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Physical and Chemical Stability of PLA in Food Packaging

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Introduction

Bioplastics are a new generation of biobased and/or biodegradable polymers (Reddy et al., 2013; European Bioplastic Association, 2018b). Conventional plastics (*i.e.* petroleum-derived and non-biodegradable) have transformed our society and are used in all aspects of our everyday life. The worldwide production of conventional plastics reached 348 million tons in 2017. Although it represents less than 1% of the world production of conventional plastics, the bioplastic market has been continuously growing over the last years, reaching around 2.11 million tons in 2018, and it is estimated to reach 2.62 in 2023 (World Economic Forum, 2016; European Bioplastic Association, 2018a). Food packaging represents one of the main applications of bioplastics. The most popular biopolymers are 30% biobased poly(ethyleneterephthalate) (Bio-PET30), biobased polyethylene (Bio-PE) and poly(lactic acid) (PLA) (European Bioplastic Association, 2018a). Among them, only the last one meets both criteria, *i.e.* being biobased and biodegradable. PLA benefits from an interesting balance between costs, functional properties and processability. The European Bioplastic Association has recently reported that the global production of PLA exceeded 210 thousand tons in 2017, and has forecast that PLA capacity will grow by 50% in 2022. PLA is compliant with European and North American legislation for food contact materials.

The first synthesis of PLA dates back to 1932 when researchers from DuPont (Carothers et al., 1932) developed a method to polymerize lactide to produce PLA that was later patented by DuPont in 1954. Due to its high costs and ability to hydrolyze in biological environments, it was firstly used only for biomedical applications. The low molar mass of PLA (<100000 g mol⁻¹) is now widely used in that field, as stents (Soares et al., 2008; Erne et al., 2006), surgical sutures (Maharana et al., 2009), and tissue cultures or drug delivery devices (Langer, 1998). In the early 1990s, the ring opening polymerization process was developed (Gruber et al., 1994; Gruber et al., 2001) to produce high molar mass PLA (>100000 g mol⁻¹) for different industrial purposes such as fibers and textiles, plasticulture, and food packaging and serviceware (Castro-Aguirre et al., 2016).

Food corporations such as Danone (Germany), Del Monte (USA) and Noble Juice (USA), as well as leading food retailers such as Wal-Mart (USA), SPAR (Austria) and Auchan (France) are already using PLA based packaging in some of their products (Castro-Aguirre et al., 2016). Various types of foods are currently packed and commercialized with PLA-based materials. These foods are characterized by different physical states, a wide range of water activity (a_w), pH and composition, and moreover different shelf lives. Some examples are potato crisps (amorphous solid, $a_w = 0.1-0.3$), fresh salads and vegetables (biological gel, $a_w > 0.99$), yogurts (gel, $a_w > 0.99$), citrus juices (acidic liquid, $a_w = 0.97-0.99$) and water (liquid, $a_w > 0.99$) (Fig. 1).

Short Overview of PLA Synthesis and Properties

The constitutive unit of PLA is lactic acid, which is derived by lactic fermentation of glucose, obtained from different vegetal sources (Fig. 2). Some examples are corn, sugar cane or sugar beet. Polymers based on lactic acid can be synthesized by different routes: i) direct lactic acid condensation, often using coupling agents to increase molecular weight and, ii) ring opening polymerization (ROP) of lactide. This sometimes leads to confusion in the nomenclature used in the literature. Polymers derived from direct polycondensation should be



*Withdrawn from the market because loud crinkling noise

Figure 1 Selected examples of commercial applications of PLA as food packaging. Images taken from NatureWorks and brands website.

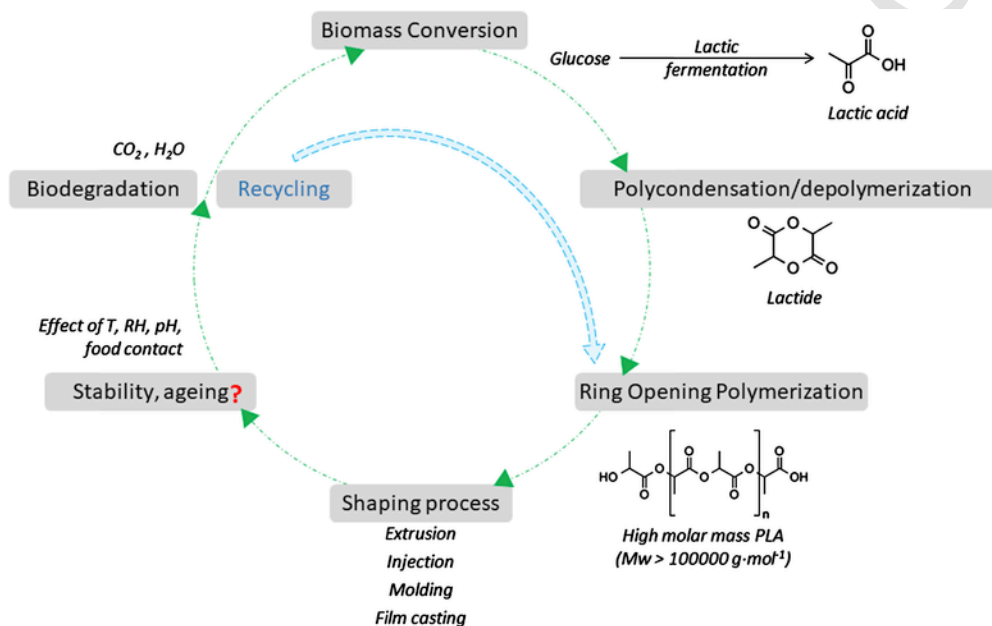


Figure 2 Production and life cycle of PLA as food packaging.

referred to as poly(lactic acid) and polymers synthesized by ROP of lactide as poly(lactide). Both types of macromolecules are generally named PLA. ROP of lactide is by far the most employed route to obtain high molecular weight polymers used in the packaging industry (Ducruet and Domenek, 2015). This route first consists of a direct polycondensation reaction to produce a low molar mass prepolymer. The prepolymer is then depolymerized in order to obtain lactides (3,6-dimethyl-1,4-dioxane-2,5-dione), being dehydrated cyclic dimers, which are the starting material for ROP into high molar mass polymers. Three forms of lactide can be obtained as a function of the stereochemistry of the feedstock, temperature and catalyst: L,L-lactide, D,D-lactide and D,L-lactide (meso-lactide) (Garlotta, 2001). The stereocontrol of the macromolecular chain can be achieved by ROP. D-lactic acid perturbs the chain packing of PLA and its quantity has therefore a large impact on the macroscopic properties of the polymer (e.g. glass transition and crystallization behavior). Enantiopure PLLA and PDLA can form a stereocomplex (Ikada et al., 1987), caused by stereoselective interactions (mostly van der Waals forces) locking the chains into a novel material with different physical properties such as changed crystalline form and higher thermal stability. Many newer technological developments are associated with this finding, and more information can be found in recent reviews, such as Bai et al. (2017).

The obtained PLA polymer can then be processed using the conventional manufacturing techniques like extrusion, injection molding, blow molding, cast film extrusion and thermoforming, in order to achieve different PLA goods such as films, rigid containers, bottles and others. PLA is a transparent polymer, glassy at room temperature, and has satisfying mechanical properties with a tensile strength ≈ 60 MPa, an elongation at break $\approx 5\%$ and a Young modulus 3–4 GPa (approximate values taken from the review of Domenek et al., 2018). After being exposed to different environmental conditions according to their application, PLA goods can be fully biodegraded or recycled (Auras et al., 2004; Castro-Aguirre et al., 2016; Jamshidian et al., 2010).

Although there is a general interest to increase the quantity of foods packed in PLA, several factors are currently limiting its application as a food packaging material. PLA displays an intermediate barrier performance to oxygen (O_2), carbon dioxide (CO_2) and

nitrogen (N₂) compared to medium or high barrier plastics such as poly(ethylene terephthalate) (PET), poly(amide) (PA), poly(vinylidene chloride) (PVDC) or poly(vinyl alcohol) (PVA) (Rocca-Smith et al., 2019). Its properties are near the benchmark poly(styrene) (PS). PLA has furthermore lower water vapor barrier properties compared to most petroleum-derived polymers. A recent review was dedicated to this subject (Sonchaeng et al., 2018). Another factor that reduces the use of PLA is its inherent water sensitivity. Even though PLA sorbs small quantities of water (Auras et al., 2004; Witzke, 1997), it readily reacts with water molecules and is hydrolyzed over time, thus compromising the performance of PLA material (Rocca-Smith et al., 2017b). Other factors which restrict its use in the market are the undesirable crackling noise that PLA makes when it is handled, its rather low thermal stability and its high price.

Stability Testing of PLA

Containment, protection and preservation represent the basic functions provided by food packaging. They can obviously be accomplished only if the material maintains its integrity in terms of chemical structure and physical state over time. Therefore, the stability of the food packaging material is intimately related to the shelf life of the product and, consequently, to the quality of the food. In the food industry, the food quality term involves a large variety of meanings which depend on the food product category. In the food technology literature, there is thus no single and simple definition of the shelf life, due to its complexity (Robertson, 2013). In general, it is described as a finite length of time, after production (including in some cases maturation or aging) and packaging, during which the food retains a required level of quality under well-storage conditions (Nicoli, 2012). According to this definition, the shelf life of food represents the failure time at which the level of quality becomes unacceptable to the consumer. Regarding European legislation, shelf life was described for the first time in Directive 13/EC (2000) on food labeling, then repealed by Regulation No 1169 (2011), as the date of minimum durability of foodstuffs. A first definition of shelf life was given in Commission Regulation (EC) 2073 (2005) based on microbiological criteria for foodstuffs. It means either the period preceding the “use by” or the “minimum durability” date as defined in the articles 9 and 10 of the European Directive 2000/13. Concerning the safety of the packaging, Commission Regulation (EC) 10 (2011) defined migration test conditions in order to validate food contact materials. In that case, food simulants are used to mimic:

- hydrophilic foods: ethanol 10% (v/v) food simulant A, acetic acid 3% (w/v) food simulant B, ethanol 20% (v/v) food simulant C.
- Lipophilic foods: ethanol 50% (v/v) food simulant D1, vegetable oil food simulant D2 (used for foods which contain free fats at the surface).
- Dry foods: poly(2,6-diphenyl-*p*-phenylene oxide), particle size 60–80 mesh, pore size 200 nm, food simulant E.

Dealing with biodegradable packaging, it is of utmost importance to ensure their stability under actual conditions of use in contact with food, in order to preserve their shelf life. The environmental factors such as relative humidity, temperature, and ultraviolet (UV) light play a key role in the stability of biodegradable packaging. These parameters also influence their biodegradation process after use (Holm, 2010). To date, neither in the scientific literature nor in the legislation, has any standard procedure been proposed for determining the stability of PLA or other biodegradable packaging during their service lifetime. Nevertheless, it is noteworthy that from an environmental point of view, the same concept applies to composting and biodegradation methods used to analyze the end of life of the material (NF 13432:2000). Concerning industrial applications other than food packaging, in the agronomic field PLA has to comply with the ultimate aerobic biodegradability in soil reported in the standard ISO 17556:2012, while in the medical domain, standard specifications for PLA and poly(lactide-co-glycolide) resin for surgical implants are provided in ASTM F2579-2010 and in ISO 13781:2017.

The inherent water sensitivity of PLA is a serious limitation for products having medium or long shelf life, as reported in different shelf life studies (Peelman et al., 2014; Romani et al., 2015; Panseri et al., 2018). In order to use PLA as a valuable packaging material for food with a long shelf life, Accelerated Shelf Life Testing (ASLT) has to be designed, as for food, in order to analyze the deterioration process under defined environmental conditions (*e.g.* temperature and relative humidity) which accelerate by a known factor the reaction rate, reducing the time of analysis (Robertson, 2010).

This article will thus focus on the importance of using appropriate storage tests to better know the stability of PLA and for later better controlling the changes according to the food application. Based on these considerations, the objective is to review the advances reached in understanding the interactions between water or food simulants and PLA, focusing on the impacts on its chemical and physical stability in its conditions of use as a food contact material.

Chemical Stability of PLA

One of the most important issues about using PLA as a food packaging material is related to its sensitivity to moisture. The hydrolysis phenomenon reduces the molecular weight of PLA, which is considered as the step preceding biodegradation (Gorrasi and Pantani, 2013). As reported in the scientific literature, the main studies on the sensitivity of PLA to water have been carried out in the biomedical field and, specifically, in contact with liquid media simulating biological systems (Li, 1999; Migliaresi et al., 1994; Tsuji et al., 2000b; Tsuji, 2010). In contrast, only limited information about the stability of PLA is reported in the literature when it is used as a food packaging material, and thus exposed to different environmental conditions in terms of temperature, relative humidity and pH.

Hydrolysis is the main route to PLA degradation. The hydrolysis kinetics of PLA under mild temperature conditions ($T < 40\text{ }^{\circ}\text{C}$) corresponding to a physiological environment, or to the storage conditions of many foods, are of importance for the design of PLA-based materials such as surgical implants or drug delivery devices. Upon immersion in aqueous environments, water only penetrates into the amorphous phase and cannot penetrate the crystallites (Sonchaeng et al., 2018). This results in primary degradation of amorphous

domains. In the presence of water and a catalyst, ester hydrolysis occurs, leading to a decrease in molecular weight. Once oligomers are small enough to dissolve, mass loss of the PLA is observed.

Main Mechanisms of Degradation in Contact With Liquid Water

The general hydrolysis reaction of the ester groups within the polymer in the presence of water can be either acid- or base-catalyzed (Lyu et al., 2007). More specifically, when PLA is used as packaging in contact with foods, which are mostly acidic products, the acid-catalyzed hydrolysis mechanism is as detailed in Fig. 3.

The hydrolytic degradation of PLA starts from the surface and its progression is dependent on the ratio of degradation kinetics and dissolution kinetics of oligomers or carboxylic acids. If the degradation products are not leached from the surface, carboxylic acid end groups accumulate in the amorphous phase where they have an autocatalytic effect (Li and Vert, 2002). In particular, in case of thick objects, the leaching of catalytic molecules from the center is slow compared to the hydrolytic degradation which evolves much faster. The amount of absorbed water, the diffusion coefficient of the chain fragments within the polymer and the solubility of degradation products are thus the main factors that control PLA hydrolysis in contact with aqueous media (Schliecker et al., 2003; Auras et al., 2010; Rocca-Smith et al., 2017b). The macroscopic outcome of this mechanism is that thick pieces liquefy at first on the inside.

Effect of Relative Humidity

Focusing in more detail on the effect of relative humidity (RH) and the physical state of water, Fig. 4 shows the evolution over time of the mean molar mass (\overline{M}_w) of PLA films (of $\sim 20 \mu\text{m}$ thickness), stored at 50°C , in various environmental conditions mimicking dry to humid foods. The progressive decrease in \overline{M}_w , from 50% to 100% RH environments, confirms that the higher the RH, the faster the hydrolysis occurs. In parallel to the decrease in the (\overline{M}_w), after 62 days at 50°C and 100% RH, the glass transition temperature (T_g) of PLA is also reduced to $\sim 46^\circ\text{C}$ and broadened (Rocca-Smith et al., 2017a). A similar decreasing trend in T_g of PLA was observed in different studies carried out under various environmental conditions (Migliaresi et al., 1994; Gonzalez et al., 1999; Tsuji et al., 2000a; Tsuji et al., 2000b; Copinet et al., 2004).

Actually, increasing the RH induces an increase in chemical potential of water, an increase of the water uptake by PLA, and, consequently, an acceleration of the hydrolysis reaction (Copinet et al., 2004). Moreover, the degradation products, accumulating in the film under high RH conditions, act as acid catalysts for the hydrolysis of PLA. However, in the case of PLA in direct contact with liquid water, the hydrolysis reaction occurs slower than for the highest RH conditions because the degradation products are solubilized into the medium in contact (Rocca-Smith et al., 2017b). When PLA is exposed to a humid environment, it can sorb small quantities of water ($<1.1 \text{ wt}\%$ at $T = 25^\circ\text{C}$ and close to saturation) (Auras et al., 2004; Witzke, 1997; Holm et al., 2006; Kucharczyk et al., 2013). It will then react with them, starting the hydrolysis phenomenon (Li, 1999; Tsuji, 2010). Whether PLA is in contact with water vapor or liquid water, its water content remains at a very low value until hydrolysis leads to a mean molar mass \overline{M}_n lower than 25000 g mol^{-1} , then increasing a lot with the absorbed water quantity (Rocca-Smith et al., 2017b; Lyu et al., 2007). Obviously, in contact with liquid aqueous media, PLA dry matter is decreasing once the hydrolysis is sufficiently advanced, due to the solubilization of degradation products which are of small size, highly polar and hydrophilic (Li and McCarthy, 1999; Tsuji et al., 2000a; Lyu et al., 2007; Rocca-Smith et al., 2017b).

Effect of pH

The pH of foods or beverages may also influence the rate of hydrolysis. Rocca-Smith, 2017 investigated this effect using McIlvaine's citric acid-phosphate buffer to control the pH of the liquid phase in contact with PLA films (for food packaging applications) in the range

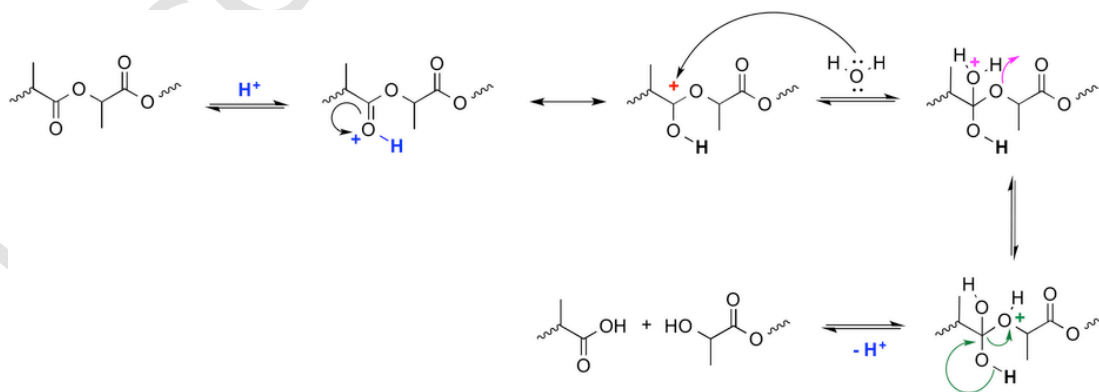


Figure 3 Schematics of ester hydrolysis (nucleophilic substitution reaction) which happens for PLA in the presence of water. Acid catalyzed hydrolysis is represented, as the main route of degradation for PLA packaging in contact with foods (which are mostly acidic).

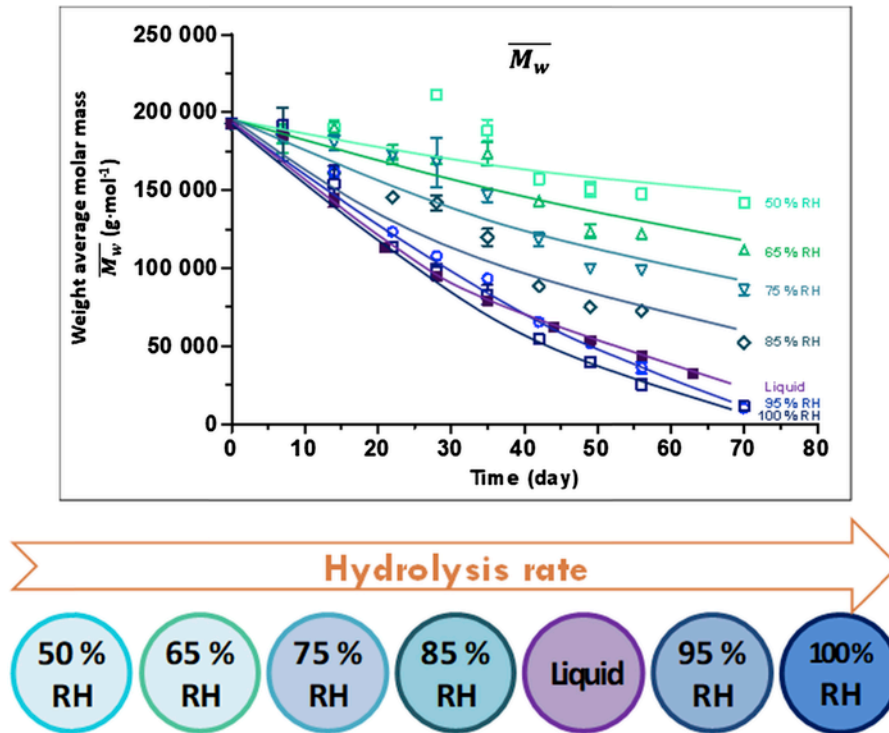


Figure 4 Kinetics of the hydrolysis rate of PLA, following the mean molar mass of PLA films stored at 50% RH, 65% RH, 75% RH, 85% RH, 95% RH, 100% RH or immersed in liquid water, at 50 °C. Error bars are standard deviations. Lines are guide for the eyes. Adapted from Rocca-Smith et al. (2017).

from 3 to 7 (under accelerated conditions at $T = 50\text{ }^{\circ}\text{C}$). The analysis of the molecular weight distribution of PLA clearly indicated that pH had no influence on the rate of hydrolysis (Fig. 5).

Similar results with no effect of pH have also been reported for amorphous polylactide used in biomedical applications (Lyu et al., 2007). In this work, the pH range was even broader (from HCl water solution at pH 0 up to NaOH water solution at pH = 12) for PLA immersed at 37 °C, for 500 days.

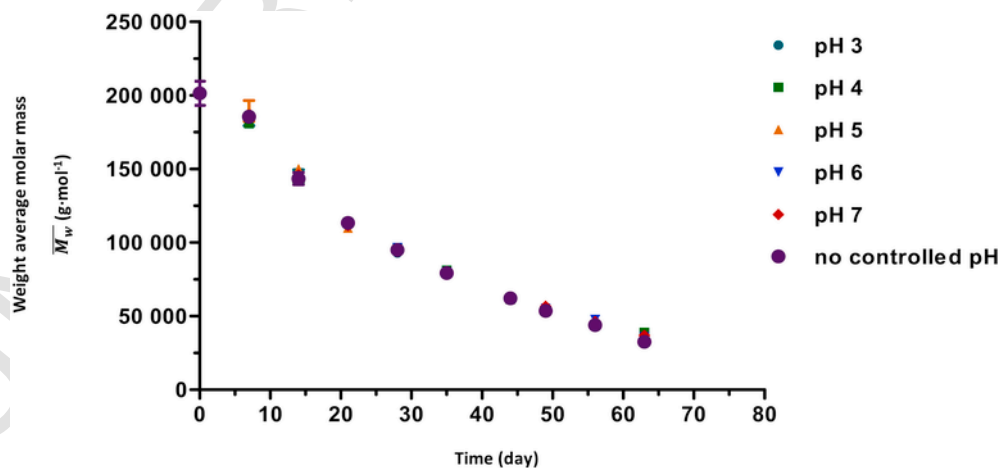


Figure 5 Kinetics of PLA films degradation, reported as the weight average molecular weight (\overline{M}_w), when immersed in aqueous media at different pH, at 50°C.

Effect of Temperature

The effect of temperature on the hydrolysis rate of PLA immersed in aqueous media is classically described by the Arrhenius model:

$$k = A \cdot e^{-\left(\frac{Ea}{RT}\right)}$$

where k is the rate constant for deteriorative reaction, A the collision frequency, Ea ($\text{J}\cdot\text{mol}^{-1}$) is the activation energy, R the gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$) and T the temperature in K . The rate at which the hydrolysis takes place obviously depends on the physical state of polymer, and thus on the temperature.

Three temperature ranges can be identified accordingly with different activation energy (Table 1) (Tsuji, 2010). Above the melting temperature of PLA, between 180–250 °C, the activation energy was found to be close to 50 kJ mol^{-1} (Tsuji et al., 2003). The activation energy in the range of temperature between 120–160 °C was reported around 70 kJ mol^{-1} (Tsuji et al., 2008). For temperatures below the glass transition temperature (T_g), between 21 and 45 °C, the kinetics of hydrolysis of PLA reached a higher value of activation energy ($>80 \text{ kJ mol}^{-1}$) (Makino et al., 1985). Hydrolysis thus occurs faster at higher temperatures and has a lower activation energy compared to temperatures below T_g . This hydrolysis phenomenon can be described in two steps: a first slow rate, followed by a second accelerated rate. This rate difference is smaller when hydrolysis occurs at high temperature, probably due to the increased chain end mobility (Lyu et al., 2007). Therefore, according to the temperature range in which the hydrolysis phenomenon is studied, different kinetic behaviors can be observed. The degradation at high temperature above T_g follows the Arrhenius model (first order kinetics), while below T_g it can more accurately be described by the Williams-Landel-Ferry model (Lyu et al., 2007).

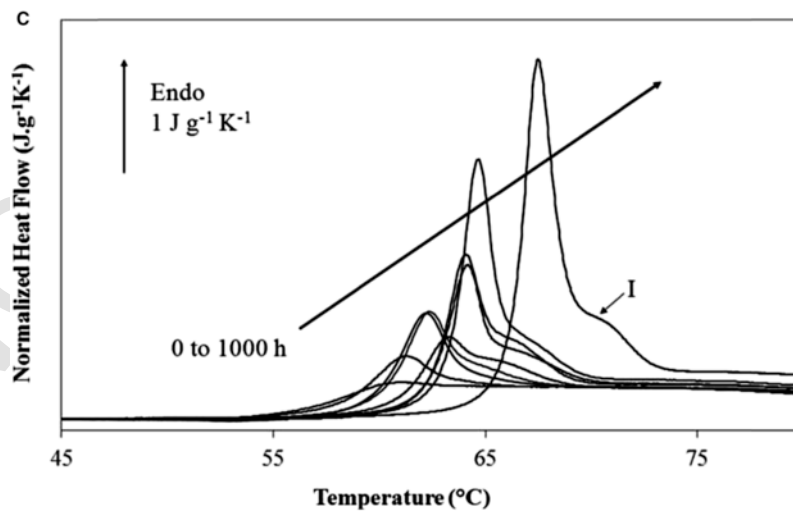
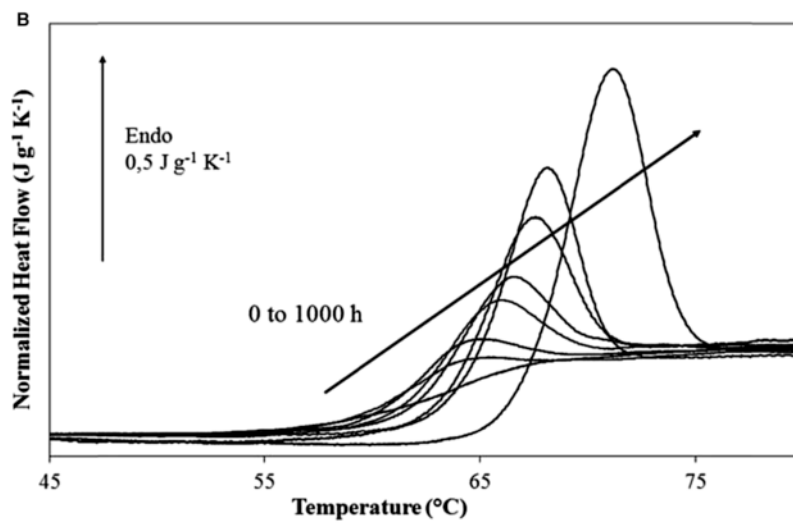
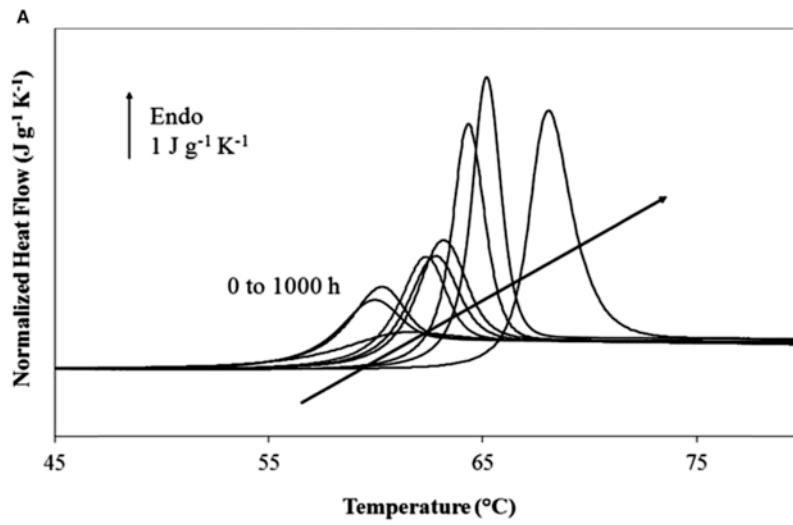
Physical Stability of PLA

When an amorphous or semi-crystalline polymer is stored at temperatures below its T_g , slow molecular rearrangements occur in the amorphous region, because only restricted motion as rotation of small groups of atoms and vibration and rotation motion of chemical bonds along the polymer can occur. Over time, the polymer relaxes towards its thermodynamic equilibrium, which causes changes in bulk properties such as volume or enthalpy. This phenomenon is called physical aging (Struik, 1977; Hutchinson, 1995). It can cause dimensional instability of the polymer, embrittlement over time and changes in gas barrier properties. Above T_g , the amorphous phase aging caused by relaxation phenomena is not thought to happen because the thermodynamic equilibrium is installed. In the case of semi-crystalline polymers, three different phases can coexist (Wunderlich, 2003). Phase coupling of amorphous and crystalline phases can give rise to an amorphous fraction with decreased macromolecular mobility, *i.e.* the Rigid Amorphous Fraction (RAF), which cannot relax at T_g . Except for the crystalline phase, the polymer needs to be described with two fractions in the amorphous phase, the Mobile Amorphous Fraction (MAF) and the RAF. The RAF vitrified at temperatures higher than T_g can be subject to physical aging.

PLA has a glass transition temperature (T_g) of approximately 60 °C and is therefore sensitive to quick physical aging at room temperature (*i.e.* storage below but near T_g). The phenomenon is often investigated by the analysis of the enthalpy recovery peak in a DSC experiment (Pan et al., 2007; Monnier et al., 2017; Dobircau et al., 2015; Righetti et al., 2017). An example of the increase in the enthalpy of recovery peak linked to T_g is given in Fig. 6 (Delpouve et al., 2014). This T_g is attributed to the MAF. Comparing Fig. 6A (amorphous PLA) and Fig. 6B (maximum crystallized PLA, $X_c = 42\%$), a broadening of this recovery peak linked to T_g can be observed due to higher heterogeneity in the mobility of the amorphous phase constrained between spherulites. In the case of insufficient crystallization, Fig. 6C (semi-crystalline PLA, $X_c = 22\%$) shows that distinct types of mobility can coexist in this amorphous fraction. Both the peak overshoots of relaxation enthalpy linked to T_g , consequently to physical aging, and corresponding to the inter-spherulitic amorphous phase and to the intra-spherulitic amorphous phase (inflection point I, Fig. 6C) are observed in that case. The RAF devitrification only occurs between 80 and 130 °C. The RAF contributes to the physical aging mainly at high undercooling (low temperature), while the structural relaxation at low undercooling (high temperature) occurs apparently via cooperative segmental motions.

Table 1 Activation energy of the hydrolysis of PLA according to the characteristic temperatures of the polymer

	Temperature range investigated	Activation energy ($\text{kJ}\cdot\text{mol}^{-1}$)	PLA material	References
$T < T_g$	21–45 °C	83.7	PLA microcapsules (1.5 μm in diameter)	Makino et al. (1985)
$T_g < T < T_m$	120–160 °C	69.0	PLLA pellets ($\overline{M}_n = 160000 \text{ g mol}^{-1}$, $X_c = 27.2\%$)	Tsuji et al. (2008)
$T > T_m$	180–250 °C	51.0 49.6	PLLA pellets ($X_c = 27\%$) PLLA pellets ($\overline{M}_n = 160000 \text{ g mol}^{-1}$, $X_c = 27.2\%$)	Tsuji et al. (2003) Tsuji et al. (2008)



At high undercooling, only small-scale local motions can take place, and this also occurs in the RAF (Righetti et al., 2017). Moreover, it has been shown that an increase of D-lactic acid content in the macromolecular structure increases the physical aging (Aou et al., 2007).

Recently, fast scanning calorimetry (FSC) was also used to study physical aging of PLA. This technique allows heating up and cooling down polymers as fast as a thousand Kelvin per second, which permits reaching the thermodynamic equilibrium of aging in relatively small time intervals (Monnier et al., 2017; Monnier et al., 2018). This provides new means for theoretically investigating the aging behavior of PLA as a function of the polymer morphology. Monnier et al., 2018 showed, for example, that constraints imposed by the RAF in the amorphous phase can decelerate the physical aging rate.

From a practical point of view, the physical aging of PLA induces embrittlement (Pan et al., 2007; Burgos et al., 2013; Avolio et al., 2015). Pan et al. (2007) showed in their pioneering work the decrease of the elongation at break of PLA during aging (Fig. 7). Burgos et al. (2013) analyzed the oxygen barrier properties of aged PLA and showed an increase of almost 20% in 90 days of aging at 25 °C and 50% RH. This decrease was even more important in the case of plasticized samples, similar to what is also observed for other types of plasticized materials (Ruellan et al., 2016). A more detailed analysis on physical aging of plasticized PLA can be found in Ruellan et al. (2015).

In addition, the physical aging of PLA in contact with water was shown to be faster compared to dry conditions. This effect could be explained by the capacity of water to form clusters inside the polymer matrix, even at very low absorbed quantities. The water clusters bring additional free volume to the structure and could thus be responsible for the acceleration of segmental motion even in the absence of any degradation due to hydrolysis (Vyavahare et al., 2014).

Effect on the Crystalline Phase of PLA

The increase in the percentage of crystallinity (X_c) is a well-known phenomenon in PLA under hydrolytic degradation which occurs also in initially amorphous PLA. Hydrolysis-induced crystallization has been confirmed by different authors, using different techniques such as DSC, WAXS (Wide-Angle X-ray Scattering) and FTIR (Fourier Transform Infrared spectroscopy). The increased chain mobility, induced by the small degradation products and water molecules, favors plasticization and also crystallization of PLA chains (Migliaresi et al., 1994; Tsuji et al., 2000a; Tsuji, 2010; Harris and Lee, 2010; Gorrasi and Pantani, 2013; Kucharczyk et al., 2013). Moreover, this phenomenon is highly influenced by the storage conditions. As an example, there was no significant change in X_c (~23%) for PLA films stored at 50% RH and 50 °C, while increasing the RH conditions up to 100%, or immersing PLA in liquid water, lead to a linear increase of X_c with time, up to ~36% (Rocca-Smith et al., 2017b). This also induced a progressive loss of the transparency of film samples (Rocca-Smith et al., 2017a). As a direct result, the melting temperature (T_m) first increased, due to an increase in the thickness of PLA crystals, favoring their thermostability (and then obviously a decrease for high hydrolysis states when chemical aging occurs). It is also worthy to note that such changes indirectly modify the respective ratios between the crystalline phase, the Rigid Amorphous Fraction (RAF), and the Mobile Amorphous Fraction (MAF) (Rocca-Smith et al., 2017b).

Conclusions and Perspectives

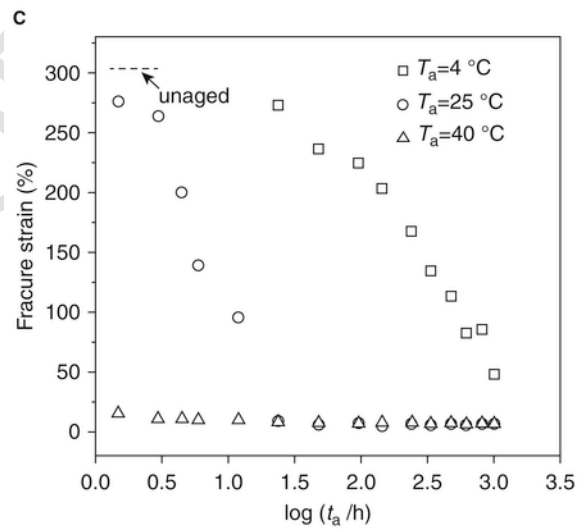
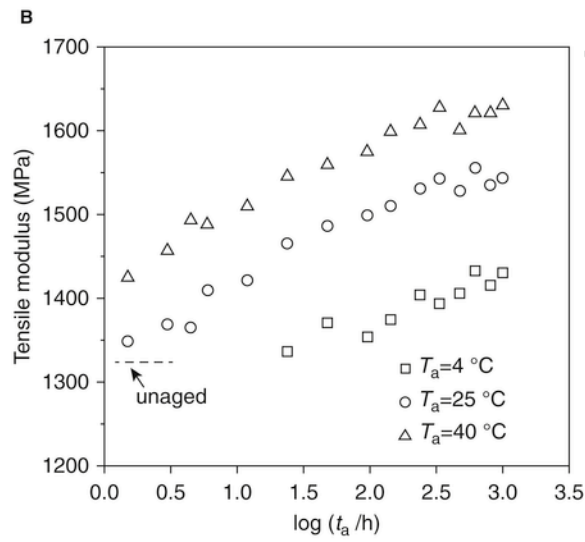
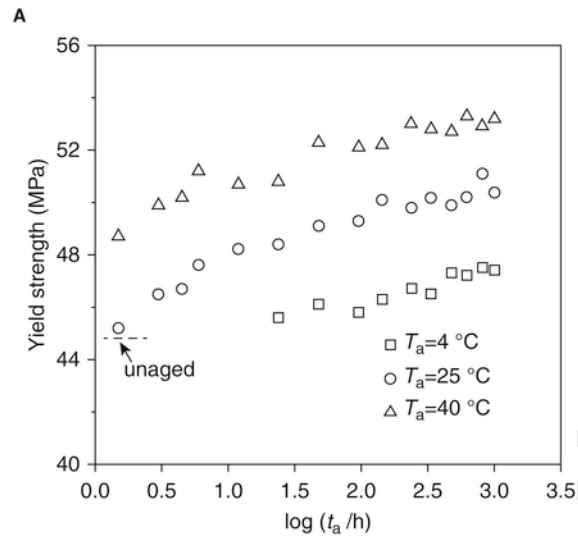
This article reports on the chemical and physical stability of PLA when stored in different environmental conditions mimicking food storage. The physical state of water plays a key role in the kinetics of the hydrolysis of PLA. Hydrolysis occurs faster when increasing relative humidity from 50% to 100%. However, when PLA is stored in direct contact with liquid water, the reaction is slower than for high RH conditions. In this latter case, the degradation products are solubilized in the liquid medium in contact. In contrast, when PLA is stored at high RH conditions, these compounds accumulate in PLA film, acting as catalyzers, and thus accelerating the hydrolysis rate (Fig. 8). Under conditions of use, it is also worth noting that physical and chemical aging of PLA will occur at the same time in most cases.

When PLA is stored at high RH conditions or immersed in liquid water, the shape of the endothermic peak associated with the glass transition becomes broader, due to the hydrolysis and plasticization effects of water that create water–water interactions (clusters) between the carbonyl groups, thus also accelerating the kinetics of physical aging. These storage conditions also lead to an increase in crystallinity (Fig. 8).

The rate of PLA hydrolysis in aqueous media depends on the temperature. For temperatures higher than the T_g , the kinetics obeys the Arrhenius model and follow a first-order reaction. Moreover, a lower activation energy is required, due to a higher increase in chain mobility. For temperatures below the T_g , the kinetics of hydrolysis can deviate from Arrhenian behavior and display a higher activation energy.

The pH does not affect the hydrolysis rate for PLA films (in the range from 3 to 7). This is key information for the application of PLA films in contact with moist foods whatever their acidity, as a very wide range of moist foods (cooked or fresh fruits and vegetables,

Figure 6 (A) DSC normalized heat flow obtained on PLA with aging times varying from 0 to 1000 h at 45 °C, at increasing time from left to right. The aging times are 30 min, 1 h, 2 h, 3 h, 5 h, 50 h, 72 h, and 1000 h. The curve corresponding to the zero aging does not exhibit any peak of recovery. (A) Amorphous PLA (B) Maximum crystallized PLA ($X_c = 42\%$). (C) Semi crystalline PLA ($X_c = 22\%$). Reproduced with permission from Delpouve et al. (2014). Copyright 2013 John Wiley and Sons.



cheeses, dairy products, meat and meat-based products, delicatessen, tomato paste, *etc.*) could be packed in PLA films or trays, provided that the shelf life of the PLA material would be longer than that of the packed product.

From a practical point of view, this overview of PLA stability indicates that PLA film is a very suitable packaging for semi-dry or dry foods, which are characterized by $a_w \leq 0.5$. In these conditions PLA is chemically stable and no hydrolysis occurs. Nevertheless, physical aging will take place, especially if the storage temperature is close to the T_g . When PLA is used to pack high moisture foods or beverages having $a_w \approx 1$, particular attention has to be paid to the stability. In such cases, shelf life testing of the packaging is required, since the PLA can highly interact with the water molecules coming from the food and therefore be altered. Consequently, the functional properties of the packaging can be modified, and the protection of the food quality can be quickly lost during time. In the case of biodegradable polymers like PLA, it thus becomes necessary to estimate the shelf life of the packaging along with the shelf life of the food according to the application targeted.

Figure 7 (A) Yield strength, (B) tensile modulus, and (C) fracture strain as a function of log (aging time, t_a/h) for PLLA samples annealed at 4, 25, and 40 °C. The dotted lines represent the data of the unaged PLLA specimen. Reproduced from **Pan et al. (2007)** Copyright © 2007 American Chemical Society with permission.

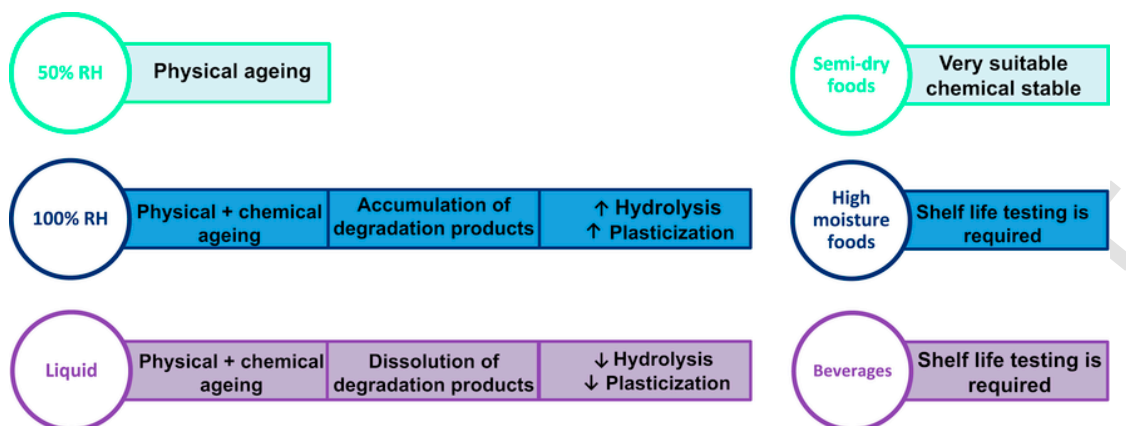


Figure 8 Main phenomena that affect PLA stability according to different storage conditions and suitability as a food packaging material.

References

- Aou, K., Hsu, S.L., Kleiner, L.W., Tang, F.-W., 2007. Roles of conformational and configurational defects on the physical aging of amorphous poly(lactic acid). *J. Phys. Chem. B* 111 (42), 12322–12327.
- ASTM F2579, 2010. Standard Specification for Amorphous Poly(Lactide) and Poly(Lactide-Co-Glycolide) Resins for Surgical Implants.
- Auras, R., Harte, B., Selke, S., 2004. An overview of polylactides as packaging materials. *Macromol. Biosci.* 4 (9), 835–864.
- Auras, R., Lim, L.-T., Selke, S., Tsuji, H., 2010. *Poly(Lactic Acid): Synthesis, Structures, Properties, Processing, and Applications*. John Wiley & Son, Inc, Hoboken, New Jersey.
- Avolio, R., Castaldo, R., Gentile, G., Ambrogio, V., Fiori, S., Avella, M., Cocca, M., Errico, M.E., 2015. Plasticization of poly(lactic acid) through blending with oligomers of lactic acid: effect of the physical aging on properties. *Eur. Polym. J.* 66, 533–542.
- Bai, H., Deng, S., Bai, D., Zhang, Q., Fu, Q., 2017. Recent advances in processing of stereocomplex-type polylactide. *Macromol. Rapid Commun.* 38 (23), 1700454.
- Burgos, N., Martino, V.P., Jiménez, A., 2013. Characterization and ageing study of poly(lactic acid) films plasticized with oligomeric lactic acid. *Polym. Degrad. Stab.* 98 (2), 651–658.
- Carothers, W.H., Dorrough, G.L., van Natta, F.J., 1932. Studies of polymerization and ring formation. X. The reversible polymerization of six-membered cyclic ester. *J. Am. Chem. Soc.* 54 (2), 761–772.
- Castro-Aguirre, E., Iñiguez-Franco, F., Samsudin, H., Fang, X., Auras, R., 2016. Poly(lactic acid) - mass production, processing, industrial applications, and end of life. *Adv. Drug Deliv. Rev.* 107, 333–366.
- Commission Regulation (EC) 2073 (2005) of 15 November 2005 on microbiological criteria for foodstuffs.
- Commission Regulation (EC) No 10 (2011) of 14 January 2011 on plastic materials and articles intended to come into contact with food.
- Copinot, A., Bertrand, C., Govindin, S., Coma, V., Couturier, Y., 2004. Effects of ultraviolet light (315 nm), temperature and relative humidity on the degradation of polylactic acid plastic films. *Chemosphere* 55 (5), 763–773.
- Delpouve, N., Arnoult, M., Saiter, A., Dargent, E., Saiter, J.-M., 2014. Evidence of two mobile amorphous phases in semicrystalline polylactide observed from calorimetric investigations. *Polym. Eng. Sci.* 54 (5), 1144–1150.
- Directive 13/EC 2000 of the European Parliament and of the Council of 20 March 2000 on the approximation of the laws of the Member States relating to the labelling, presentation and advertising of foodstuffs.
- Dobircan, L., Delpouve, N., Herbinet, R., Domenek, S., Le Pluart, L., Delbreilh, L., Ducruet, V., Dargent, E., 2015. Molecular mobility and physical ageing of plasticized poly(lactide). *Polym. Eng. Sci.* 55 (4), 858–865.
- Domenek, S., Fernandes-Nassr, S., Ducruet, V., 2018. Rheology, mechanical properties, and barrier properties of poly(lactic acid). In: Di Lorenzo, M.L., Androsch, R. (Eds.), *Synthesis, Structure and Properties of Poly(lactic Acid)*. Springer International Publishing, Cham, pp. 303–341.
- Ducruet, V., Domenek, S., 2015. Characteristics and applications of PLA. In: Kalia, S., Averous, L. (Eds.), *Biodegradable and Biobased Polymers for Environmental and Biomedical Applications*. Scrivener Publishing LLC, Beverly, MA, pp. 171–224.
- Erne, P., Schier, M., Resink, T.J., 2006. The road to bioabsorbable stents: reaching clinical reality?. *Cardiovasc. Interv. Radiol.* 29 (1), 11–16.
- European Bioplastic Association, 2018a. Global Production Capacities of Bioplastics 2018–2023.
- European Bioplastic Association, 2018b. What Are Bioplastics? Material Types, Terminology, and Labels - an Introduction.
- Garlotta, D., 2001. A literature review of poly(lactic acid). *J. Polym. Environ.* 9 (2), 63–84.
- Gonzalez, M.F., Ruseckaitė, R.A., Cuadrado, T.R., 1999. Structural changes of polylactic-acid (PLA) microspheres under hydrolytic degradation. *J. Appl. Polym. Sci.* 71 (8), 1223–1230.
- Gorrasi, G., Pantani, R., 2013. Effect of PLA grades and morphologies on hydrolytic degradation at composting temperature: assessment of structural modification and kinetic parameters. *Polym. Degrad. Stab.* 98, 1006–1014.
- Gruber, P.R., Hall, E.S., Kolstad, J.J., Iwen, M.L., Benson, R.D., Borchardt, R.L., 1994. U.S. Patent 5,357,035.
- Gruber, P.R., Hall, E.S., Kolstad, J.J., Iwen, M.L., Benson, R.D., Borchardt, R.L., 2001. U.S. Patent 6,326,458.
- Harris, A.M., Lee, E.C., 2010. Heat and humidity performance of injection molded PLA for durable applications. *J. Appl. Polym. Sci.* 115 (3), 1380–1389.
- Holm, V.K., 2010. Shelf life of foods in biobased packaging. In: Robertson, G.L. (Ed.), *Food Packaging and Shelf Life: A Practical Guide*. CRC Press, Boca Raton, pp. 353–362.
- Holm, V.K., Ndoni, S., Risbo, J., 2006. The stability of poly(lactic acid) packaging films as influenced by humidity and temperature. *J. Food Sci.* 71 (2), E40–E44.

- Hutchinson, J.M., 1995. Physical aging of polymers. *Prog. Polym. Sci.* 20 (4), 703–760.
- Ikada, Y., Jamshidi, K., Tsuji, H., Hyon, S.H., 1987. Stereocomplex formation between enantiomeric poly(lactides). *Macromolecules* 20 (4), 904–906.
- ISO 17556, 2012. Plastics - Determination of the Ultimate Aerobic Biodegradability of Plastic Materials in Soil by Measuring the Oxygen Demand in a Respirometer or the Amount of Carbon Dioxide Evolved.
- ISO 13781, 2017. Implants for Surgery - Homopolymers, Copolymers and Blends on Poly(lactide) - in Vitro Degradation Testing.
- Jamshidian, M., Tehrani, E.A., Imran, M., Jacquot, M., Desobry, S., 2010. Poly-Lactic Acid: production, applications, nanocomposites, and release studies. *Compr. Rev. Food Sci. Food Saf.* 9 (5), 552–571.
- Kucharczyk, P., Hnatkova, E., ZdenekDvorak, Sedlarik, V., 2013. Novel aspects of the degradation process of PLA based bulky samples under conditions of high partial pressure of water vapour. *Polym. Degrad. Stab.* 98 (1), 150–157.
- Langer, R., 1998. Drug delivery and targeting. *Nature* 392, 5–10.
- Li, S., 1999. Hydrolytic degradation characteristics of aliphatic polyesters derived from lactic and glycolic acids. *J. Biomed. Mater. Res.* 48 (3), 342–353.
- Li, S., McCarthy, S., 1999. Further investigations on the hydrolytic degradation of poly (DL-lactide). *Biomaterials* 20 (1), 35–44.
- Li, S.M., Vert, M., 2002. Biodegradation of aliphatic polyester. In: Scott, G. (Ed.), *Degradation of Polymers: Principles and Applications*. Springer Netherlands.
- Lyu, S., Schley, J., Loy, B., Lind, D., Hobot, C., Sparer, R., Untereker, D., 2007. Kinetics and time-temperature equivalence of polymer degradation. *Biomacromolecules* 8 (7), 2301–2310.
- Maharana, T., Mohanty, B., Negi, Y.S., 2009. Melt–solid polycondensation of lactic acid and its biodegradability. *Prog. Polym. Sci.* 34 (1), 99–124.
- Makino, K., Arakawa, M., Kondo, T., 1985. Preparation and in vitro degradation properties of polylactide microcapsules. *Chem. Pharm. Bull.* 33 (3), 1195–1201.
- Migliaresi, C., Fambri, L., Cohn, D., 1994. A study on the in vitro degradation of poly (lactic acid). *J. Biomater. Sci. Polym. Ed.* 5 (6), 591–606.
- Monnier, X., Saiter, A., Dargent, E., 2017. Physical aging in PLA through standard DSC and fast scanning calorimetry investigations. *Thermochim. Acta* 648, 13–22.
- Monnier, X., Fernandes Nassar, S., Domemek, S., Guinault, A., Sollogoub, C., Dargent, E., Delpouve, N., 2018. Reduced physical aging rates of polylactide in polystyrene/polylactide multilayer films from fast scanning calorimetry. *Polymer* 150, 1–9.
- NF EN 13432 2000. Requirements for Packaging Recoverable through Composting and Biodegradation.
- Nicoli, M.C. (Ed.), 2012. *Shelf Life Assessment of Food*. CRC Press, Boca Raton, FL.
- Pan, P., Zhu, B., Inoue, Y., 2007. Enthalpy relaxation and embrittlement of poly(l-lactide) during physical aging. *Macromolecules* 40 (26), 9664–9671.
- Panseri, S., Martino, P.A., Cagnardi, P., Celano, G., Tedesco, D., Castrica, M., Balzaretto, C., Chiesa, L.M., 2018. Feasibility of biodegradable based packaging used for red meat storage during shelf-life: a pilot study. *Food Chem.* 249, 22–29.
- Peelman, N., Ragaert, P., Vandemoortele, A., Verguldt, E., De Meulenaer, B., Devlieghere, F., 2014. Use of biobased materials for modified atmosphere packaging of short and medium shelf-life food products. *Innovat. Food Sci. Emerg. Technol.* 26, 319–329.
- Reddy, M.M., Vivekanandhan, S., Misra, M., Bhatia, S.K., Mohanty, A.K., 2013. Biobased plastics and bionanocomposites: current status and future opportunities. *Prog. Polym. Sci.* 38 (10), 1653–1689.
-) Regulation No 1169 (2011) of the European Parliament and of the Council of 25 October 2011 on the provision of food information to consumers.
- Righetti, M.C., Gazzano, M., Delpouve, N., Saiter, A., 2017. Contribution of the rigid amorphous fraction to physical ageing of semi-crystalline PLLA. *Polymer* 125, 241–253.
- Robertson, G.L., 2010. *Food Packaging and Shelf Life: A Practical Guide*. CRC Press, Boca Raton, FL.
- Robertson, G.L., 2013. *Food Packaging: Principles and Practice*. CRC Press, Boca Raton, FL.
- Rocca-Smith, J.R., 2017. *A Contribution of Understanding the Stability of Commercial PLA Films for Food Packaging and its Surface Modifications*. PhD thesis. University of Burgundy, & University of Udine.
- Rocca-Smith, J.R., Chau, N., Champion, D., Brachais, C.H., Marcuzzo, E., Sensidoni, A., Piasente, F., Karbowski, T., Debeaufort, F., 2017a. Effect of the state of water and relative humidity on ageing of PLA films. *Food Chem.* 236, 109–119.
- Rocca-Smith, J.R., Whyte, O., Brachais, C.-H., Champion, D., Piasente, F., Marcuzzo, E., Sensidoni, A., Debeaufort, F., Karbowski, T., 2017b. Beyond biodegradability of poly (lactic acid): physical and chemical stability in humid environments. *ACS Sustain. Chem. Eng.* 5 (3), 2751–2762.
- Rocca-Smith, J.R., Pasquarelli, R., Lagorce-Tachon, A., Rousseau, J., Fontaine, S., Aguié-Béghin, V., Debeaufort, F., Karbowski, T., 2019. Toward sustainable PLA-based multilayer complexes with Improved barrier properties. *ACS Sustain. Chem. Eng.* <https://doi.org/10.1021/acssuschemeng.8b04064>.
- Romani, S., Tappi, S., Balestra, F., Rodriguez Estrada, M.T., Siracusa, V., Rocculi, P., Dalla Rosa, M., 2015. Effect of different new packaging materials on biscuit quality during accelerated storage. *J. Sci. Food Agric.* 95 (8), 1736–1746.
- Ruellan, A., Ducruet, V., Domemek, S., 2015. Plasticization of poly(lactide). In: Alfonso, J., Peltzer, M., Ruseckaite, R. (Eds.), *Poly(Lactic Acid) Science and Technology: Processing, Properties, Additives and Applications*. The Royal Society of Chemistry, Cambridge, United Kingdom, pp. 124–170.
- Ruellan, A., Ducruet, V., Gratia, A., Saelices Jimenez, L., Guinault, A., Sollogoub, C., Chollet, G., Domemek, S., 2016. Palm oil deodorizer distillate as toughening agent in polylactide packaging films. *Polym. Int.* 65 (6), 683–690.
- Schliecker, G., Schmidt, C., Fuchs, S., Kissel, T., 2003. Characterization of a homologous series of D,L-lactic acid oligomers; a mechanistic study on the degradation kinetics in vitro. *Biomaterials* 24 (21), 3835–3844.
- Soares, J.S., Moore, J.E.J., Rajagopal, K.R., 2008. Constitutive framework for biodegradable polymers with applications to biodegradable stents. *Am. Soc. Artif. Intern. Organs J.* 54 (3), 295–301.
- Sonchaeng, U., Iñiguez-Franco, F., Auras, R., Selke, S., Rubino, M., Lim, L.-T., 2018. Poly(lactic acid) mass transfer properties. *Prog. Polym. Sci.* 86, 85–121.
- Struik, L.C.E., 1977. Physical aging in plastics and other glassy materials. *Polym. Eng. Sci.* 17 (3), 165–173.
- Tsuji, H., 2010. Hydrolytic degradation. In: Auras, R., Lim, L.-T., Selke, S.E.M., Tsuji, H. (Eds.), *Poly(Lactic Acid): Synthesis, Structures, Properties, Processing, and Applications*. John Wiley & Sons, Inc, Hoboken, New Jersey, pp. 345–376.
- Tsuji, H., Mizuno, A., Ikada, Y., 2000a. Properties and morphology of poly(l-lactide) 4. Effects of structural parameters on long-term hydrolysis of poly(l-lactide) in phosphate-buffered solution. *Polym. Degrad. Stab.* 67 (1), 179–189.
- Tsuji, H., Mizuno, A., Ikada, Y., 2000b. Properties and morphology of poly(L-lactide). III. Effects of initial crystallinity on long-term in vitro hydrolysis of high molecular weight poly(L-lactide) film in phosphate-buffered solution. *J. Appl. Polym. Sci.* 77 (7), 1452–1464.
- Tsuji, H., Daimon, H., Fujie, K., 2003. A new Strategy for recycling and preparation of poly(l-lactic acid): Hydrolysis in the Melt. *Biomacromolecules* 4 (3), 835–840.
- Tsuji, H., Saeki, T., Tsukegi, T., Daimon, H., Fujie, K., 2008. Comparative study on hydrolytic degradation and monomer recovery of poly(l-lactic acid) in the solid and in the melt. *Polym. Degrad. Stab.* 93 (10), 1956–1963.
- Vyavahare, O., Ng, D., Ling Hsu, S., 2014. Analysis of structural rearrangements of poly(lactic acid) in the presence of water. *J. Phys. Chem. B* 118 (15), 4185–4193.

- Witzke, D.R., 1997. Introduction to Properties, Engineering, and Propsects of Polylactide polymers. PhD thesis. Michigan State University, East Lansing, MI.
- World Economic Forum, 2016. The New Plastic Economy: Rethinking the Future of Plastics.
- Wunderlich, B., 2003. Reversible crystallization and the rigid–amorphous phase in semicrystalline macromolecules. *Prog. Polym. Sci.* 28 (3), 383–450.

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