Hydrolysis and biodegradation of poly(lactic acid)

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Abstract   In this work, a review is presented concerning hydrolytic degradation and biodegradation of Poly(lactic acid) (PLA). Hydrolytic degradation, that induces morphological and compositional changes, is considered the most important step in determining the bio-degradation. The main factors influencing the hydrolytic degradation, such for instance temperature, pH, sample morphology, molecular weight, are considered and analyzed. An overview on the biodegradation in composting conditions is also reported. Finally, the chapter analyses also the possibilities of modulating degradation and biodegradation rates in function of the expected lifetime of the objects made in PLA. This can be considered a frontier of research in this field.

Keywords   PLA, hydrolysis, biodegradation, modeling, composting

Contents

Nomenclature

K_{BB}	Kinetic constant of the backbiting mechanism
K_D^α	Kinetic constant of the terminal hydrolysis
K_D^β	Kinetic constant of the backbone hydrolysis
K_{RH}	Kinetic constant of the random hydrolysis
K_w	Kinetic constant of the non-catalyzed hydrolysis
$\%C_{mat}$	Percentage organic carbon content of the sample
C_A	Concentration of water
C_A^*	Concentration of water in reference conditions
C_{A0}	Initial concentration of water inside the sample
C_C	Concentration of carboxylic end-groups
C_E	Concentration of ester groups
C_{E0}	Initial concentration of ester groups
C_{H+}	Concentration of positive ions
C_n	Concentration of chains having n monomeric units
C_{OH-}	Concentration of negative ions
C_{ol}	Concentration of oligomers
D_A	Effective diffusivity of wter inside the sample
D_{ol}	Effective diffusivity of the oligomers inside the sample
DP	Average degree of polymerization
E_C	Constant in Arrhenius equation describing the effect of temperature on water sorption
E_D	Constant in Arrhenius equation describing the effect of temperature on water diffusivity
E_R	Constant in Arrhenius equation describing the effect of temperature on hydrolysis
gCO_2	Grams of evolved carbon dioxide in the sample and the positive control
$gCO_{2,b}$	Grams of evolved carbon dioxide in the blank
g_{mat}	Mass of the sample in grams
j_M	Mass flux of the oligomers leaving the sample the surface, as a result of hydrolysis
K_a	Acid dissociation constant
K_R	Kinetic constant of hydrolysis from experimental data
K_R	Kinetic constant of hydrolysis
K_t	Kinetic constant of thermal degradation

M	Molecular weight of the repeating unit
Ma	Mass of amorphous phase inside the sample
Mc	Mass of crystalline phase inside the sample
M_n	Number average molecular weight
Mo	Initial mass of the sample
Mt	Total mass of the sample
M_W	Weight average molecular weight
r_m	Mass of polymer metabolized by the microorganisms per unit time and per unit sample surface
R_{ol}	Number of oligomers produced per unit volume
R_S	Scissions of polymeric chains per unit volume
S	Sample surface
Tg	Glass transition temperature
$Tref$	Reference temperature
Xc	Absolute crystallinity degree
z	Polydispersity
δ	Characteristic dimension of the sample in the thickness direction
η	Viscosity
ϱ	Density of the sample

Introduction

In recent years, research activity on biodegradable polymers gained great interest because of their increasingly applications in biomedical, packaging, environmental and agricultural applications [1]. Undoubtedly biodegradable polyesters play a key role in the category of biodegradable polymers. The highly hydrolyzable ester bonds make this class of polymers highly subject to degradation in humid environments, which is favorable for biodegradation mechanisms. The knowledge of the hydrolytic degradation of PLA is essential for the plastics industry, in order to meet the current environmental issues and regulations. Furthermore, the control of its hydrolytic degradation and biodegradation is fundamental for medical applications. Hydrolysis of PLA has been reported to proceed either at the surface or within the bulk and it is determined by several variables, i.e. chemical composition, stereochemistry, sequence distribution, molecular weight and molecular weight distribution, sample morphology, chain orientation, the presence of residual monomers and the environmental degradation conditions. Most of the studies on PLA degradation are related to the abiotic hydrolysis [2,3] and have found that, very often an uncontrolled hydrolytic degradation rate of PLA matrix limits its applications [4]. Numerous hydrolytic degradation tests have been performed on PLA to simulate its degradation process in the human body (T $\cong$ 37°C) [5-11] and in natural media as soil or compost (25°C < T < 58°C)[12-15], all reporting that PLA can be hydrolyzed to give water soluble oligomers. Most of the studies report that the hydrolytic degradation of PLA takes place mainly in the bulk of the material rather than on the surface, and it is quite generally accepted that it follows an autocatalytic hydrolysis [16-18]. The formation of lactic acid oligomers, which follows the chain scission, increases the concentration of the carboxylic acid end groups in the degradation medium, making the hydrolytic degradation of PLA a self-catalyzed and self-maintaining process thanks to the catalytic action of these end groups. At the same time, the structural and morphological organization of PLA has been demonstrated to strongly affect its hydrolytic degradation mechanism. It has been found that the hydrolytic chain cleavage proceeds preferentially in the amorphous regions, leading to the increase in polymer crystallin-

ity [19]. The rate of the degradation reaction is also affected by the structure of the macromolecules and the shape of the specimen, as well as by the conditions under which the hydrolysis is performed, including pH and temperature [20]. The chemical hydrolysis reduces the molecular weight of the PLA, and only subsequently the micro-organisms can utilize the lactic acid oligomers as an energy source [21,22]. The analysis of the hydrolysis mechanisms is, thus, of fundamental importance, because it occurs before any biotic attack. The end result of the whole process is a quantitative release of CO_2 back into the atmosphere. The aerobic degradation is known to be strictly temperature dependent [23], with essentially complete biodegradation in around 3-4 months at 55-60°C, and a marginal degradation at mesophilic temperatures (20-45 °C).

In this chapter we draw an outline of the current knowledge about degradation and biodegradation of PLA, underlining the effects of the main variables affecting these processes.

Degradation in the molten state: a processing concern

One of the main drawbacks of PLA is its tendency to undergo degradation during processing from the molten state. This is the first issue that the users of PLA have to face. This phenomenon is extremely accelerated if the material is not correctly dried. As an example, in **Fig. 1** and **Fig. 2** we report the pressure evolutions measured along the flow-path during injection molding of a PLLA grade (Natureworks 2002D). In particular, **Fig. 1** refers to the material accurately dried as suggested by the supplier. The pressure drops between transducer positions are quite high, and the material does not reach the tip of the cavity, resulting in an incomplete part. The molded sample (shown on the right in **Fig. 1**) results to be transparent, and without any visible sign of thermal degradation.
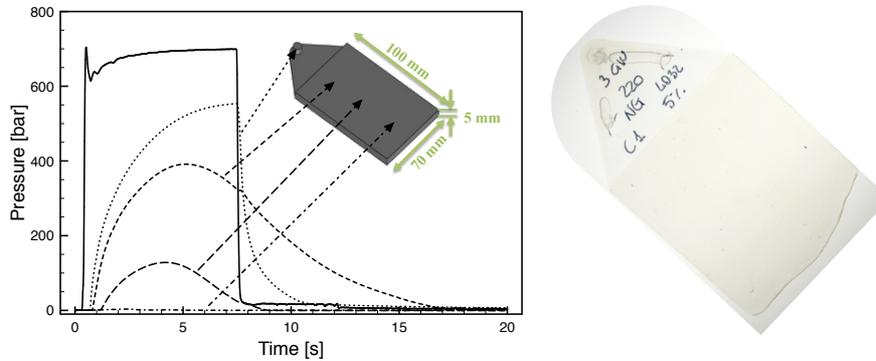
Fig. 1 Pressure curves measured during injection molding of a PLLA grade (Natureworks 2002D), previously dried overnight under vacuum at 60°C. A picture of the obtained sample is reported on the right side of the figure: the sample results clear and transparent, although not complete due to the excessive viscosity

Vice versa, **Fig. 2** refers to the same material injected without any drying. The advantages in terms of fluidity are evident: the pressure drops are much lower, and a significant pressure is recorded at the tip of the cavity. In this case the part is complete. However, visible evidence of degradation is present in the sample in the form of dark halos, as clear from the picture reported in the same figure.
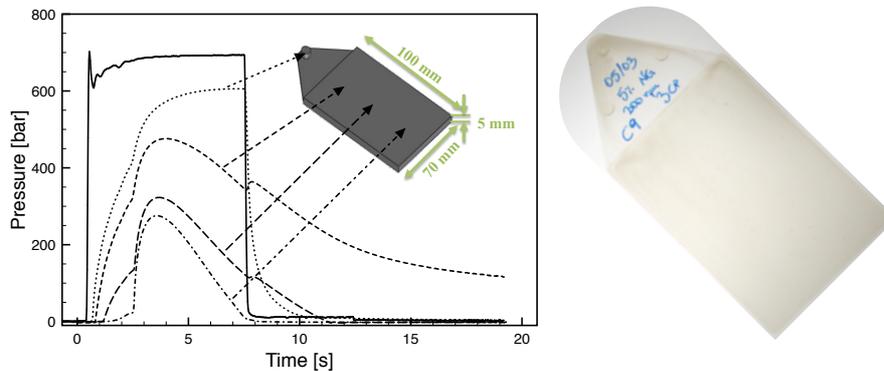
Fig. 2 Pressure curves measured during injection molding of a PLLA grade (Natureworks 2002D), injection molded without any drying step (i.e. in equilibrium with environmental moisture). A picture of the obtained sample is reported on the right side of the figure: the sample clearly present signs of degradation, although being complete.

Carrasco et. al [24] reported similar degradation signs in PLLA samples of the same grade subjected to consecutive extrusion and injection molding steps. They stressed the fact that, as a consequence of processing, the melt flow index increases (namely the viscosity decreases), the molecular weight drops and the polydispersity index rises.

An analysis of the effects of several processing variables on the degradation of a PLLA (a grade supplied by Neste Oy, Finland) was carried out by Taubner and Shishoo [25]. It was evidenced that an increase of temperature, residence time in the screw and relative humidity induce a faster decrease of molecular weight. The presence of humidity, above all, was found to be a critical factor.

In **Fig. 3** we report original data collected on a PLLA (4032D Natureworks) during compounding in a micro-compounder (Haake Minilab II, Thermo Scientific, Germany – twin screws, counter rotating), at different temperatures, screw velocity and water contents. The dried samples were dried overnight under vacuum at 60°C, the undried samples were processed without any drying step, namely with a water content in equilibrium with environment. The adopted micro-compounder is able to estimate the viscosity of the material during compounding [26].
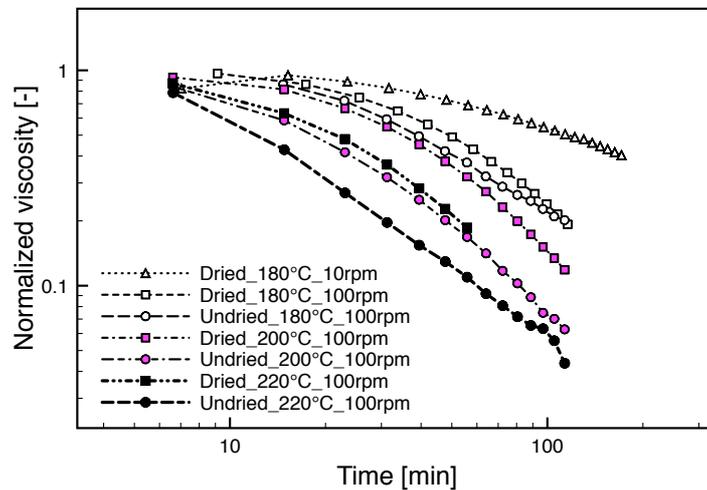
Fig. 3 Evolution of normalized viscosity (with respect to the maximum measured value) during time in a micro-compounder (Haake Minilab II, Thermo Scientific, Germany – twin screws, counter rotating), at different temperatures, screw velocity and water contents.

On increasing temperature, the reduction of viscosity is faster. Also a larger mechanical work (applied to the polymer by increasing the screw rotation speed) has the same effect of increasing the viscosity drop. Finally, the presence of water surely enhances the phenomenon, since for the same conditions the undried samples present a much faster viscosity decrease.

Similar results concerning the effect of temperature, mechanical work and water content are also reported in the literature [27,28]. As a result of literature studies, it can be summarized that processing temperatures lower than 180°C, coupled with a drying step according to the producer's indications can surely minimize the effects of degradation during times consistent with a melt processing step.

Concerning the effect of processing on other properties it is reported [29] that on increasing the residence time in the barrel, the modulus of PLLA (3051D by Natureworks) increases and the tensile strength decreases. An increase of shear rate and of nozzle temperature also induces similar effects, though to a less extent. The degradation in the molten state also causes changes in the crystallization kinetics. Some literature values [30] of the crystallization half time are reported in **Fig. 4** for virgin, extruded and injected material as a function of temperature. It is evident that the processing induces a faster crystallization kinetics, as a consequence of degradations which results in more mobile chains.
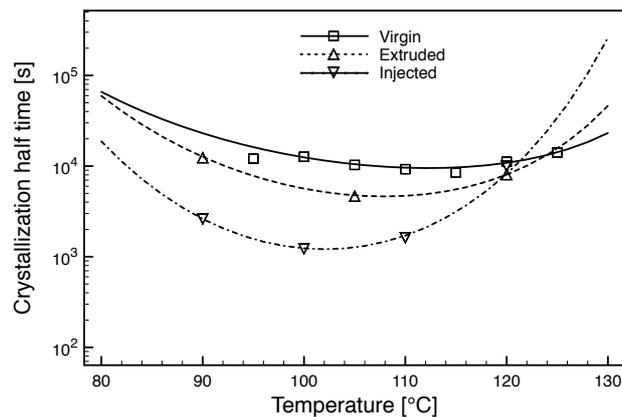
Fig. 4 Crystallization half times as a function of temperature for virgin PLLA Natureworks 2002D and for the same material after extrusion or injection molding (adapted from ref. [30])

The physical reasons of the degradation reported above are the combined effect of hydrolysis and thermal degradation. When exposed to moisture the ester groups of the main chain of PLA are cleaved, and this results in a decrease of molecular weight and the release of oligomers and monomers. This phenomenon will be more deeply described in the following section "Modeling hydrolytic degradation". Thermal degradation is due to chain scission and inter and/or intra trans-esterification reactions [31]. It is strongly influenced by the presence of impurities (mainly residual metals, which can catalyze the depolymerization of PLA to form lactide) [32].

Some stabilizers have been tested in the literature to reduce the process-induced degradation. Benzoyl peroxide was found to stabilize the polymer against thermal degradation by deactivating the catalyst residues for PLLA prepared by ring-opening polymerization in the melt using stannous octoate as catalyst [33]. An antioxidant (B900 - tris(2,4-di -tert-butylphenyl)phosphite) was also found to be able to minimize the PLLA degradation during consecutive processing cycles, preventing chain scission [34]. The incorporation of a chain extension/branching agent (Joncryl ADR-4368), by reaction extrusion, also showed an improvement of thermal stability [35].

Hydrolytic degradation of PLA

The most critical issue in the application of PLA and of biomaterials based on this polymer is the control of in vitro and in vivo degradation, both of which occur in presence of water [1-3,36-38]

As widely reported, the hydrolytic degradation of PLA typically occurs in stages:

1. diffusion of water into the material;
2. hydrolysis of the chains in the amorphous region, because of the lower resistance to water attack;
3. diminution of molecular weight due to the hydrolytic cleavage of ester bonds and formation of water-soluble compounds;
4. hydrolysis of the lamellae of the crystalline phase, which can occur through an autocatalytic mechanism by the acidic deg-

radation products as well as by the increasing concentration of carboxylic acid at chain end [39-43]

In the following, the effect of several main parameters on the evolution of hydrolytic degradation is reported.

Temperature

It has been widely demonstrated that the temperature can accelerate the hydrolytic degradation of PLA. In **Fig. 5** we report some data of degradation kinetics as collected from different literature papers. In order to compare the results, we took the slope of the linear (namely initial) part of the plots reporting the reciprocal of the number average molecular weight ($1/M_n$) versus time. The results obtained were then divided by the initial water concentration, C_{A0}, which, if not given in the original reference, was assumed to be 700mol/m^3, which is a reasonable estimate for samples immersed in water in the temperature range from 37°C to 90°C [44].

The kinetic constant of hydrolysis was then assumed to be

$$K_R = \frac{1}{C_{A0}} \frac{d}{dt}\left(\frac{1}{M_n}\right) \qquad 1$$

It can be noticed from **Fig. 5** that the data collected in the molten state [45], when extrapolated to lower temperature assuming an Arrhenius-like dependence,

$$K_R(T) = K_R(T_{ref})e^{-E_R\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)} \qquad 2$$

are consistent with the data collected at temperatures equal or higher to Tg (about 60°C for PLA). The value of E_R is about 10000K. If temperatures lower than Tg are considered, kinetics become much slower, about two order of magnitude on the adopted scale at 37°C.
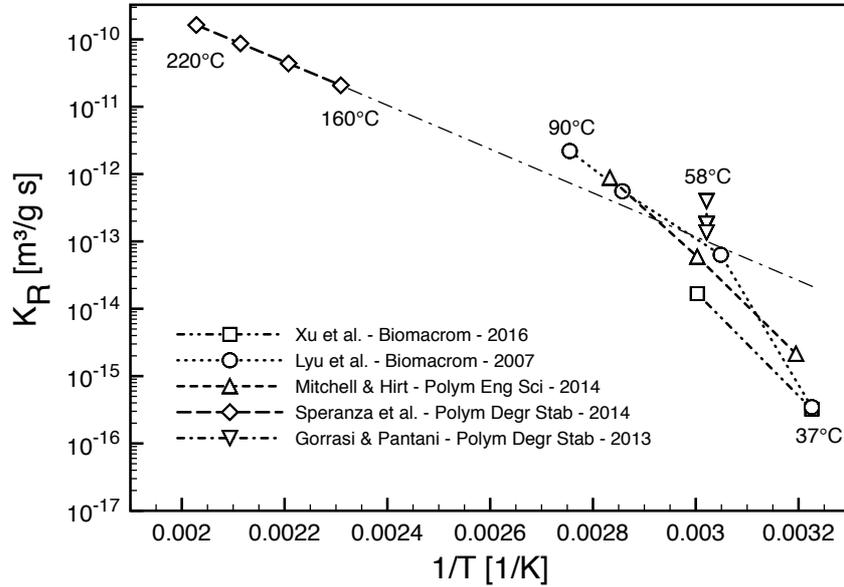
Fig. 5 Data of kinetics of hydrolysis at different temperatures as collected from literature [45-48,15]

This change of slope at temperatures lower than Tg has been noticed also on other systems: for instance [49] the activation energies for the degradation reaction in 50 : 50 poly(lactic-co-glycolic acid) (PLGA) copolymers at temperatures below and above Tg were different and suggested that tests performed at T>Tg can not be used to predict the polymer degradation trend at T<Tg; also on systems PLA/PGA in neutral conditions the hydrolytic degradation rate dramatically increased when the degradation temperature was over Tg [50]. This is the main reason why at mesophilic temperatures, marginal degradation of PLA is observed [51].

pH

pH has a very strong impact on the PLA degradation, because it acts both on the reaction mechanism and on the reaction kinetics. In the frame of biomedical applications, the understanding of the kinetics dependence upon pH is of crucial importance considering im-

plants or drug release, as in the human body the pH values can range from strongly acidic (in the stomach the pH is about 1-2) [52] to almost neutral (in the blood pH = 7.4) [53]. Therefore, according to the environment where degradation takes place, degradation and subsequent release from the same device might occur at largely different rates. Generally, for polyester degradation, it was reported that the reaction occurs by hydrolytic degradation of the ester groups followed by different paths: acid-catalyzed, base-catalyzed and non-catalyzed [54-56]. In the specific case of PLA, two main mechanisms were reported depending on the nature of the medium. In acidic media, the hydrolysis of the ester bonds catalyzed by protons is predominant. In particular, in the case of the degradation of PLA oligomers, it was found that the overall kinetic constant is chain length dependent up to oligomer with chain length equal to about seven. This dependence was found to be related to the different reactivity of the ester bonds: a distinction between the reactivity of the terminal and backbone ester groups showed that terminal esters degrade faster compared to the back-bone ones according to the preferential chain end scission mechanism [57,58]. It is often reported that the hydrolysis mechanism at acidic pH proceeds via chain-end scission [59,58]. In this case, the cleavage of terminal esters induces a faster weight loss, due to the production of soluble low molecular weight oligomers. Vice versa, the cleavage of back-bone esters causes a faster drop in the properties of the polymer. A preferential backbiting mechanism leading to the formation of lactide, the cyclic dimer of lactic acid, was also observed at higher pH [60]. The reaction was found to be chain length independent, and occurring through the terminal -OH group. Only a few papers quantify the impact of pH on the lactic acid degradation [61], by measuring the rate constants at specific pH values (i.e. pH = 2 [62] and pH = 7.2 [60]). In **Fig. 6** we report some literature data [59] of degradation kinetics constants collected at 37°C and at different pH on lactic acid oligomer with a DP = 7. It is clear that on increasing pH values from 1 to 10 the values of the observed constants first decrease, reach a minimum at pH of about 4 and then increase for higher pH values. The increase is extremely significant (about 4 orders of magnitude).
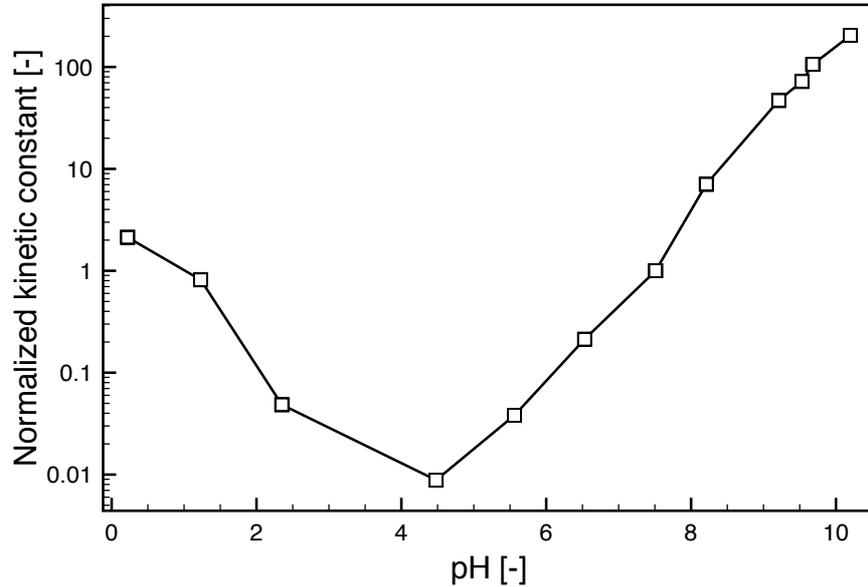
Fig. 6 data of first order degradation kinetic constant (normalized with respect to the value measured at pH = 7.5) for lactic acid oligomer with a DP = 7 (adapted from ref. [59])

The presence of a minimum in the degradation kinetic constant at intermediate pH was evidenced also by Jung et al. [61], and confirms that hydrolysis is either acid- or base- catalyzed. The specific mechanism in the presence of low or high pH values is commented in the following section "More detailed approaches to hydrolytic degradation".

Molecular weight

Molecular weight is one of the most crucial factors for the hydrolytic degradation rate of PLA-based materials. The effect of different molecular weights of PLLA species on hydrolytic degradation was evaluated in neutral conditions [63,64]. It was found that in the range of M_n from $8 \cdot 10^4$ to $4 \cdot 10^5$ g/mol the effect of molecular weight on the degradation rate of PLLA was not significant, observing similar decreases in the M_n of PLLA matrix against degradation time. However, at M_n values lower than $4 \cdot 10^4$ g/mol the hydrolytic degra-

dation resulted considerably accelerated by decreasing molecular weight. This last phenomenon was explained considering that at low molecular weight values higher molecular mobility, higher density of hydroxyl groups and hydrophilic terminal carboxyl- and higher probability of formation of water-soluble oligomers and monomers could take place, thus increasing the water diffusion rate and content, and catalyzing PLLA degradation [63].

Crystallinity

As reported above, the crystalline regions of PLA are hydrolysis-resistant compared to those in the amorphous regions because the access of water molecules to chains inside the rigid crystalline regions is highly restricted. This causes predominantly or selective hydrolytic cleavage of chains in the amorphous regions and removal of hydrolysis-formed water-soluble oligomers and monomers, with only some residual crystalline regions [65]. Considerably higher degradation in the sample weight of fully amorphous PLA as compared to those reported in the literature for semicrystalline PLA under similar conditions of hydrolytic degradation (phosphate-buffered solution pH = 4.0 at 37°C) was observed [66]. It was reported that after 18 weeks, amorphous PLLA presented a weight decrease by about 14% with respect to its initial mass, whereas other observed similar weight losses for a semicrystalline PLA by hydrolysis in phosphate buffered saline with pH = 3.4 at 37°C, but only after 20 months [67,68]. These results indicate that the hydrolysis level obtained for the amorphous PLLA matrix is reasonably high and attributed to the easier hydrolytic attack of ester bonds in amorphous polymer matrices as compared to crystalline polymers. An increase in polymer crystallinity should generally decrease polymer degradation rates, as extensively reported for PLA matrices under alkaline hydrolytic degradation conditions [69]. Other papers [18,70] reported an accelerated hydrolysis in neutral media with increasing polymer crystallinity for PLLA [11,71] and PLLA/PDLA blends [72]. Such behavior was justified by the fact that, upon crystallization of PLLA, hydrophilic terminal groups (-COOH and -OH) can be included in the amorphous area between the crystalline regions (in fig.

12 of ref. [71] a scheme is provided). The high density of the hydrophilic terminal groups can cause loosening of chain packing in the amorphous area between the crystalline regions, compared to the chain packing in completely amorphous regions, enhancing the diffusion of water molecules into the bulk material.

The high level of absorbed water and the catalytic effect by the high density of carboxylic groups can subsequently accelerate the hydrolytic degradation of crystallized PLLA samples. Moreover, the terminal groups are sites for the formation of lactoyl-lactic acid and lactic acid, which could catalyze the hydrolytic degradation of the polymer.

During the hydrolysis, an initial increase of crystallinity degree is observed, sometimes followed by a decrease. The increase of crystallinity can be ascribed to two main reasons: the preferred degradation of amorphous phase and the generation of new crystalline entities transformed from the amorphous chains. This last phenomenon is probably accelerated by neighboring water molecules, oligomers or monomers that can facilitate the chain mobility [73,74].

Gorrasi and Pantani [15] proposed a method to analyze the crystallinity evolution during hydrolytic degradation. They started from assuming that crystallinity degree can increase by effect of two possible phenomena: crystallization of the amorphous parts and erosion of the amorphous parts.

The crystallinity degree, Xc, was defined as

$$Xc = \frac{Mc}{Mt} = \frac{Mc}{Mc + Ma} \qquad 3$$

where Mt is the mass of the sample, Ma and Mc are the masses of the amorphous and crystalline parts, respectively.

Assuming that Mc does not change during time (namely that no crystallization or hydrolysis of crystal portions occur), the time derivative of eq. 3 results in

$$\frac{dln(Xc)}{dt} = \frac{dln\left(\frac{Mo}{Mt}\right)}{dt} \qquad 4$$

in which Mo is the initial mass of the sample. Eq. 4 states that, if the mass of the crystal inside the sample does not change with time (namely if the crystallinity degree increases just by effect of the erosion of the amorphous portions) a plot reporting the logarithm of the crystallinity degree versus the logarithm of the reciprocal of the ratio

Mo/Mt would present a slope equal to 1. A larger slope would indicate that the crystallinity degree increases also by effect of the crystallization of the amorphous parts; a smaller slope would mean that also crystalline portions are eroded. The results obtained with several PLA grades hydrolyzed in water at 58°C are summarized in **Fig. 7**
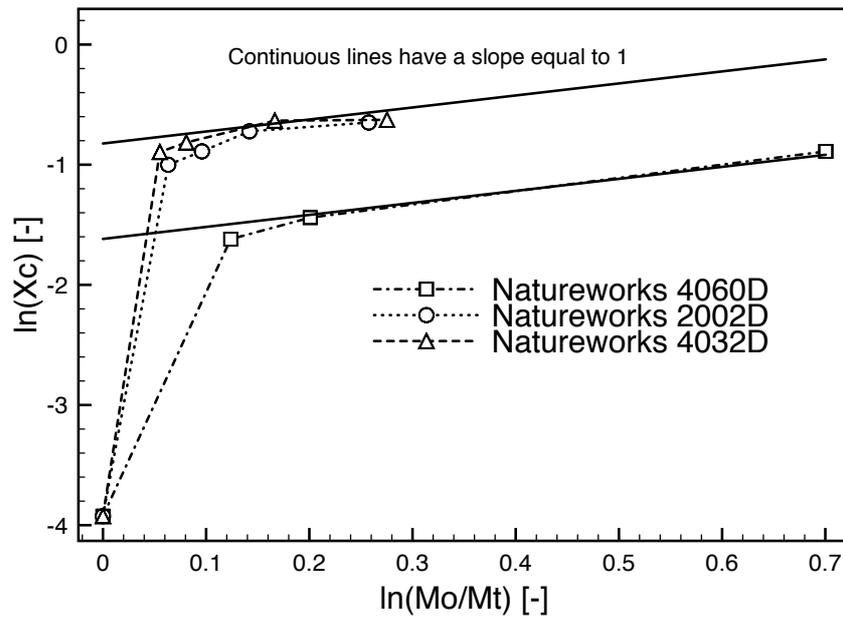
Fig. 7 Crystallinity evolution versus weight loss data during hydrolysis tests. The slope of the continuous lines is equal to 1 and indicates a crystallinity increase consistent with the erosion of the amorphous parts (adapted from ref. [15]) D-isomer contents of 4060D, 2002D and 4032D are 12%, 4% and 2%, respectively. The molecular weight Mw is in the range 190-230 KDa for all of them.

It can be noticed that at early times the slope is much larger than 1; at longer times the slope becomes equal to 1, indicating that the crystallinity degree increases by effect of the erosion of the amorphous parts. The latest points present a slope slightly smaller than 1, indicating that hydrolysis is attacking also the crystalline regions.

Effect of L-Lactide content

The stereoisomery of PLA is of special importance, considering that the amount of D-lactic acid strongly affects material properties such for instance crystallization rate, which play a crucial role on hydrolysis and biodegradation of poly(lactic acid). The influence of stereoregularity of PLA on crystallization rare is detailed in Chapter 7 of this volume. Tsuji [75] analyzed the autocatalytic hydrolysis phenomenon of amorphous polylactides, considering the effects of L-lactide content, tacticity and enantiomeric polymer blending. Poly (D,L-lactide) (PDLLA), Poly (L-lactide) (PLLA), and Poly (D-lactide) (PDLA) were synthetized with similar molecular weight. The non-blended PDLLA, PLLA, and PDLA films and PLLA/PDLA 1/1 blend film were also prepared in the amorphous state. The conditions were pH = 7.4 (phosphate-buffered solution) and Temperature = 37 °C for a time of hydrolysis up to 24 months. The results of gravimetry, gel permeation chromatography, and mechanical properties showed that the autocatalytic hydrolyzabilities of polylactides, PLAs, in the amorphous state decreased in the following order: nonblended PDLLA > nonblended PLLA, non blended PDLA >PLLA/PDLA 1/1 blend. The higher hydrolyzability of the nonblended PDLLA film compared with those of the nonblended PLLA and PDLA films was ascribed to the lower tacticity of PDLLA chains, which decreases their intramolecular interaction and therefore the PDLLA chains are more susceptible to the attack from water molecules. In contrast, the slower hydrolysis of PLLA/PDLA 1/1 blend film compared with those of the nonblended PLLA and PDLA films was attributable to stronger interaction between PLLA and PDLA chains in the blend, resulting in the "unfavoured" interaction of PLLA or PDLA chains and water molecules. The X-ray diffractometry and differential scanning calorimetry elucidated that all the initially amorphous PLA films remained amorphous even after the autocatalytic hydrolysis for 16 (PDLLA film) and 24 (nonblended PLLA and PDLA films, PLLA/PDLA 1/1) blend film) months. The melting temperatures, observed at around 170 °C and 220 °C, for the PLLA/PDLA 1/1 blend film after the hydrolysis for 24 months were ascribed to those of homo- and stereocomplex crystal-

lites, respectively, formed during heating at around 100 °C and 200 °C, but not during the autocatalytic hydrolysis

Commercial grades and laboratory synthesized polymers

One of the most important key questions is whether the knowledge of the degradation of PLLA is directly transferable to the degradation of industrial PLA. For this purpose, Höglund et al. compared the rate of degradation of large-scale synthesized polylactide (PLA) of industrial origin with that of laboratory-scale synthesized poly(L-lactide) (PLLA) of similar molar mass [76]. Generally PLA of industrial origin is a stereo-copolymer with some percentage of D-units in the poly(L-lactide) chain, with wide molar mass distribution. Industrial PLA commonly formulated with several additives, such as stabilizers, nucleating agents, and other additives important for processing and stability. These additives are known to be important contributors to the degradation of PLA-type polymers. It was found that the rate of degradation of industrial polylactide (PLA) was substantially faster than that of laboratory-scale synthesized poly(L-lactide) with similar molar mass. Incorporation of small amounts of D-units in the poly(L-lactide) chain and higher molar mass distribution enhanced the hydrolytic degradation. Furthermore, the PLA material maintained its physical properties for a longer period of time than PLLA, which loose its mechanical properties (fragmented into small pieces) earlier. A comprehensive picture of the rate of degradation of industrial PLA was then established. The degree of crystallinity had a greater influence than the degradation environment on the hydrolysis rate. The molar mass of the PLA materials decreased very rapidly and significantly faster than the mass loss, and this effect was observed regardless of temperature.

Thus, predicting the degradation of industrial PLA based on a knowledge of laboratory-scale synthesized PLLA is not properly straightforward, and the appropriate PLA grade must be chosen on the basis of the conditions prevailing in the degradation environment.

Control of hydrolytic degradation

As reported above, the main driving force of the PLA degradation has been recognized to be the hydrolysis inducted by water transport [76-79]. This inspires the rational design of usage-adaptive degradation properties, which is academically and commercially attractive to prompt a broader range of applications for PLA [63,80-83]. The most generally used approaches to tailor the hydrolytic degradation of PLA are:

- generation of hydrophilic surfaces by copolymerization, grafting reactions, and cross-linking [84-90]
- addition of hydrophilic fillers or polymers [91] and generation of porous structures [92,93];
- facilitation of hydrolytic attack by incorporation of selected proteinase [94-96];
- control of the activation energy for hydrolysis by using nanoparticles [97].

The application of the above mentioned methods is necessary for the design of molecular architectures and structural features that render the ability to interact with surrounding water molecules in a controlled manner [98-101].

Arias et al. [100] have controlled and predetermined degradation profiles of PLLA-based materials during hydrolytic degradation thorough melt-blending with different polyesters. However, this route changes the physical properties of the material, including the desired ones. The use of additives which can change the rate of hydrolysis is a route which preserves the nature and properties of PLA. Recently, Stloukal et al. [102], investigated the stabilization effect of a commercially available aromatic carbodiimmide-based anti-hydrolysis agent (which could modify the diffusion of water into the polymer matrix), intended to improve the hydrolysis resistance of PLA based materials and prevent their degradation during processing. Even more recently, Benali et al. [103] used silanized zinc oxide nanofiller (ZnOs) to tune the hydrolytic degradation of PLA.

In contrast to the numerous attempts made to tailor the hydrolytic behavior of PLA, quite limited progress can be evidenced in understanding the fundamental mechanisms for hydrolysis-triggered

chemical and physical transformation, particularly in the long-term [104-106].

Modeling hydrolytic degradation

The reaction of hydrolysis taking place inside the samples can be written as:

$H_2O + ester \rightleftarrows -COOH + -OH$ 5

The carboxylic end-groups concentration, C_C, and the ester concentration, C_E, can be related to the molecular weight as follows [45,107,108]:

$$C_C = \frac{\rho}{M_n}$$ 6

$$C_E = \frac{\rho}{M_n}(DP - 1)$$ 7

In these equations ρ is the density of the polymer sample (equal to 1.2 g/cm³) and DP is the average degree of polymerization, defined as the ratio *Mn/M* (*M* is the molecular weight of the repeating unit, 71 g/mol).

The rate of hydrolysis can be assumed to be proportional to the water concentration inside the sample, C_A, and to the ester bounds concentration. Several studies [109,110] pointed out that the reaction of hydrolysis is autocatalytic, namely that the increase of carboxylic end-groups concentration increases the rate of the reaction. When this mechanism is taken into account the rate of hydrolysis should be dependent on C_C. However, it is still unclear if the catalytic effect is due to the carboxylic end groups in their undissociated form. It has been reported [110,111] that the catalytic effect is due to the acid part of the dissociated form of the carboxylic end groups. In this case, being

$$K_a = \frac{C_{H^+} C_{-COO^-}}{C_C}$$ 8

where K_a is the acid dissociation constant, and being $C_{H^+} = C_{-COO^-}$, the concentration of the species acting as catalysis should be proportional to $C_C^{0.5}$.

In summary, the rate of scission of polymeric chains, dR_S/dt, can be written as:

$$\frac{dR_S}{dt} = K_h C_E C_A C_C{}^a + K_t C_E \qquad 9$$

in which a is a constant (equal to 0, if the catalytic effect is not considered, or to 1, if the catalytic effect is due to the undissociated carboxylic end groups, or to 0.5 if catalytic effect is due to the dissociated form of the carboxylic end groups), K_h is the constant of hydrolysis, and the last term keeps into account the thermal breakdown reaction (thermal degradation) which can be assumed to be a first order reaction [45] whose kinetic constant, K_t, depends on temperature.

The autocatalytic effect becomes dominant at longer times, whereas it can be neglected at short times [42,48].

Several modifications have been proposed to eq. 9. For instance, it was assumed [111-113] that only the carboxylic groups belonging to oligomers act as catalysts, being mobile enough to take part to hydrolysis. In this case, it is necessary to add a rate of production of oligomers. On the basis of statistical considerations [111] an empirical relationship was assumed between the oligomer produced, R_{ol}, and the scissions of polymeric chains:

$$\frac{R_{ol}}{C_{E0}} = \alpha \left(\frac{R_s}{C_{E0}} \right)^{\beta} \qquad 10$$

where C_{E0} represents the initial concentration of ester bonds and α and β are two constants. Eq. 10 is versatile enough to account for chain scission taking place at chain ends (in this case both α and β are equal to one) or randomly along the polymer chain. In the original paper by Han et al. [111] α and β were set to 0.4 and 1, respectively.

It is interesting to notice that, once the concentration of oligomers is estimated, it is also possible [111] to consider the diffusion of these small molecules according to the following balance equation:

$$\frac{\partial C_{ol}}{\partial t} = \frac{dR_{ol}}{dt} + \bar{\nabla} \cdot D_{ol} \bar{\nabla} C_{ol} \qquad 11$$

in which D_{ol} is the effective diffusivity of the oligomers inside the sample, which can be considered a function of the amount of degradation and of the crystallinity degree [111]. The diffusion of oligo-

mers causes the mass loss from the sample when immersed in a degradation medium.

Also the water concentration inside the material can be described by a balance equation keeping into account both reaction and diffusion:

$$\frac{\partial C_A}{\partial t} = -K_h C_E C_A C_C{}^a + \bar{\nabla} \cdot D_A \bar{\nabla} C_A \quad \text{12}$$

in which the last term of right hand side, RHS, keeps into account the water diffusion due to a gradient of concentration; D_A is the water diffusivity inside the sample.

Bulk and surface erosion

Two erosion paths are described in the literature: bulk and surface erosion. The first scenario occurs when water diffusion is faster than polymer degradation, leading to a homogeneous degradation of the sample. On the other hand, in the case of surface erosion the sample is eroded starting from the external surface and the erosion front moves towards the interior, as a consequence of the fact that polymer degradation is faster than water diffusion.

Following eq. 12, the two competing mechanisms appear clearly: the reaction reduces the water amount, and the molecular diffusion aims at keeping the water concentration homogeneous inside the sample. Assuming that the water concentration on the outer surfaces of the sample is fixed to an equilibrium value (which is reasonable especially when the sample is immersed in an aqueous medium), it is clear from eq. 12 that on increasing the distance δ from the surfaces, the effect of diffusion reduces with the square of δ. This means that for thick samples, the internal parts do not receive water enough and only the regions closer to the surface undergo hydrolysis. In these cases, the so-called "surface erosion" is present [114]. On the contrary, if the samples are thin, water is homogenous inside the sample and so is the hydrolytic degradation. We have thus the so-called "bulk erosion" [114]. In order to quantify how thick the samples must be to have surface erosion, it is necessary to analyze the orders of magnitude of the two terms appearing on the RHS of eq. 12.

The first term represents the reaction, and following equations 6 and 7 it can be quantified from experimental data as

$$\rho \frac{d}{dt}\left(\frac{1}{M_n}\right)e^{-E_R\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)} \qquad 13$$

in which M_n is the experimentally determined change of number averaged molecular weight at a given temperature T_{ref}, and an Arrhenius like equation is assumed to consider the effect of temperature. According to literature indications [45,47,48] (**Fig. 5**) , in water, at temperatures in the range 55 °C-60 °C the order of magnitude of the result of eq. 13 is 10^{-4} mol/m^{3}s.

The second term represents the diffusion, and its order of magnitude can be estimated as

$$\frac{D_{A,ref}C^*_{A,ref}e^{-(E_D+E_C)\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)}}{\delta^2} \qquad 14$$

in which the water diffusivity and the equilibrium water content, C^*_A are evaluated at the reference temperature, and again an Arrhenius-like dependence is assumed to consider the effect of temperature. E_D and E_C are the constants that describe the effect of temperature on diffusion and sorption, respectively.

According to literature indications [115,116] for amorphous PLLA samples at a temperature of 58 °C, the diffusivity of water is of the order of 10^{-11} m^2/s and the equilibrium water content is about 700 mol/m^3.

Considering δ as the distance from the surface at which the orders of magnitude of reaction and diffusion are comparable, after eq. 13 and 14 one obtains

$$\delta \sim \sqrt{\frac{D_{A,ref}C^*_{A,ref}e^{-(E_D+E_C-E_R)\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)}}{\rho\frac{d}{dt}\left(\frac{1}{M_n}\right)}} \qquad 15$$

At temperatures in the range 55-60 °C, δ results to be about 5mm. This means that only samples thicker than about 1cm should present surface erosion. On changing temperature, E_R of the order of 10^4 K [45,47] or even larger (**Fig. 5**) whereas the sum (E_D+E_C) is of about 4000 K [117,116]. Thus, the reaction term is dominant and δ decreases on increasing temperature and increases on decreasing temperatures.

Following this analysis, surface erosion should hardly take place in solid PLA samples.

Obviously, other factors could change the results of this analysis. For instance, the crystallinity degree can lower the order of magnitude of the numerator in eq. 15 thus lowering the value of δ.

Furthermore, at different pH of the degradation medium, the reaction kinetics can change, thus affecting the value of δ.

Finally, with the ongoing of degradation and the production of oligomers which can catalyze the reaction, the denominator can increase [42]. To this regard, the counter-diffusion of oligomers (after eq. 11) can be determining. For samples of large dimensions the oligomers can't diffuse fast enough, so they accumulate in the bulk of the sample creating a pH gradient from the center to the surface, that determines a profile of degradation rates [118,119]. This justifies the phenomenon sometimes reported in the literature [120] of a faster degradation inside the sample than at the surfaces. For small size samples, such as nano and microparticles, the characteristic size of the device is smaller than the outer diffusion layer and, since the diffusion of the oligomers is not limiting, degradation proceeds invariably through a bulk erosion path [17,121,122].

More detailed approaches to hydrolytic degradation

The models summarized above can describe the change in the average molecular weight, but not its distribution. Other approaches have been proposed in the literature which explicitly describe the molecular weight distribution by applying a population balance on the molecular chains.

An example of this approach can be found in a recent work by Lazzari et al. [123]: the population balance of molecular chains having n monomeric units was expressed as

$$\frac{d}{dt}C_n = -2K_D^\alpha C_A C_{H+} C_n - (n-3) K_D^\beta C_A C_{H+} C_n$$

$$+2K_D^\alpha C_A C_{H+} C_{n+1} + 2K_D^\beta C_A C_{H+} \sum_{i=n+2}^{\infty} C_i$$

$$-K_{BB} C_{OH-} C_n - (n-1) K_{RH} C_A C_{OH-} C_n$$

$$+K_{BB} C_{OH-} C_{n+2} + 2K_{RH} C_A C_{OH-} \sum_{i=n+1}^{\infty} C_i$$

$$-(n-1) K_W C_A C_n + 2K_W C_A \sum_{i=n+1}^{\infty} C_i$$

16

In eq. 16, C_{H+} and C_{OH-} are the concentration of positive and negative ions to consider the effect of pH. By adopting the population balance, the contributions due to terminal (kinetic constant K_D^α – acid-catalyzed), backbone (kinetic constant K_D^β – acid-catalyzed), back-biting (kinetic constant K_{BB} – base-catalyzed), random (kinetic constant K_{RH} – base-catalyzed) and non-catalyzed hydrolysis (kinetic constant K_W) hydrolysis are explicitly accounted for. Source terms (with positive contribution) are also considered from the scission of longer molecules.

Obviously, the computation efforts arising from considering the whole population of macromolecules are considerably higher, also because some of the kinetic constants are in principle depending on the chain length. Concerning this point, the authors assume that this length dependence is negligible when n is larger than 4.

Degradation in the molten state: modeling viscosity changes

The zero-shear rate viscosity of a polymer can be related to the molecular weight of the polymer by the following equation

$$\eta = c\, z^a M_n^a$$

17

in which z is the polydispersity (M_w/M_n), a is an exponent whose value is generally accepted to be 3.4 and c is a parameter depending on temperature. A discussion on the origin of eq. 17 and on the meaning of its parameters can be found in the literature [124]. For PLA, during degradation in the molten state at relatively short times, it can be assumed that polydispersity does not change significantly

with time: Mohd-Adnan et al. [125] showed that during hydrolysis at 110°C the polydispersity remained essentially the same; Le Marec et al. [27] also report a constant polydispersity index for degradation in the molten state in the temperature range 170-210°C for times up to 30 min.

According to eq. 17, once the models depicted above can be applied to describe the evolution of M_n with time, the viscosity is simply calculated. Since the exponent a makes the viscosity extremely sensitive to changes in molecular weight (a factor 2 decrease of M_n causes a decrease of viscosity of a factor 10), rheological measurements are an extremely powerful mean for assessing the kinetics of reaction in the molten state [45].

Biodegradation in composting conditions

Some confusion still persists about the difference between a degradable and a biodegradable plastic. Many international standards were developed in order to clarify the possible misconceptions. The ASTM D883-12 standard establishes that a degradable plastic is a plastic that undergoes a significant change in its chemical structure under specific environmental conditions resulting in a loss of some properties. The degradation of the plastic can be induced by chemical or biological means, through heat or by ultraviolet light. Depending on the process of degradation, the material can be classified as photodegradable, when degradation is by UV light, or biodegradable when degradation is performed by micro-organisms [126]. This international standard defines biodegradable plastics as plastics in which degradation results from the action of naturally occurring microorganisms such as bacteria, fungi and algae. Biodegradation of plastics could be aerobic or anaerobic, depending on the environment in which they are degrading. The degradation behavior of PLA under anaerobic conditions has been less studied with respect to aerobic ones [51] although anaerobic conditions are important for landfill, marine disposal, anaerobic digestion systems. This is probably due to the extremely low degradation rate of PLA at low temperatures. The behaviour of Ingeo polylactides (PLA) in landfills was analyzed through two studies aimed at generating reliable infor-

mation on the anaerobic biodegradation of PLA, under conditions of extended time and relatively low temperatures [50]. These two tests accelerated the biological degradation sufficiently that they were quite equivalent to approximately a century of a "typical" biologically active landfill: 1) an accelerated landfill conditions test was conducted at 21°C, and three moisture levels, extending to 390 days, 2) a high solids anaerobic digestion test under optimal and significantly accelerated conditions was conducted at 35°C for 170 days. The semicrystalline polylactide samples did not produce a statistically significant quantity of biogas during either test. The amorphous PLA generated a small amount of biogas in the test at 35°C, but none in the test at 21°C. It was underlined that the tests were conducted under accelerated, optimal landfill conditions, and the biodegradation was observed in a 100 year timeframe and the market volume of amorphous PLA considered was low. Authors concluded that semicrystalline PLA (typical of >96 wt% of resin used to manufacture products), under anaerobic biological conditions typical of a landfill at moderate temperatures (where PLA hydrolysis is slow), will not lead to significant generation of methane, and that no significant population of organisms is available under anaerobic conditions to directly degrade high molecular weight PLA. Because there was no direct biological degradation of PLA under the anaerobic conditions, it is likely that any degradation of PLA in a landfill would require a chemical hydrolysis step prior to any biodegradation, which is analogous to the situation in aerobic composting.

Degradation in aerobic conditions, which essentially takes place during composting has been more deeply investigated. The compostability is a very important characteristic for a polymeric material [127].
The terms "biodegradable polymer", "biodegradation", and "compostability" are frequently misused and they are often a source of misunderstanding. For instance, solubility in water is considered as a synonym of biodegradability, and biodegradability as a synonym of compostability. The term biodegradable by itself is not useful, since biodegradation is not always ensured. If the environment is not favorable for the degradation, the material will not degrade in a short time, even with the presence of enzymes that could speed up the

breaking rate of the chemical bonds. Therefore, it is important to couple the term biodegradable with the specification of the particular environment where the degradation is expected to happen, during the time scale of the process [128].

Composting includes extremely complex interactions between a complex system and the polymer. A systematic study is not available in the literature. In the following, some main aspects of the phenomena involved are schematized.

Composting is a natural process in which organic materials are decomposed into humus, a soil like substance. Decomposition is principally operated by microorganisms, but also small insects, earthworms, and other soil inhabiting organisms. The major groups of thermophilic and mesophilic microorganisms involved in composting are fungi, bacteria and actinomycetes. The organic matter represents the food source for these organisms. The process requires carbon, oxygen, nitrogen, water and heat. Organisms that decompose organic matter utilize carbon as a source of energy and nitrogen for building cell structures. A 30:1 carbon to nitrogen is the ideal ratio for reproduction of thermophilic microorganisms [129]. Generally, a compost pile goes through two steps: an active composting step and a curing period step. In the first step, the temperature increases as long as oxygen is available, producing a strong microbial activity. During this step, the temperature can rise well above 60 °C when many microorganisms become dormant or start to die. After this, the temperature starts to stabilize or may even decrease. In the curing step, the material continues to compost but at a much slower rate. The rate of oxygen consumption decreases, and the compost can be piled without turning or forced aeration. The composting process proceeds until the remaining nutrients are consumed by the last microorganisms and until almost all the carbon is converted to carbon dioxide.

Biodegradation is generally assessed by measuring the amount of carbon by-products that are produced by the biodegradation process:

$$\% mineralization = 100 \cdot \frac{gCO_2 - gCO_{2,b}}{g_{mat}\frac{\%C_{mat}}{100}\frac{44}{12}} \qquad 18$$

where gCO_2 represents the amount of evolved carbon dioxide in grams in the sample and the positive control; $gCO_{2,b}$ is the amount of evolved carbon dioxide in grams in blank; g_{mat} is the mass of the

sample; $\%C_{mat}$ is the percentage organic carbon content of the sample.

It has been proved that composting conditions are governed by the outer atmosphere, the type of compost, and the compost parameters (temperature, moisture, pH). Hence, they may differ from the simulated or controlled composting conditions as proposed by ASTM for materials and whole packages. Due to the elevated temperature conditions and high moisture and content of microorganisms, compost has been proved to be the most suitable environment for biodegradation of PLA.

PLA with high molecular weight is colonized by relatively few microorganisms [130-132]. Up to date, only few reports give evidence of the ability of microorganisms or enzymes to cleave high molecular weight PLA directly [23,133,134] The ability of PLA degradation by several *actinomycetes* [135] and thermophilic PLA-degrading bacteria such as *Bacillus licheniformis, Bacillus brevis, Bacillus stearothermophilus, Geobacillus thermocatenulatus, Nonomureae terrinata, Micromonospora viridifaciens, Micromonospora echinospora, Laceyella sacchari, Thermoactinomyces vulgaris*, and *Nonomureae fastidiosa* have been reported [136], and it has been demonstrated that microorganisms are only able to assimilate oligomers or low molecular weight products released from the polymer matrix as a consequence of the prior abiotic hydrolysis of PLA.

Kale et al. [137] investigated and compared the degradation of two commercially available biodegradable packages of PLA under real compost conditions and under ambient exposure. Both packages were subjected to composting and ambient exposure conditions for 30 days, and the decay of the physical properties was evaluated at 1, 2, 4, 6, 9, 15 and 30 days. PLA containers composed of 96% L-lactide exhibited lower degradation than PLA bottles made of 94% L-lactide, mainly due to their highly ordered structure and, therefore, their higher degree of crystallinity. The degradation rate changed as the initial crystallinity and the L-lactide content of the specimens varied. Temperature, relative humidity and pH of the compost played a significant role in the rate of degradation of the packages. First-order degradation kinetics and linear degradation trends were observed for both samples subjected to composting conditions. The

same authors [138] investigated the biodegradation of PLA bottles under simulated composting conditions according to ASTM D5338 and ISO 14885-1 standards. Two simulated composting methods were used to assess biodegradability of PLA bottles: (i) a gravimetric measurement respirometric (GMR) system, (ii) a cumulative measurement respirometric (CMR) system. Both methods showed similar trends of biodegradation for PLA bottles and at the end of the 58th day the mineralization 77.8±10.4% and 84.2±0.9%, respectively. PLA bottle biodegradation in real composting conditions was correlated to their breakdown and variation in molecular weight. Sikorska et al [139] reported the degradability of PLA under industrial composting conditions of multi-reprocessed PLLA. PLLA materials were degraded in selected environments: a composting system (an industrial composting pile) and in water (abiotic conditions) at 70 °C. The repeated processing experiments of PLLA in the extruder did not significantly affect the rate of degradation and only slightly affected the disintegration progress of the PLLA samples. The progress of the degradation process was monitored by measurements of sample weight loss and variation in the PLLA molecular weight, as well as through surface changes. The molecular level structure of the water soluble degradation products of PLLA samples was determined by electrospray ionization multistage mass spectrometry (ESI-MSn). Lactic acid monomer and its oligomeric species, terminated by carboxyl and hydroxyl end groups were identified as hydrolytic degradation products. The results indicated that in selected environments (industrial composting and incubation under abiotic conditions) hydrolytic degradation via random ester bond scission occurs preferentially. It was demonstrated, that multi re-processing of PLLA did not significantly affect the rate of degradation and only slightly affected the disintegration progress of the PLLA samples.

Pantani and Sorrentino [115] analyzed the effect of crystallinity on the biodegradation rate of injection molded PLLA parts. Their results confirmed that the initial morphology strongly affect the degradation rate. They also reported that the crystals formed during degradation have less connectivity and are thus less efficient to prevent the complete swelling of the polymer, whereas the crystals formed before degradation present a higher connectivity that guarantee a

denser structure more impermeable to the enzymatic attach and to oligomer diffusion.

The control of the degradation process has received only limited attention [102]. It has been reported [140,141] that the enzymatic hydrolysis of PLA can be inhibited by rutile-type TiO_2 particles. In a recent paper, it was demonstrated that adding silver nanoparticles to PLA significantly decreased the degree of biodegradation even at very low concentrations (0.01wt%) [142].

Phenomenological interpretation of biodegradation data in composting conditions

Despite the complexity of the phenomena involved in the biodegradation of PLA, a simplified interpretation of biodegradation data can be carried out assuming that:

- the oligomers produced from hydrolysis diffuse from the sample toward the surfaces, with a diffusion parameter which is a strong (decreasing) function of crystallinity degree.
- the microorganisms attack the surface of the samples and they metabolize the oligomers diffusing from the bulk of the sample toward the surface.

On these bases, a balance can be carried out on the mass metabolized by the microorganism as

$$r_m S = -\rho S \frac{d\delta}{dt} + j_M S \qquad 19$$

in which j_M is the mass flux of the oligomers leaving the sample the surface, as a result of hydrolysis; r_m is mass of polymer metabolized by the microorganisms per unit time and per unit sample surface; δ is sample thickness; S is sample surface. The first term at the RHS of eq. 19 represents the surface erosion, whereas the second term the bulk erosion.

At a first approximation, surface erosion should be about constant with time, giving a linear contribution to the metabolized mass. For the same polymer mass, surface erosion is inversely proportional to

sample thickness (because the total surface is inversely proportional to thickness).

Concerning the bulk erosion, at a first approximation it can be assumed that

$$\dot{j}_M \approx \frac{D_{ol}}{\delta} C_{ol} \qquad\qquad 20$$

where C_{ol} is the (mass) concentration of oligomers inside the sample, which increases first (hydrolysis) and then decreases at long times (less available mass)

A sigmoidal expression is thus expected for the contribution of bulk erosion to the metabolized mass.

Crystallinity is expected to play a role on both mechanisms:
 - on surface erosion because crystalline regions are more indigestible to microorganisms;
 - on diffusion term because:
 a) hydrolysis is slower on crystalline regions,
 b) the diffusion parameter can be much lower for semicrystalline polymers.

In **Fig. 8** two curves of mineralization collected during biodegradation in composting conditions [115] are reported for two samples of Natureworks PLA 2002D having different thickness, namely 2 mm and 1 mm. The samples were previously kept at 105°C for 8h, in order to allow complete crystallization. It can be noticed that both the curves are nearly linear, and the slopes are indeed inversely proportional to the thickness (namely directly proportional to the surface). According to the equations reported above, this is consistent with a surface erosion mechanism. When an amorphous sample is considered (**Fig. 9**) the mineralization curve starts following the same trend of the crystalline sample, however it soon shows a higher rate and a sigmoidal shape. In this case, probably the bulk erosion becomes soon dominant.
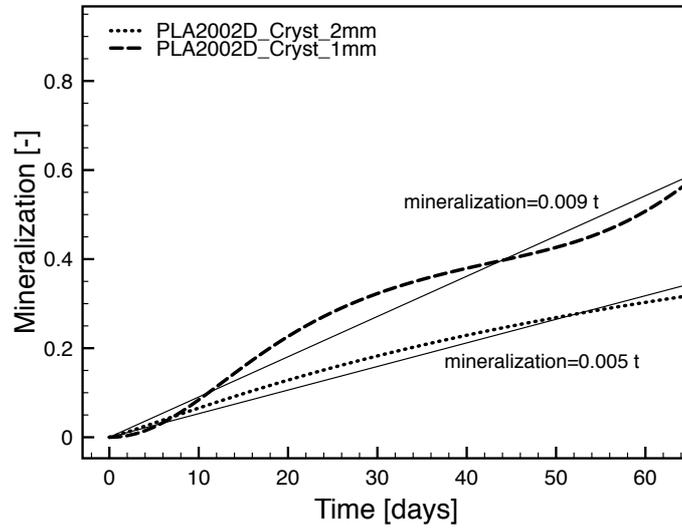
Fig. 8 mineralization for two crystalline samples of Natureworks 2002D in composting conditions at 58 °C according to the protocol reported in ref [115]. Samples are either 2 mm or 1 mm thick.
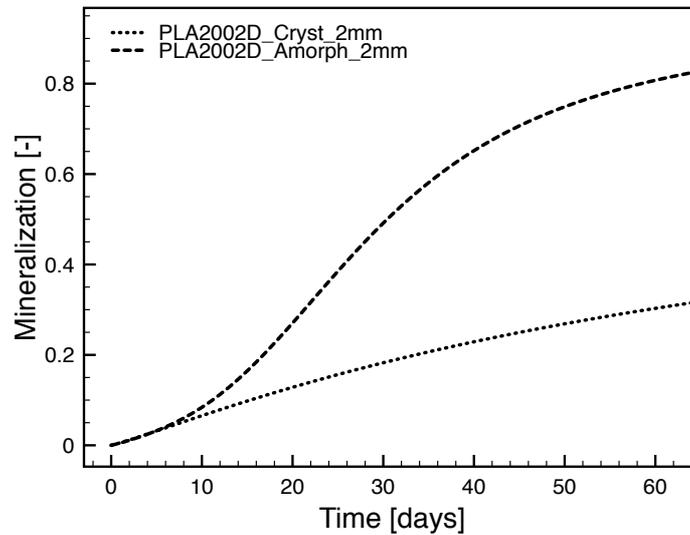
Fig. 9 mineralization for two samples of Natureworks 2002D, an amorphous one and a crystalline one in composting conditions at 58 °C according to the protocol reported in ref [115]. Samples are 2 mm.

Final comments and perspectives

The analysis of degradation and biodegradation of PLA has been conducted thoroughly in the last twenty years. The mechanisms of the reactions involved are now clearer and the effects of the several variables are being understood. The efforts to be made in order to make PLA a serious competitor of traditional polymers are toward the control of degradation and biodegradation. Indeed, the characteristics of being degradable represent the main advantage of the use of PLA, but also its main limitation. The ideal material should be stable when processed from the molten state, resistant to the environmental agents during the use, and readily biodegradable at the end of life. This goal is particularly challenging, especially for durable products with long-term performance such as in the automotive, electronic and agricultural industries. It has to be mentioned that, somewhat surprisingly, for some applications, mainly when living organisms are involved (tissue engineering or plant nursery), also a readily degradable material like PLA disappears in times too long for many uses. The perfect material should disappear in times comparable to the use. The case of pots for plants is a good example: it would be perfect if the pot could disappear (namely biodegrade) in times consistent with the plant growth, so to protect the young plant but to avoid to be a limitation for the growth of the roots when the plant becomes older. The same condition happens every time an artifact made in PLA has to interact with a living organism (i.e. in tissue engineering).

It is clear that the tuning of degradation and biodegradation rates can be attained only through a deep understanding of the chemical and physical mechanisms which control the phenomena. This is surely a challenge which researchers must face in the next years.

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