INFLUENCE OF PLASTICIZERS ON THE COMPOSTABILITY OF POLYLACTIC ACID

Marina P. Arrieta [ORCID]

Departamento de Ingeniería Química Industrial y del Medio Ambiente, Universidad Politécnica de Madrid, E.T.S.I. Industriales, Calle José Gutiérrez Abascal 2, 28006, Madrid, Spain.

Grupo de Investigación: Polímeros, Caracterización y Aplicaciones (POLCA) Madrid, Spain.

Abstract:

Poly(lactic acid) (PLA) has gained considerable attention as an interesting biobased and biodegradable polymer for film for food packaging applications, due to its many advantages such as biobased nature, high transparency and inherent biodegradable/compostable character. With the dual objective to improve PLA processing performance and to obtain flexible materials, plasticizer are use as strategy for extending PLA applications as compostable film for food packaging applications. Several plasticizers (i.e.: citrate esters, polyethylene glycol (PEG), oligomeric lactic acid (OLA), etc.) as well as essential oils and maleinized and/or epoxidized seed oils are widely used for flexible PLA film production. This article reviews the most relevant compostable PLA-plasticized flexible film formulations with an emphasis on plasticizer effect on the compostability rate of PLA polymeric matrix with the aim to get information of the possibility to use plasticized PLA-based formulatios as compostable films for sustainable industrial packaging production.

Keywords: Biobased polymers, Biodegradable polymers, Polylactic acid, Plasticizers, Compostability.

1. Introduction

In the last few years, biodegradable polymer industry has considerably increased as an alternative to non-degradable traditional polymers with the main objective to address the problems generated by plastic waste accumulation in landfill and oceans, particularly in short term applications such as food packaging, agricultural mulch films, disposable cutlery, etc. Simultaneously, the use of biobased polymeric formulations is currently growing in order to reduce the consumption of non-renewable resources. Among others biopolymers, poly(lactic acid) (PLA) is one of the most important biobased and biodegradable polymer candidates for short term applications due to its many advantages.

2. PLA production and properties

PLA environmentally beginning characteristics are related with the fact that it is a thermoplastic biopolyester derived from renewable resources, such as the fermentation of simple sugars (mainly starch and sugar cane). PLA is currently available in the market at a competitive cost (Arrieta, Samper, Aldas, & López, 2017; Auras, Harte, & Selke, 2004; Luzi et al., 2015). Bioplastics (biobased and/or biodegradable plastics) represent nowadays only about one per cent of the global annual production of plastics (Bioplastics, 2020) (about 359 million tonnes annually) (Figure 1) (Plastic Europe, 2019). In fact, the bioplastic production has reached 2.11 million tonnes in 2019 (Bioplastics, 2020), being 13.9% of this production of PLA. Nevertheless, as demand is rising, each year the

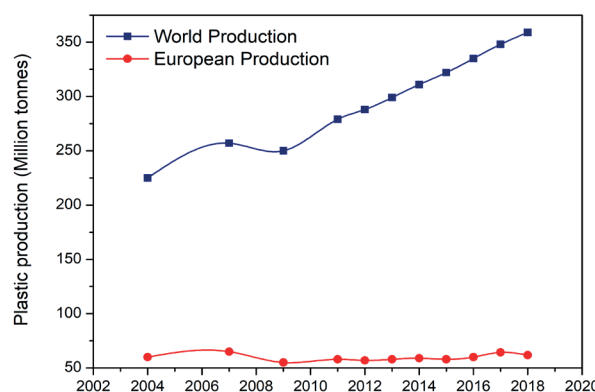bioplastic market (including that of PLA) is growing very dynamically (Bioplastics, 2020).

Figure 1: World and European Plastic production. Data obtained from Reference (Plastic Europe, 2019).

A schematic representation of the industrial PLA production is showed in Figure 2. Lactic acid manufacture utilizes the homofermentative pathway of dextrose, generally mediated by *Lactobacillus* (operating at pH between 5.4 and 6.4, 38–42 °C and a low oxygen concentration) (Auras et al., 2004; Madhavan, Nimisha Rajendran, & Rojan Pappy, 2010), to obtain the lactic acid monomers (D(-)-lactic acid and L(+)-lactic acid) which are then pre-polymerized to obtain an intermediate low molecular mass poly(lactic acid) pre-polymer (Auras et al., 2004) with water remove under mild conditions (Vink, Rábago, Glassner, & Gruber, 2003). The low molecular mass pre-polymer is further catalytically converted into lactide

*Corresponding author: Marina P. Arrieta, m.arrieta@upm.es

stereoisomers, the cyclic dimers of lactic acid (Auras et al., 2003; Vink et al., 2003), mainly in the form of the *L*-isomer (Lim, Auras, & Rubino, 2008). Then, purified lactide by distillation is further polymerized in a solvent free ring-opening polymerization (ROP) process to obtain high molecular weight PLA, with controlled optical purity (Auras et al., 2004). The final properties of PLA are determined by the weight ratio of the two lactic acid stereoisomers and, thus, PLA can vary from totally amorphous (with 50–93% L-lactic acid) to semi-crystalline (containing more than 93% of L-lactic acid) (Auras et al., 2004; Petersson, Kvien, & Oksman, 2007).
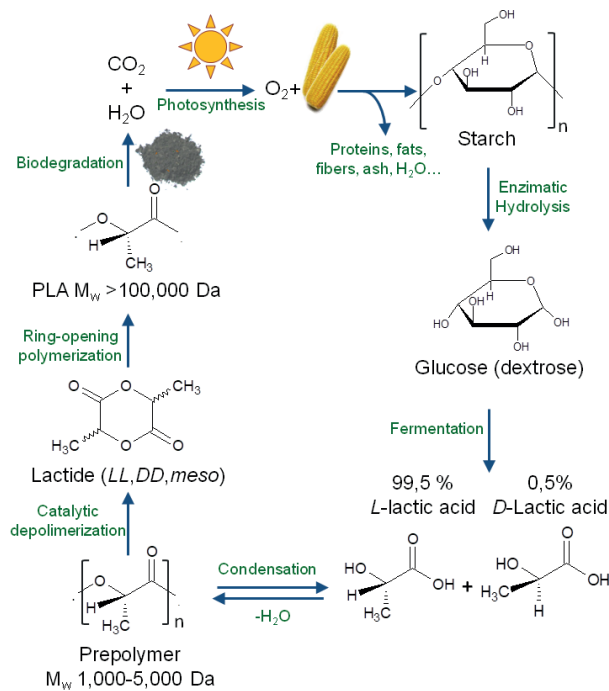

Figure 2: Schematic representation of high molecular weight PLA production at industrial level.

Another important point is that PLA is ease of processing by already available thermoplastic technologies at industrial level such as melt-blending, extrusion, injection molding, blow molding, film forming and thermoforming (Arrieta, Fortunati, et al., 2014a). Therefore, high amount of the plastic production is demanded by the packaging sector (Figure 3), which are commonly short term applications.
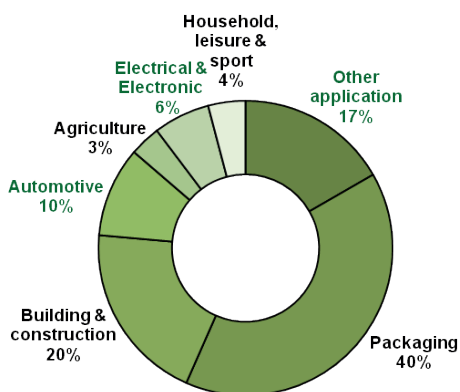

Figure 3: Plastic demand by sector in Europe in 2019. Data obtained from Reference (Plastic Europe, 2019).

In this sense, PLA possesses several interesting properties for the food packaging industry. First of all, it is classified as generally recognized as safe (GRAS) by the Food and Drug Administration (FDA) and, thus, it is safe for food related applications (Arrieta, Samper, et al., 2017; Jamshidian, Tehrany, Imran, Jacquot, & Desobry, 2010). PLA also has excellent printability (Fortunati et al., 2012). It is high transparent, and this is why it is highly appreciated for film production intended for food packaging purposes, since seeing through the packaging film is one of the most important requirements for consumers (Arrieta, Fortunati, et al., 2014a; Auras et al., 2004; Fortunati, Armentano, Iannoni, & Kenny, 2010). In fact, PLA sheeting shows transparency around 95% (transmission of visible light in the range 540–560 nm) (Auras et al., 2004). PLA has high mechanical strength and stiffness, being often compared to polystyrene (PS) or polyethylene terephthalate (PET) (Auras et al., 2004; Petersson et al., 2007; Villegas et al., 2019). Conversely, the use of PLA in film food packaging applications has been somewhat limited due to its poor ductility, reduced thermal stability and low barrier properties when compared to equivalent petroleum based and non-compostable polymers (Arrieta, Samper, et al., 2017; Burgos, Martino, & Jiménez, 2013; Luzi et al., 2015). These problems have been solved or at least reduced by co-polymerization (Arrieta & Peponi, 2017; Shinoda et al., 2003) or by plasticization either with plasticizers (Abdelwahab et al., 2012; Burgos et al., 2013; Fortunati et al., 2014) or by several kind of oils: essential oils (Arrieta, López, Hernández, & Rayón, 2014; Luzi et al., 2019; Villegas et al., 2019) as well as epoxidized and/or maleinized seed oils (Carbonell-Verdu et al., 2018; Carbonell-Verdu, Garcia-Garcia, et al., 2017; Carbonell-Verdu, Samper, Garcia-Garcia, Sanchez-Nacher, & Balart, 2017; Garcia-Garcia, Carbonell-Verdu, Arrieta, López-Martínez, & Samper, 2020; Pawlak, Aldas, Parres, López-Martínez, & Arrieta, 2020; Quiles-Carrillo et al., 201b8). From an industrial point of view, plasticization approaches are preferred since can be easily transfer from laboratory scale level to industrial level. The modification of PLA by increasing the polymer chain mobility by means of the above mentioned approaches could also affect the hydrolytic disintegration rate of PLA under composting, and thus offering the opportunity to modulate the compostability.

3. PLA wastes

PLA wastes are potentially recyclable (Agüero et al., 2019; Beltrán, Arrieta, Gaspar, de la Orden, & Urreaga, 2020; Beltrán, Lorenzo, de la Orden, & Martínez-Urreaga, 2016), but although the corresponding sorting technology is already available, no separate recycling stream yet exists (Bioplastics, 2020). Additionally, consumers also have low information regarding where they have to throw away biodegradable plastics after their useful life (Arrieta, Samper, et al., 2017). Therefore, biodegradable PLA products are commonly disposed with traditional plastics and if the required sorting step is not implemented, PLA wastes can contaminate traditional recycled plastics, interfering with traditional non-degradable plastic recycling efforts (Samper, Arrieta, Ferrándiz, & López, 2014; Samper, Bertomeu, Arrieta, Ferri, & López-Martínez, 2018). It is expected that the recycling of so called post consumer PLA, which is a treatment option which ranks

higher on the European waste hierarchy, will be easily feasible as soon as the commercial volumes of PLA increases sufficiently to cover the investments required (Bioplastics, 2020). Thus, compostability represents a clear benefit for its end-life mainly when PLA items are mixed with biowastes (Bioplastics, 2020). The PLA compostability is managed by aerobic fermentation that ultimately results in humus-rich soil (Figure 4) (Arrieta, Fortunati, et al., 2014b). Meanwhile, the degradation of waste in landfills is mediated by anaerobic fermentation, which is considerably less odorous than its aerobic counterpart, but it takes longer time (Yagi, Ninomiya, Funabashi, & Kunioka, 2013).
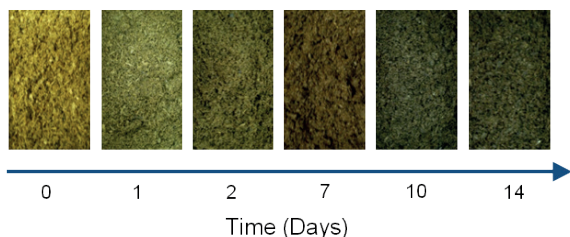

Figure 4: Visual appearance evolution of compost soil during PLA-based film formulations disintegration under composting following the European standard ISO 20200 (films thickness between 10 and 30 μm). Reprinted with permission of references (Arrieta, Fortunati, et al., 2014b).

As it was already commented, PLA composting within a time frame of 6-12 weeks under composting controlled conditions (temperature = 58 °C, water content = 60%, pH ≅ 7.5, C/N relationship between 20:1 and 40:1 as well as aeration) (Arrieta, Samper, et al., 2017; Kale et al., 2007) is managed by aerobic fermentation (Bioplastics, 2020), but it begins with a random non-enzymatically surface hydrolysis, that leads in a significantly molar weight reduction followed by the enzymes action all over the bulk of PLA-based material (Arrieta, López, Rayón, & Jiménez, 2014a; Kale, Auras, & Singh, 2006; Kale et al., 2007). PLA has ester linkages in the polymer backbone which play a predominant role as biodegradable plastic due to their potentially hydrolysable ester bonds (Madhavan et al., 2010; Shah, Hasan, Hameed, & Ahmed, 2008). As a result, PLA is finally disintegrated in low-molecular weight species (Kale et al., 2007; Song, Murphy, Narayan, & Davies, 2009) (Figure 5) and the resultant breakdowns are suitable for further degradation mediated by the micro-organisms. It has been observed that that during the first days of composting process, PLA-based samples immediate increases in thickness, ascribed to the swelling phenomenon as a consequence to the high temperature levels and the enlarged porous structure due to hydrolysis of the polymer. For instance the wall of PLA-based bottles doubled the thicknesses after the first day in the compost pile (Kale et al., 2006). Similarly, Balart et al. (2018) studied the disintegration under composting conditions of PLA plasticized with epoxidized linseed oil (ELO) and reinforced with hazelnut shell flour (HSF). They observed that the diffusion of water from the soil to the plasticized PLA-based composites promotes overall swelling and this phenomenon prompts the microorganism attack (Balart et al., 2018). Initially, a change in the refraction index of PLA takes place due to the water absorption as well as the presence of shorter polymer chains formed during the hydrolytic degradation process, which results in a loss

of the high transparency of PLA (Arrieta, López, et al., 2014a; Fortunati, Puglia, Santulli, Sarasini, & Kenny, 2012b). Then, as the hydrolysis process progress, PLA-based samples decrease in size evidenced by a reduction of the sample thickness accompanied with an increase in PLA fragility (Arrieta, Fortunati, et al., 2014a; Siracusa, Rocculi, Romani, & Rosa, 2008). Several bacterial strains, for instance those belonging to the genera *Actinomadura*, *Streptomyces* and *Laceyella*, utilize polyesters as a carbon source having good polyester-degrading activity (Sriyapai, Chansiri, & Sriyapai, 2018). Depolymerase enzymes (i.e.: lipase, esterase, proteinase K, alcalase and protease) have the ability to degrade biopolyester and they can accelerate the PLA degradation in compost (Arrieta, Samper, et al., 2017; Musioł et al., 2016; Sriyapai et al., 2018). PLA amorphous regions are firstly attacked by microorganisms, contributing to reduce the PLA high transparency (Arrieta, Samper, et al., 2017; Fortunati et al., 2012b). The crystalline regions are the latest which disintegrate in compost, while at the end of the process the resulting end-products are carbon dioxide, water and a small amount biomass (Bioplastics, 2020; Kale et al., 2006; Kale et al., 2007).
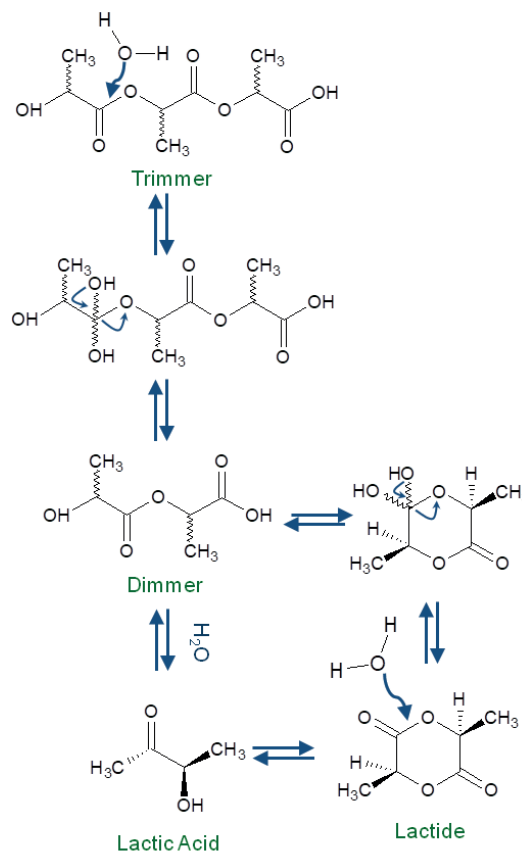

Figure 5: Schematic representation of PLA hydrolysis process and molecular weight reduction. Adapted from Kale et al. (Kale et al., 2006).

The relationship between *meso*-lactide and lactide (either *L*- or *D*-lactide) forms has been used as a semi-quantitative signal of the degradation mechanism of PLA in biotic media (Arrieta et al., 2014; Khabbaz, Karlsson, & Albertsson, 2000). In fact, microorganisms prefer de *L*-lactide than *D*-lactide form (Khabbaz et al., 2000). For that reason, the relationship between *meso*-lactide and lactide decrease

during composting as a consequence of the *meso*-lactide form increases in the remaining polymeric matrix during compostability, as it was measured by Pyrolysis-Gas Chromatography–Mass Spectrometry device (Py-GC/MS) (Arrieta et al,. 2014). Moreover, changes in compost colour take place as a consequence of the aerobic fermentation that results in dark humus-rich soil (Arrieta, López, Rayón, & Jiménez, 2014b).

4. PLA plasticization effect on PLA compostability

The use of plasticizers is a regular practice performed at plastic processing industry to both, facilitate the PLA processability as well as to obtain PLA-based flexible materials (i.e.: for film manufacturing). An optimal additive for sustainable films production should promote the hydrolysis rate of biodegradable plastic, without changing their inherent properties (strength, modulus, elongation, transparency, etc.) (Shinoda et al., 2003). Several authors have studied the polymer disintegration under composting following the European standard ISO 20200 (UNE-EN ISO, 2016). In general, the presence of plasticizers speed up the PLA disintegration under composting due to the increased polymer chain mobility. Although the time required to completely disintegrated PLA-plasticized films its strongly dependant of the film thickness, it generally takes around 1 month (i.e. films with thickness between 200-500 µm (Arrieta, López, et al., 2014a). While in the case of injecteinjection-molded pieces (with thickness of 4 mm) the required time is between 6 and 8 weeks) (Quiles-Carrillo, Montanes, Lagaron, Balart, & Torres-Giner, 2018a). For instance, typical plasticizers for PLA are poly(ethylene glycol) (PEG) (Arrieta, J. López, et al., 2014a) and acetyl-tri- butyl citrate (ATBC) (Aragón-Gutierrez, Arrieta, López-González, Fernández-García, & López, 2020; Arrieta, Fortunati, Dominici, López, & Kenny, 2015; Arrieta, López, et al., 2014a; Arrieta, Peponi, López, & Fernández-García, 2018), and both are able to increase the PLA disintegration in compost (see **Figure 6**).
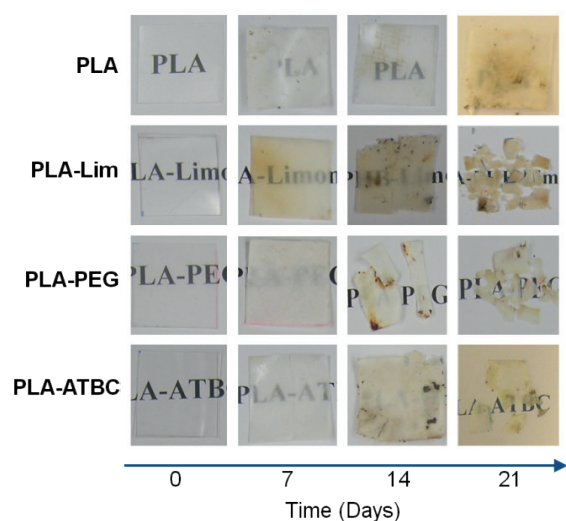

Figure 6: Visual appearance of PLA and plasticized PLA films with D-limonene essential oil as well as PEG and ATBC plasticizers. Reprinted with permission of references (Arrieta et al., 2014; Arrieta, López, et al., 2014a).

For instance, Arrieta et al. (2014) have studied the influence of PEG and ATBC plasticizers on the disintegration rate as well on the loss of the mechanical properties of PLA films with thickness around 200±50 µm. Although, both plasticizers speed up the disintegration rate of PLA, PEG produce a faster disintegration rate than ATBC. Similarly, the diminution in hardness and reduced modulus was more evident in films plasticized with PEG, than in films plasticized with ATBC and ascribed to the more hydrophilic nature of PEG (Arrieta, López, et al., 2014a). In the meantime, for PLA-ATBC plasticized thicker films (thickness ranged from 10 to 30 µm) while neat PLA film requires 2 weeks to reach the goal of the disintegrability test, PLA-ATBC based films were disintegrated in 1 week (Arrieta et al., 2015). Similarly, the incorporation of other typical PLA plasticizer into PLA-based formulations such as oligomeric lactic acid (OLA) also speed up the degradation kinetic of PLA under composting respect to neat PLA films (Arrieta, García, López, Fiori, & Peponi, 2019; Arrieta, Perdiguero, Fiori, Kenny, & Peponi, 2020; Burgos et al., 2017; Luzi et al., 2019).

The presence of other additives able to increase the crystallinity of PLA will delay the disintegration process. For instance, the presence of more crystalline polymeric matrix such as polyhydroxybutyrate (PHB), widely used to produce PLA-PHB blends, delay the disintegration process of plasticized PLA systems (Arrieta et al., 2015; Arrieta, López, et al., 2014a; Burgos et al., 2017; Luzi et al., 2019). In the case of plasticized-PLA multiphase systems, different behaviours have been observed. For instance, Arrieta et al. incorporated organic micro fillers such as chitosan (Arrieta, López, López, Kenny, & Peponi, 2016b), catechin (Arrieta et al., 2016b), and nanofillers such as cellulose nanocrystals (CNC) (Arrieta et al., 2015; Arrieta, López, López, Kenny, & Peponi, 2016a) or lignocellulose nanoparticles (Arrieta et al., 2018) to ATBC-based plasticized systems and observed although the particles increased the crystallinity of ATBC-based PLA systems (with 15 wt.% of ATBC), all of them speed up the disintegration under composting conditions ascribed to the high amount of -OH groups able to interact with water in the initial steps of the disintegration and, thus, accelerating the overall disintegration process (Arrieta et al., 2015; Arrieta et al., 2016a, 2016b). Similarly, OLA-based PLA systems loaded with CNC showed that the combined effect of catechin (Arrieta et al., 2019) or CNC (Burgos et al., 2017; Luzi et al., 2019) and OLA accelerate the disintegration under composting of PLA-based formulations. On the other hand, Aragon-Gutierrez et al. have recently developed PLA plasticized with 15 wt.% of ATBC and further loaded with silica aerogel and founded that both additives provided opposites effects. While ATBC leads to a expected increase in the disintegration rate, the silica aerogel promoted a higher degree of crystallinity, which was enhanced at the temperature of the composting test, which entails a decrease in the disintegration rate (Aragón-Gutierrez et al., 2020).

5. Essential, maleinized and epoxidized vegetable oils and their effect on PLA compostability

Natural occurring oils are increasingly being used as environmentally friendly plasticizers. In this context,

Arrieta et al. (2014) developed plasticized PLA films with 15 wt.% of D-limonene essential oil and it speed up the disintegration process of PLA (Figure 6), the quantification of D-limonene by Py-GC/MS showed that D-limonene amount was reduced from 6%, 3.5%, 2.5% to 2% in PLA-LIM systems at 0, 7, 14 and 21 days, respectively, under composting, showing that it degrades or it is lost firstly than polymeric matrix (Arrieta et al. 2014). Fortunati et al. studied the combined effect of D-limonene as PLA plasticizer and CNC as reinforcing nanofillers and obtained lower disintegration rate which was attributed to the increasing crystallinity due to CNC presence, hence affecting the water diffusion through the PLA matrix and, consequently the reducing the disintegration kinetics with respect to neat PLA (Fortunati et al., 2014). Ramos et al. 2016 developed PLA added with thymol for active film for food packaging production and observed that hydroxyl groups of thymol contributed to PLA hydrolysis, resulting in a noticeable enhancement in disintegrability of PLA-thymol formulations (Ramos et al., 2016). While the incorporation of silver nanoparticles did not significantly affected the disintegrability governed by the thymol presence which composting takes around a month (Ramos et al., 2016). Luzi et al. also used thymol as active agent to produce antibacterial active PLA-based formulations and in the same way observed that the plasticizing effect increased the disintegration under composting of PLA samples, obtaining thin PLA-based fims that were disintegrated in around 17 days (Luzi et al., 2019). Higher rates of disintegration than neat PLA were also observed by Villegas et al. 2019 in PLA films added with essential oils such as thymol and cinnamaldehyde. This behaviour was ascribed to the plasticization effect which increased the polymer chain mobility facilitating the penetration of water as well as to the more hydrophilic surfaces provided by both essential oils, particularly in the case of thymol which showed higher water affinity than cinnamaldehyde and, as a consequence, higher disintegration rate (Villegas et al., 2019). This formulations were also loaded with cloisite nanoclay and the rate of disintegration under composting conditions was slightly longer for PLA-essential oil loaded Cloisite formulations but still higher than meat PLA or PLA-Cloisite nanocomposite, being all formulations completelly disintegrated in less than two weeks (Villegas et al., 2019). Similarly, the addition of clay such as montmorillonite somewhat delay on the disintegration rate of PLA-thymol film formulations (Ramos et al., 2020). Nevertheless, it should be highlighted that all formulations were completely disintegrated in 35 days (Ramos et al., 2020).

Regarding vegetable maleinized and epoxidized oils, which are widely used as PLA plasticizers (Quiles-Carrillo et al., 2018), it seems that they are also able to increase the disitegration rate of PLA. For instance, Carbonell-Verdú et al. 2017 plasticized PLA with maleinized cottonseed oil (MCSO) and maleinized linseed oil (MLO) and observed that plasticized films become firstly fragile than neat PLA (for a composting time of 6 days) and this fragility was much more evident with increasing composting time. PLA took 14 days to disintegrate, while plasticized films with 5 wt.% of both MCSO or MLO, required 11 days to achieve the complete disintegration, suggesting that MCSO and MLO accelerated the disintegration process in controlled compost soil (Carbonell-Verdu, Garcia-Garcia, et al., 2017). Similarly, García-García et al.

(2020) plasticized PLA with epoxidized karanja oil (EKO) speed up the disintegration of PLA and ascribed this behaviour to the increased polymer chain mobility as a consequence of temperature of the composting experiment which took place at 58 °C, close to the T_g of these formulations (Garcia-Garcia et al., 2020). Quiles-Carrillo et al. (2018) used acrylated epoxidized soybean oil (AESO) as PLA plasticizer for injection-molded pieces and it was observed that AESO slightly speed up the disintegration of neat PLA (Quiles-Carrillo et al., 2018b). On the other hand, Balart et al. (2018) studied the already commented plasticized PLA-ELO composites reinforced with HSF and founded that the addition of lignocellulosic particles delayed the disintegration rate under composting. This behaviour was directly related to the fact that HSF increased the degree of crystallinity of neat PLA (Balart et al., 2018).

6. Lactic acid co-polymerization and its effects in PLA compostability

Co-polymers of lactide acid have been also used as PLA plasticizers. However, those formulations are nor commercial grade and, thus, are still not used at industrial level. For instance, poly(aspartic acid-co-lactide) (PAL) oligomer has been also used as degradation accelerator for PLA (Oyama, Tanishima, & Maekawa, 2016; Shinoda et al., 2003). In this sense, Shinoda et al. blended PLA with low amounts of PAL (up to 5 wt.%) and observed that while the transparency and the mechanical properties of PLA/PAL blends were comparable to that of neat PLA film, PAL was effective additive to increase the thermal resistance and for accelerating the hydrolytic disintegration of PLA. The degradation under composting (temperature: 58 °C and water content: 60%) and in soil was faster for PLA/PAL blend films than that of the neat PLA film (Shinoda et al., 2003). Nevertheless, it should be mentioned that the disintegration under composting conditions took less than one month, while the degradation rate in soil required almost one year to lose its integrity brooking into small pieces. Arrieta et al. (Arrieta & Peponi, 2017) used PLA and PCL tri-block co-polymer (PLLA-b-PCL-b-PLLA) to produced a polyester urethane with shape memory properties (Navarro-Baena, Marcos-Fernández, Fernández-Torres, Kenny, & Peponi, 2014) and further incorporated with catechin to produce an antioxidant packaging high flexible films with thickness around 500 μm (Arrieta & Peponi, 2017). The active materials were disintegrated under composting at laboratory scale level (Arrieta, Sessini, & Peponi, 2017). During the 50 days required to completely disintegrate the films, materials were exposed to temperatures at which the PCL block is above the melt state, leading to an increase on the polymer chain mobility which facilitates the water penetration. The presence of antioxidant additive further accelerates the disintegration process due the presence of high amount of -OH groups which are more predisposed to water attack (Arrieta, Sessini, et al., 2017). However, it should be mentioned, that although the materials were compostable, PCL is not biobased polymer and thus this formulations posses less environmental positive characteristics.

7. Conclusions

The plasticized PLA-based formulations facilitate the PLA processing, increasing the flexibility of PLA and maintained the optical transparency of the PLA matrix. Therefore, plasticized PLA system are highly interesting for the production of biobased and biodegradable films for food packaging. Several plasticizers have been widely used, mainly citrate esters (ie.: ATBC, PEG and OLA) and more recently essential oils as well as maleinized and/or epoxidized seed oils. Moreover, plasticized PLA-based formulations showed increased disintegration rate in composting, which can be delayed by the presence of other additives such as micro- or nanoparticles or another more crystalline polymeric matrix. Thus, plasticized PLA-based formulations are interesting for the production of flexible films with tuneable disintegration rate under composting conditions, showing their interest for compostable film applications.

Acknowledgements

References

Abdelwahab, M.A., Flynn, A., Chiou, B.S., Imam, S., Orts, W., Chiellini, E. (2012). Thermal, mechanical and morphological characterization of plasticized PLA-PHB blends. *Polymer Degradation and Stability, 97*(9), 1822-1828. https://doi.org/10.1016/j.polymdegradstab.2012.05.036

Agüero, A., Morcillo, M.C., Quiles-Carrillo, L., Balart, R., Boronat, T., Lascano, D.,... Fenollar, O. (2019). Study of the influence of the reprocessing cycles on the final properties of polylactide pieces obtained by injection molding. *Polymers, 11*(12), 1908. https://doi.org/10.3390/polym11121908

Aragón-Gutierrez, A., Arrieta, M.P., López-González, M., Fernández-García, M., López, D. (2020). Hybrid Biocomposites Based on Poly (Lactic Acid) and Silica Aerogel for Food Packaging Applications. *Materials, 13*(21), 4910. https://doi.org/10.3390/ma13214910

Arrieta, M.P., Fortunati, E., Dominici, F., López, J., Kenny, J.M. (2015). Bionanocomposite films based on plasticized PLA-PHB/cellulose nanocrystal blends. *Carbohydrate Polymers, 121*(0), 265-275. https://doi.org/10.1016/j.carbpol.2014.12.056

Arrieta, M.P., Fortunati, E., Dominici, F., Rayón, E., López, J., Kenny, J.M. (2014a). Multifunctional PLA-PHB/cellulose nanocrystal films: Processing, structural and thermal properties. *Carbohydrate Polymers, 107*(0), 16-24. https://doi.org/10.1016/j.carbpol.2014.02.044

Arrieta, M.P., Fortunati, E., Dominici, F., Rayón, E., López, J., Kenny, J.M. (2014b). PLA-PHB/cellulose based films: Mechanical, barrier and disintegration properties. *Polymer Degradation and Stability, 107*, 139-149. https://doi.org/10.1016/j.polymdegradstab.2014.05.010

Arrieta, M.P., García, A.D., López, D., Fiori, S., Peponi, L. (2019). Antioxidant bilayers based on PHBV and plasticized electrospun PLA-PHB fibers encapsulating catechin. *Nanomaterials, 9*(3). https://doi.org/10.3390/nano9030346

Arrieta, M.P., López, J., Hernández, A., Rayón, E. (2014). Ternary PLA-PHB-Limonene blends intended for biodegradable food packaging applications. *European Polymer Journal, 50*, 255-270. https://doi.org/10.1016/j.eurpolymj.2013.11.009

Arrieta, M.P., López, J., López, D., Kenny, J.M., Peponi, L. (2016a). Biodegradable electrospun bionanocomposite fibers based on plasticized PLA-PHB blends reinforced with cellulose nanocrystals. *Industrial Crops and Products, 93*, 290-301. https://doi.org/10.1016/j.indcrop.2015.12.058

Arrieta, M.P., López, J., López, D., Kenny, J.M., Peponi, L. (2016b). Effect of chitosan and catechin addition on the structural, thermal, mechanical and disintegration properties of plasticized electrospun PLA-PHB biocomposites. *Polymer Degradation and Stability, 132*, 145-156. https://doi.org/10.1016/j.polymdegradstab.2016.02.027

Arrieta, M.P., López, J., Rayón, E., Jiménez, A. (2014b). Disintegrability under composting conditions of plasticized PLA-PHB blends. *Polymer Degradation and Stability*. https://doi.org/10.1016/j.polymdegradstab.2014.01.034

Arrieta, M.P., Peponi, L. (2017). Polyurethane based on PLA and PCL incorporated with catechin: Structural, thermal and mechanical characterization. *European Polymer Journal, 89*, 174-184. https://doi.org/10.1016/j.eurpolymj.2017.02.028

Arrieta, M.P., Peponi, L., López, D., Fernández-García, M. (2018). Recovery of yerba mate (Ilex paraguariensis) residue for the development of PLA-based bionanocomposite films. *Industrial Crops and Products, 111*, 317-328. https://doi.org/10.1016/j.indcrop.2017.10.042

Arrieta, M.P., Perdiguero, M., Fiori, S., Kenny, J.M., Peponi, L. (2020). Biodegradable electrospun PLA-PHB fibers plasticized with oligomeric lactic acid. *Polymer Degradation and Stability, 179*. https://doi.org/10.1016/j.polymdegradstab.2020.109226

Arrieta, M.P., Samper, M.D., Aldas, M., López, J. (2017). On the use of PLA-PHB blends for sustainable food packaging applications. *Materials, 10*(9), 1008. https://doi.org/10.3390/ma10091008

Arrieta, M.P., Sessini, V., Peponi, L. (2017). Biodegradable poly(ester-urethane) incorporated with catechin with shape memory and antioxidant activity for food packaging. *European Polymer Journal, 94*, 111-124. https://doi.org/10.1016/j.eurpolymj.2017.06.047

Auras, R.A., Harte, B., Selke, S., Hernandez, R. (2003). Mechanical, physical, and barrier properties of poly(lactide) films. *Journal of Plastic Film and Sheeting, 19*(2), 123-135. https://doi.org/10.1177/8756087903039702

Auras, R., Harte, B., Selke, S.E. (2004). An overview of polylactides as packaging materials. *Macromolecular Bioscience, 4*(9), 835-864. https://doi.org/10.1002/mabi.200400043

Balart, J., Montanes, N., Fombuena, V., Boronat, T., Sánchez-Nacher, L. (2018). Disintegration in compost conditions and water uptake of green composites from poly (lactic acid) and hazelnut shell flour. *Journal of Polymers and the Environment, 26*(2), 701-715. https://doi.org/10.1007/s10924-017-0988-3

Beltrán, F.R., Arrieta, M.P., Gaspar, G., de la Orden, M.U., Urreaga, J.M. (2020). Effect of lignocellulosic nanoparticles extracted from yerba mate (Ilex paraguariensis) on the structural, thermal, optical and barrier properties of mechanically recycled poly(lactic acid). *Polymers, 12*(8). https://doi.org/10.3390/polym12081690

Beltrán, F.R., Lorenzo, V., de la Orden, M.U., Martínez-Urreaga, J. (2016). Effect of different mechanical recycling processes on the hydrolytic degradation of poly(L-lactic acid). *Polymer Degradation and Stability, 133*, 339-348. https://doi.org/10.1016/j.polymdegradstab.2016.09.018

Bioplastics, E. (2020). from https://www.european-bioplastics.org/bioplastics/materials/

Burgos, N., Armentano, I., Fortunati, E., Dominici, F., Luzi, F., Fiori, S.,... Kenny, J.M. (2017). Functional Properties of Plasticized Bio-Based Poly(Lactic Acid)_Poly(Hydroxybutyrate) (PLA_PHB) Films for Active Food Packaging. *Food and Bioprocess Technology, 10*(4), 770-780. https://doi.org/10.1007/s11947-016-1846-3

Burgos, N., Martino, V.P., Jiménez, A. (2013). Characterization and ageing study of poly(lactic acid) films plasticized with oligomeric lactic acid. *Polymer Degradation and Stability, 98*(2), 651-658. https://doi.org/10.1016/j.polymdegradstab.2012.11.009

Carbonell-Verdu, A., Ferri, J.M., Dominici, F., Boronat, T., Sanchez-Nacher, L., Balart, R., Torre, L. (2018). Manufacturing and compatibilization of PLA/PBAT binary blends by cottonseed oil-based derivatives. *Express Polymer Letters, 12*(9), 808-823. https://doi.org/10.3144/expresspolymlett.2018.69

Carbonell-Verdu, A., Garcia-Garcia, D., Dominici, F., Torre, L., Sanchez-Nacher, L., Balart, R. (2017). PLA films with improved flexibility properties by using maleinized cottonseed oil. *European Polymer Journal, 91*, 248-259. https://doi.org/10.1016/j.eurpolymj.2017.04.013

Carbonell-Verdu, A., Samper, M.D., Garcia-Garcia, D., Sanchez-Nacher, L., Balart, R. (2017). Plasticization effect of epoxidized cottonseed oil (ECSO) on poly(lactic acid). *Industrial Crops and Products, 104*, 278-286. https://doi.org/10.1016/j.indcrop.2017.04.050

Fortunati, E., Armentano, I., Iannoni, A., Kenny, J. (2010). Development and thermal behaviour of ternary PLA matrix composites. *Polymer Degradation and Stability, 95*(11), 2200-2206. https://doi.org/10.1016/j.polymdegradstab.2010.02.034

Fortunati, E., Armentano, I., Zhou, Q., Puglia, D., Terenzi, A., Berglund, L.A., Kenny, J. (2012a). Microstructure and nonisothermal cold crystallization of PLA composites based on silver nanoparticles and nanocrystalline cellulose. *Polymer Degradation and Stability, 97*(10), 2027-2036. https://doi.org/10.1016/j.polymdegradstab.2012.03.027

Fortunati, E., Luzi, F., Puglia, D., Dominici, F., Santulli, C., Kenny, J.M., Torre, L. (2014). Investigation of thermo-mechanical, chemical and degradative properties of PLA-limonene films reinforced with cellulose nanocrystals extracted from Phormium tenax leaves. *European Polymer Journal, 56*(1), 77-91. https://doi.org/10.1016/j.eurpolymj.2014.03.030

Fortunati, E., Puglia, D., Santulli, C., Sarasini, F., Kenny, J.M. (2012b). Biodegradation of Phormium tenax/poly(lactic acid) composites. *Journal of Applied Polymer Science, 125*(SUPPL. 2), E562-E572. https://doi.org/10.1002/app.36839

Garcia-Garcia, D., Carbonell-Verdu, A., Arrieta, M.P., López-Martínez, J., Samper, M.D. (2020). Improvement of PLA film ductility by plasticization with epoxidized karanja oil. *Polymer Degradation and Stability, 179*. https://doi.org/10.1016/j.polymdegradstab.2020.109259

Jamshidian, M., Tehrany, E.A., Imran, M., Jacquot, M., Desobry, S. (2010). Poly-Lactic Acid: Production, Applications, Nanocomposites, and Release Studies. *Comprehensive Reviews in Food Science and Food Safety, 9*(5), 552-571. https://doi.org/10.1111/j.1541-4337.2010.00126.x

Kale, G., Auras, R., Singh, S.P. (2006). Degradation of Commercial Biodegradable Packages under Real Composting and Ambient Exposure Conditions. *Journal of Polymers and the Environment, 14*(3), 317-334. https://doi.org/10.1007/s10924-006-0015-6

Kale, G., Kijchavengkul, T., Auras, R., Rubino, M., Selke, S.E., Singh, S.P. (2007). Compostability of bioplastic packaging materials: An overview. Macromolecular *Bioscience, 7*(3), 255-277. https://doi.org/10.1002/mabi.200600168

Khabbaz, F., Karlsson, S., Albertsson, A.C. (2000). PY-GC/MS an effective technique to characterizing of degradation mechanism of poly (L-lactide) in the different environment. *Journal of Applied Polymer Science, 78*(13), 2369-2378. https://doi.org/10.1002/1097-4628(20001220)78:13<2369::AID-APP140>3.0.CO;2-N

Lim, L.T., Auras, R., Rubino, M. (2008). Processing technologies for poly(lactic acid). *Progress in Polymer Science (Oxford), 33*(8), 820-852. https://doi.org/10.1016/j.progpolymsci.2008.05.004

Luzi, F., Dominici, F., Armentano, I., Fortunati, E., Burgos, N., Fiori, S.,... Torre, L. (2019). Combined effect of cellulose nanocrystals, carvacrol and oligomeric lactic acid in PLA_PHB polymeric films. *Carbohydrate Polymers, 223*. https://doi.org/10.1016/j.carbpol.2019.115131

Luzi, F., Fortunati, E., Puglia, D., Petrucci, R., Kenny, J.M., Torre, L. (2015). Study of disintegrability in compost and enzymatic degradation of PLA and PLA nanocomposites reinforced with cellulose nanocrystals extracted from Posidonia Oceanica. *Polymer Degradation and Stability, 121*, 105-115. https://doi.org/10.1016/j.polymdegradstab.2015.08.016

Madhavan, N.K., Nimisha Rajendran, N., Rojan Pappy, J. (2010). An overview of the recent developments in polylactide (PLA) research. *Bioresource Technology, 101*(22), 8493-8501. https://doi.org/10.1016/j.biortech.2010.05.092

Musioł, M., Sikorska, W., Adamus, G., Janeczek, H., Richert, J., Malinowski, R.,... Kowalczuk, M. (2016). Forensic engineering of advanced polymeric materials. Part III - Biodegradation of thermoformed rigid PLA packaging under industrial composting conditions. *Waste Management, 52*, 69-76. https://doi.org/10.1016/j.wasman.2016.04.016

Navarro-Baena, I., Marcos-Fernández, A., Fernández-Torres, A., Kenny, J.M., Peponi, L. (2014). Synthesis of PLLA-b-PCL-b-PLLA linear tri-block copolymers and their corresponding poly (ester-urethane) s: effect of the molecular weight on their crystallisation and mechanical properties. *RSC advances, 4*(17), 8510-8524. https://doi.org/10.1039/c3ra44786c

Oyama, H.T., Tanishima, D., Maekawa, S. (2016). Poly(malic acid-co-L-lactide) as a superb degradation accelerator for Poly(l-lactic acid) at physiological conditions. *Polymer Degradation and Stability, 134*, 265-271. https://doi.org/10.1016/j.polymdegradstab.2016.10.016

Pawlak, F., Aldas, M., Parres, F., López-Martínez, J., Arrieta, M.P. (2020). Silane-functionalized sheep wool fibers from dairy industry waste for the development of plasticized pla composites with maleinized linseed oil for injection-molded parts. *Polymers, 12*(11), 1-22. https://doi.org/10.3390/polym12112523

Petersson, L., Kvien, I., Oksman, K. (2007). Structure and thermal properties of poly(lactic acid)/cellulose whiskers nanocomposite materials. *Composites Science and Technology, 67*(11), 2535-2544. https://doi.org/10.1016/j.compscitech.2006.12.012

Plastic Europe. (2019). Plastics - the Facts 2019. An analysis of European plastics production, demand and waste data., from https://www.plasticseurope.org/es/resources/publications/1804-plastics-facts-2019

Quiles-Carrillo, L., Montanes, N., Garcia-Garcia, D., Carbonell-Verdu, A., Balart, R., Torres-Giner, S. (2018b). Effect of different compatibilizers on injection-molded green composite pieces based on polylactide filled with almond shell flour. *Composites Part B: Engineering, 147*, 76-85. https://doi.org/10.1016/j.compositesb.2018.04.017

Quiles-Carrillo, L., Montanes, N., Lagaron, J.M., Balart, R., Torres-Giner, S. (2018a). On the use of acrylated epoxidized soybean oil as a reactive compatibilizer in injection-molded compostable pieces consisting of polylactide filled with orange peel flour. *Polymer International, 67*(10), 1341-1351. https://doi.org/10.1002/pi.5588

Ramos, M., Fortunati, E., Beltrán, A., Peltzer, M., Cristofaro, F., Visai, L.,... Garrigós, M.C. (2020). Controlled Release, Disintegration, Antioxidant, and Antimicrobial Properties of Poly (Lactic Acid)/Thymol/Nanoclay Composites. *Polymers, 12*(9), 1878. https://doi.org/10.3390/polym12091878

Ramos, M., Fortunati, E., Peltzer, M., Jimenez, A., Kenny, J.M., Garrigós, M.C. (2016). Characterization and disintegrability under composting conditions of PLA-based nanocomposite films with thymol and silver nanoparticles. *Polymer Degradation and Stability, 132*, 2-10. https://doi.org/10.1016/j.polymdegradstab.2016.05.015

Samper, M.D., Arrieta, M.P., Ferrándiz, S., López, J. (2014). Influence of biodegradable materials in the recycled polystyrene. *Journal of Applied Polymer Science, 131*(23). https://doi.org/10.1002/app.41161

Samper, M.D., Bertomeu, D., Arrieta, M.P., Ferri, J.M., López-Martínez, J. (2018). Interference of biodegradable plastics in the polypropylene recycling process. *Materials, 11*(10). https://doi.org/10.3390/ma11101886

Shah, A.A., Hasan, F., Hameed, A., Ahmed, S. (2008). Biological degradation of plastics: A comprehensive review. *Biotechnology Advances, 26*(3), 246-265. https://doi.org/10.1016/j.biotechadv.2007.12.005

Shinoda, H., Asou, Y., Kashima, T., Kato, T., Tseng, Y., Yagi, T. (2003). Amphiphilic biodegradable copolymer, poly(aspartic acid-co-lactide): acceleration of degradation rate and improvement of thermal stability for poly(lactic acid), poly(butylene succinate) and poly(ε-caprolactone). *Polymer Degradation and Stability, 80*(2), 241-250. https://doi.org/10.1016/S0141-3910(02)00404-4

Siracusa, V., Rocculi, P., Romani, S., Rosa, M.D. (2008). Biodegradable polymers for food packaging: a review. *Trends in Food Science and Technology, 19*(12), 634-643. https://doi.org/10.1016/j.tifs.2008.07.003

Song, J.H., Murphy, R.J., Narayan, R., Davies, G.B.H. (2009). Biodegradable and compostable alternatives to conventional plastics. *Philosophical Transactions of the Royal Society of London B: Biological Sciences, 364*(1526), 2127-2139. https://doi.org/10.1098/rstb.2008.0289

Sriyapai, P., Chansiri, K., Sriyapai, T. (2018). Isolation and characterization of polyester-based plastics-degrading bacteria from compost soils. *Microbiology, 87*(2), 290-300. https://doi.org/10.1134/S0026261718020157

UNE-EN ISO. (2016). Plastics - Determination of the degree of disintegration of plastic materials under simulated composting conditions in a laboratory-scale test (ISO 20200:2015).

Villegas, C., Arrieta, M.P., Rojas, A., Torres, A., Faba, S., Toledo, M.J.,... Valenzuela, X. (2019). PLA/organoclay bionanocomposites impregnated with thymol and cinnamaldehyde by supercritical impregnation for active and sustainable food packaging. *Composites Part B: Engineering, 176*. https://doi.org/10.1016/j.compositesb.2019.107336

Vink, E.T.H., Rábago, K.R., Glassner, D.A., Gruber, P.R. (2003). Applications of life cycle assessment to NatureWorks™ polylactide (PLA) production. *Polymer Degradation and Stability, 80*(3), 403-419. https://doi.org/10.1016/S0141-3910(02)00372-5

Yagi, H., Ninomiya, F., Funabashi, M., Kunioka, M. (2013). Thermophilic anaerobic biodegradation test and analysis of eubacteria involved in anaerobic biodegradation of four specified biodegradable polyesters. *Polymer Degradation and Stability, 98*(6), 1182-1187. https://doi.org/10.1016/j.polymdegradstab.2013.03.010