P., 2011. Comparative Study of PLA Nanocomposites Reinforced with Clay and Silica Nanofillers and Their Mixtures. *Journal of Applied Polymer Science* 122, 1519.

Leroux, F., Taviot-Gueho, C., 2005. Fine tuning between organic and inorganic host structure: new trends in layered double hydroxide hybrid assemblies. *J. Mater. Chem.* 15, 3628-3642.

Li, X., Yin, J., Yu, Z., Yan, S., Lu, X., Wang, Y., Cao, B., Chen, X., 2009. Isothermal Crystallization Behavior of Poly(L-lactic acid)/Organo-Montmorillonite Nanocomposites. *Polym. Compos.* 30, 1338-1344.

Lincoln, D.M., Vaia, R.A., Krishnamoorti, R., 2004. Isothermal crystallization of nylon-6/montmorillonite nanocomposites. *Macromolecules* 37, 4554-4561.

Maiti, P., Nam, P.H., Okamoto, M., Hasegawa, N., Usuki, A., 2002a. Influence of crystallization on intercalation, morphology, and mechanical properties of polypropylene/clay nanocomposites. *Macromolecules* 35, 2042-2049.

Maiti, P., Yamada, K., Okamoto, M., Ueda, K., Okamoto, K., 2002b. New Polylactide/Layered Silicate Nanocomposites: Role of Organoclays. *Chem. Mater.* 14, 4654-4661.

Marega, C., Causin, V., Marigo, A., Ferrara, G., Tonnaer, H., 2009. Perkalite as an Innovative Filler or Isotactic Polypropylene-Based Nanocomposites. *Journal of Nanoscience and Nanotechnology* 9, 2704-2714.

Mehta, S., Mirabella, F.M., Rufener, K., Bafna, A., 2004. Thermoplastic Olefin/Clay Nanocomposites: Morphology and Mechanical Properties. *J. Appl. Polym. Sci.* 92, 928-936.

Neppalli, R., Causin, V., Marega, C., Saini, R., Mba, M., Marigo, A., 2011. Structure, Morphology, and Biodegradability of Poly( $\epsilon$ -caprolactone)-Based Nanocomposites. *Polym. Eng. Sci.* 51, 1489-1496.

Nieddu, E., Mazzucco, L., Gentile, P., Benko, T., Balbo, V., Mandrile, R., Ciardelli, G., 2009. Preparation and biodegradation of clay composites of PLA. *Reac. Funct. Polymers* 69, 371-379.

Ogata, N., Jimenez, G., Kawai, H., Ogihara, T., 1997. Structure and thermal/mechanical properties of poly (l-lactide)-clay blend. *J. Polym. Sci. Phys.* 35, 389-396.

Pan, P., Zhu, B., Dong, T., Inoue, Y., 2008. Poly(L-Lactide)/Layered Double Hydroxides Nanocomposites: Preparation and Crystallization Behavior. *J. Polym. Sci. Phys.* 46, 2222-2233.

Paul, M.A., Delcourt, C., Alexandre, M., Degee, P., Monteverde, F., Dubois, P., 2005. Polylactide/montmorillonite nanocomposites: study of the hydrolytic degradation. *Polym. Degrad. Stab.* 87, 535-542.

Picard, E., Gauthier, H., Gerard, J.F., Espuche, E., 2007. Influence of the intercalated cations on the surface energy of montmorillonites: Consequences for the morphology and gas barrier properties of polyethylene. *J. Colloid Interface Sci.* 307, 364-376.

Ray, S.S., Okamoto, M., 2003. Biodegradable Polylactide and Its Nanocomposites: Opening a New Dimension for Plastics and Composites. *Macromol. Rapid Commun.* 24, 815-840.

Ray, S.S., Ramontjia, J., 2009. Polylactide-based nanocomposites, in: Yu, L. (Ed.), *Biodegradable Polymers Blends and Composites from Renewable Resources*. Wiley, Hoboken, NJ, pp. 389-414.

Ray, S.S., Yamada, K., Okamoto, M., Ueda, K., 2003a. New polylactide-layered silicate nanocomposites. 2. Concurrent improvements of material properties, biodegradability and melt rheology. *Polymer* 44, 857-866.

Ray, S.S., Yamada, K., Okamoto, M., Ueda, K., 2003b. Control of biodegradability of polylactide via nanocomposite technology. *Macromol. Mater. Eng.* 288, 203-208.

Ray, S.S., Yamada, K., Okamoto, M., Ueda, K., 2002. Polylactide-Layered Silicate Nanocomposite: A Novel Biodegradable Material. *Nano Lett.* 2, 1093-1096.

Strawhecker, K.E., Manias, E., 2003. Crystallization behavior of poly(ethylene oxide) in the presence of Na<sup>+</sup> montmorillonite fillers. *Chem. Mater.* 15, 844-849.

Tabatabaei, S.H., Ajji, A., 2011. Orientation, mechanical and optical properties of poly(lactic acid) nanoclay composite films. *Polym Eng Sci* 51, 2151-2158.

Tsuji, H., Suzuyoshi, K., 2002. Environmental degradation of biodegradable polyesters 1. Poly(epsilon-caprolactone), poly[(R)-3-hydroxybutyrate], and poly(L-lactide) films in controlled static seawater. *Polym. Degrad. Stab.* 75, 347-355.

Urayama, H., Kanamori, T., Kimura, Y., 2002. Properties and Biodegradability of Polymer Blends of Poly(L-lactide)s with Different Optical Purity of the Lactate Units. *Macromol. Mater. Eng.* 287, 116-121.

Vaia, R.A., Liu, W., 2002. X-ray powder diffraction of polymer/layered silicate nanocomposites: Model and practice. *J. Polym. Sci. Polym. Phys.* 40, 1590-1600.

Zhang, Z., Zhang, L., Li, Y., Xu, H., 2005. New fabricate of styrene-butadiene rubber/montmorillonite nanocomposites by anionic polymerization. *Polymer* 46, 129-136.

Zhou, Q., Xanthos, M., 2008. Nanoclay and crystallinity effects on the hydrolytic degradation of polylactides. *Polym. Degrad. Stab.* 93, 1450-1459.