



# Effect of solid-state polymerization on the structure and properties of mechanically recycled poly(lactic acid)

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## ABSTRACT

Poly(lactic acid) (PLA) is one of the most important alternatives to fossil-fuel based polymers due to its biodegradability and good properties. However, the growing production along with the increasing resistance to degradation of the newer grades could lead to waste management problem. The application of mechanical recycling, which could be the best valorization method for biodegradation-resistant PLA residues, is limited by the degradation of the polymer, which decreases its performance, so it is interesting to develop simple and acceptable methods to improve the recycled plastic. The aim of this work is to study the effect of thermal treatments of PLA residues (with two levels of degradation) on the structure and properties of recycled PLA. During thermal treatments, both polycondensation and degradation reactions take place, and the net result depends on the degradation level of the residue and the time and temperature of the treatment. In adequate conditions, polycondensation reactions increase the molecular weight of the residue and lead to significant improvements of the mechanical and thermal properties of the recycled plastic. These results suggest that thermal treatments represent a simple, cost-effective and environmentally friendly method to improve the recyclability of PLA and, hence, the environmental impact of this plastic.

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## 1. Introduction

The large production, and consumption, of plastics has led to an important waste management problem, which could have pernicious consequences for the environment. One of the alternatives proposed to face this problem is the utilization of bioplastics. Among these materials, poly(lactic acid) (PLA) plays a prominent role due to its biodegradability, good processability, and acceptable optical and mechanical properties [1,2]. Furthermore, the continuous development of this material is leading to new grades with better thermal and mechanical properties [3], making it suitable for applications in a wide variety of industries, such as textile,

automobile and packaging. This increasing variety of applications results in a continuous growth in the production of PLA, exceeding 200 kt/year in 2016, and with an expected growth of 10% per year [4].

The progressive substitution of fossil fuel-based plastics with bioplastics, such as PLA, presents several environmental advantages. However, this increase of the production, and consumption, of PLA is not without problems. On the one hand, the production of the raw materials used in the manufacture of PLA requires large amounts of croplands, which could affect the supply and price of some food products, especially in developing countries [5]. On the other hand, the low degradation rate of PLA [6,7] along with an inadequate management of the wastes could generate the accumulation of residues [8]. Several authors have reported that potential alternatives for the management of PLA residues include energy recovery, composting and chemical and mechanical recycling [9,10]. Mechanical recycling is especially interesting in the valorization of the residues coming from high-performance PLA

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grades, since these grades could not be suitable for composting due to its high resistance to degradation. Furthermore, mechanical recycling allows to reduce the consumption of raw materials, decreasing the environmental impact (according to different Life Cycle Assessment studies) of the use of PLA [11–13].

Although mechanical recycling poses several advantages, there are two main concerns with its feasibility. Firstly, the need of adapting the current plastic recovery processes to introduce a new stream for PLA. Secondly, previous studies, such as those conducted by Beltrán et al. [10] and Botta et al. [14] report that important properties such as viscosity, thermal stability and gas barrier properties are negatively affected by mechanical recycling. This decrease on the properties might reduce the demand for recycled PLA, and hence negatively affect the recyclability of the polymer. Therefore, the development of easy, cost-effective and environmentally friendly methods for improving the performance of the recycled plastic becomes crucial [9]. In this regard, previous works report that through the utilization of functionalized nanoclays [15] and reactive extrusion [16] the degradation of PLA during the mechanical recycling, concretely during the reprocessing step, could be limited, obtaining a recycled material with improved properties, and thus, more attractive to the plastics market.

Beside the previously cited upgrading methods, another alternative for improving the properties of recycled PLA is the utilization of thermal treatments. Several authors have pointed out that thermal treatments below the melting temperature could increase some properties of PLA. Nascimento et al. [17] subjected reprocessed PLA to an annealing treatment at 120 °C for 6 h, reporting an increase on the crystallinity and an improvement of the mechanical properties of the samples. Thermal treatments could also be used to increase the molecular weight of PLA. This process is called solid state polymerization (SSP). Vouyiouka et al. reported increases of up to 67% after submitting a low molecular weight PLA to a thermal treatment at 120 °C during 32 h in nitrogen atmosphere. However, it is important to carefully study the conditions of the SSP, since degradation reactions (such as lactide and/or vinyl ends formations) can take place, decreasing the molecular weight [18]. It is also worth to note that thermal treatments present some technical advantages, since they don't require the utilization of any additive or solvent, nor complex synthesis procedures, which makes them a potential environmentally friendly, and cost-effective, method for improving the properties of mechanically recycled PLA.

The aforementioned studies point out that it is possible to increase the molecular weight and improve some properties of PLA using thermal treatments, which are very interesting due to their simple application and low environmental impact. However, there are no studies that consider the different levels of degradation that might be found in PLA after its service life, and the effect these might have on the effectiveness of the thermal treatments. Therefore, the main aim of this work is to analyze the effects of different thermal treatments in the structure of recycled PLA subjected to two different ageing protocols. On the one hand, to simulate the degradation of a post-consumer material, PLA was subjected to an extrusion and compression molding process. Then, the obtained films were subjected to an accelerated ageing process comprising photochemical, thermal and hydrolytic degradation. Lastly, the aged films were washed at 85 °C. On the other hand, in order to consider the possibility of severely degraded wastes, another batch of neat PLA was degraded by hydrolysis at 60 °C during 5 days. Both post-consumer and hydrolyzed PLA were then subjected to different thermal treatments in vacuum or under dry nitrogen, at temperatures between 110 and 140 °C, and times ranging from 8 h to 48 h. After the treatment, the samples were processed by melt extrusion and compression molding, and then characterized by means of intrinsic viscosity measurements (IV), gel permeation

chromatography (GPC), Fourier transform infrared (FTIR) and UV–Vis spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), nanoindentation and microhardness measurements.

## 2. Materials and methods

### 2.1. Materials

A commercial grade of PLA, designed for packaging applications, labeled as Ingeo™ 2003D was used. It has a melt mass-flow rate of 6 g/10 min (2.16 kg at 210 °C).

### 2.2. Preparation of the samples

The procedure followed for the preparation of the samples is presented in Scheme 1. For the obtainment of simulated post-consumer PLA, the Ingeo 2003D PLA was melt processed by extrusion using a Rondol Microlab twin-screw microcompounder with L/D = 20 and a screw speed of 60 rpm. The used temperature profile was, from hopper to die: 125, 160, 190, 190, 180 °C. The material was transformed into films (200 ± 10 µm) using an IQAP-LAP hot-plate press at 190 °C (PLAV). The obtained films were then subjected to an accelerated ageing protocol, in order to simulate the degradation during service life. The ageing protocol included (i) 40 h of photochemical degradation in an Atlas UVCON chamber, equipped with eight F40UVB lamps; (ii) 468 h of thermal degradation in a convection oven at 50 °C and (iii) 240 h of hydrolytic degradation in demineralized water at 25 °C. Subsequently, the aged material was washed following the procedure suggested in previous studies by our research group [16] (PLAP). A severely degraded PLA was obtained by immersion of neat PLA in demineralized water at 60 °C for five days (PLAH).

Afterwards, both simulated post-consumer and hydrolyzed PLA were subjected to thermal treatments at temperatures between 110 and 140 °C, and for times going from 8 to 48h. The treated samples have been labeled as PLAPT-X-Y and PLAHT-X-Y, where X corresponds to the hours and Y to the temperature of the treatment. The thermal treatments were carried out in a vacuum oven and/or in a reactor under nitrogen atmosphere. The reactor consisted in a quartz tube, which was heated using a tubular oven (see supporting information). The reactor was fed with previously heated N<sub>2</sub> (99.98% purity), whose flow was controlled using a rotameter.

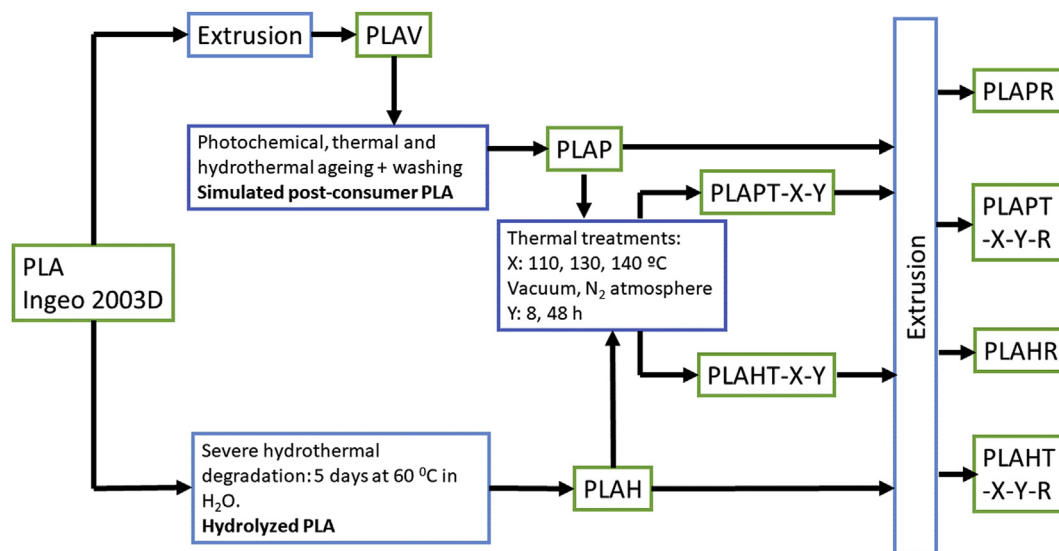
The resulting materials were then processed using the same conditions of the first processing step (samples with the letter –R). It is worth to note that, prior to processing, all the materials were dried for 2 h, in a vacuum oven at 85 °C.

### 2.3. Characterization techniques

Gel permeation chromatography (GPC) was used to measure weight-average molecular weight ( $M_w$ ) and number-average molecular weight ( $M_n$ ) of the different materials. A chromatographic system (Waters) equipped with a refractive index detector and Styragel packed Waters columns (HR 0.5, HR 1 and HR 4, 7.8 mm × 300 mm) was used. The eluent (tetrahydrofuran, 99.9%, Aldrich) flow rate was 1 mL/min at 35 °C. Polystyrene standards were used as reference for molecular weight.

The intrinsic viscosity of the samples was measured at 25 °C, using an Ubbelohde viscometer and chloroform as solvent.

UV–Vis spectra were recorded in a Shimadzu 2401 PC UV–Vis spectrophotometer, at a scanning rate of 200 nm/min. ISO 13468 standard was used for the determination of the overall transmittance in the visible light. A Nicolet iS10 spectrometer, equipped with a diamond Attenuated Total Reflectance (ATR) accessory was



Scheme 1. Recycling process and thermal treatments applied to PLA.

used to record Fourier-transform infrared (FTIR) spectra of the different samples. The spectra were recorded using 16 scans and a resolution of  $4\text{ cm}^{-1}$ . FTIR-ATR spectra were corrected and normalized using the band at  $1451\text{ cm}^{-1}$ , which has been reported as an internal standard [19,20].

Thermogravimetric analysis (TGA) were conducted in a TA Instruments TGA2050 thermobalance. Samples (12 mg) were heated from room temperature to  $800\text{ °C}$  in dry nitrogen (30 mL/min), using a heating rate of  $10\text{ °C/min}$ . The thermal transitions and structure of the materials were analyzed using DSC tests, which were performed in a TA Instruments Q20 calorimeter. Samples of approximately 5 mg were placed in aluminum pans. The scans were performed under nitrogen atmosphere (50 mL/min). The protocol consisted of (i) a first heating, from  $30$  to  $180\text{ °C}$  at  $5\text{ °C/min}$ . (ii) An isothermal step at  $180\text{ °C}$  for 3 min (iii) a cooling scan from  $180\text{ °C}$  to  $0\text{ °C}$  at  $5\text{ °C/min}$ . (iv) an isothermal step at  $0\text{ °C}$  for 1 min and a (v) second heating, at  $5\text{ °C/min}$ , until  $180\text{ °C}$ .  $X_c$  was calculated using equation (1):

$$\chi_c(\%) = \frac{\Delta H_M - \Delta H_{CC}}{\Delta H_\infty} \times 100 \quad (1)$$

where  $\Delta H_\infty$  is  $93.1\text{ J/g}$  [10].

Vickers hardness of the samples was measured using a Type M Shimadzu microhardness tester. A load of 25 g was applied during 10 s using a Vickers pyramidal indenter. Each measurement was repeated six times. Young modulus of the samples was measured by means of instrumented nanoindentation in a Shimadzu DUH-211S dynamic Ultra-Microhardness Tester at room temperature. A loading rate of  $1.4632\text{ mN/s}$ , a load time of 5 s and a maximum load of 10 mN were selected. Each measurement was replicated six times.

### 3. Results and discussion

The different ageing, washing and reprocessing steps to which the different PLA samples were subjected can affect the chemical structure of the polymer. According to the literature, a Norrish type II mechanism is the main responsible of the generation of C=C bonds and carboxyl terminal groups during photochemical degradation. During thermal degradation, a wide variety of chain scission processes, such as degradation, hydrolysis, backbiting reactions and

intermolecular transesterifications take place. Lastly, at neutral and alkaline pH conditions lactide and, in the long term, lactoyl lactic acid and lactic acid are generated during hydrolytic degradation, due to the occurrence of backbiting reactions [16,21,22]. Overall, the photochemical, thermal and hydrolytic degradation result in the generation of  $-\text{COOH}$  terminal groups in PLA.

The degradation of PLA during ageing and melt processing was followed by means of intrinsic viscosity measurements. Besides the relationship between intrinsic viscosity and molecular weight, intrinsic viscosity plays a very important role on the processing of plastics. This is due to industrial forming processes being designed to operate with plastics at specific viscosity conditions [16]. Results point out that the first processing step leads to a 6% decrease of the intrinsic viscosity of the polymer due to the thermomechanical degradation of PLA during the melt compounding. Furthermore, PLAPR presents a viscosity of  $118 \pm 1\text{ mL/g}$ , which is 11% lower than of PLAV. This result suggests that the ageing processes and the reprocessing step lead to a further degradation of the plastic. This behavior could be due to the generation of carboxyl end groups in PLA during the ageing and washing processes. These groups might have a catalytic effect in some of the degradation processes that take place during the reprocessing step, resulting in an important decrease of the viscosity.

Regarding the hydrolyzed PLA samples, PLAH has an intrinsic viscosity value 50% lower than that of PLAV. This difference is consequence of the chain scission reactions that take place during the hydrolytic degradation of PLA at  $60\text{ °C}$ . Previous works [10,16] point out that the decrease of the intrinsic viscosity observed in both post-consumer and hydrolyzed PLA samples leads to a reduction of some key properties in packaging applications, such as mechanical and gas barrier properties. This decrease of the performance represents a problem for the potential market of recycled plastic. Therefore, is important to find cost-effective and environmentally friendly methods to improve the properties of recycled PLA. In this regard, thermal treatments could play a very important role, due to their simplicity, low cost and very low environmental impact.

#### 3.1. Effects of the thermal treatments on the intrinsic viscosity of aged PLA samples

Thermal treatments could improve the average molecular

weight of PLA, but also could induce the thermal degradation of the polymer. Therefore, adequate conditions must be established to guarantee a recycled PLA with good properties. The effect of different thermal treatments on the intrinsic viscosity of post-consumer and hydrolyzed PLA is presented in Fig. 1.

Fig. 1a shows that, although the changes are small, the thermal treatments cause an increase of the intrinsic viscosity. However, the resulting intrinsic viscosity varies with the temperature and atmosphere at which the treatment is carried out. To explain this behavior, one should consider that at temperatures between  $T_g$  and  $T_m$  both degradation and polycondensation reactions could occur in the amorphous regions of PLA [18]. Polycondensation to produce poly(lactic acid) depends on two thermodynamic equilibria, namely the hydrolysis/condensation (for ester formation) and the ring/chain equilibrium (for the formation of lactide), which are shown in Scheme 2 [23]. The removal of the condensation byproducts from the surface of the material is necessary to promote the polycondensation reactions, which lead to higher molecular weights [24]. The removal of these byproducts could be done either by evaporation in vacuum conditions or by driving them away using a carrier gas (like  $N_2$ ).

Fig. 1a also shows that the intrinsic viscosity values of post-consumer PLA treated at 130 °C under vacuum is slightly higher than that of  $N_2$  atmosphere. Furthermore, the formation of significant amounts of a white powder, which was identified as lactide, was noticed inside the reactor using  $N_2$ . These results suggest that the vacuum conditions promote a better removal of the condensation products, concretely water, which favors the polycondensation and results in higher intrinsic viscosity values.

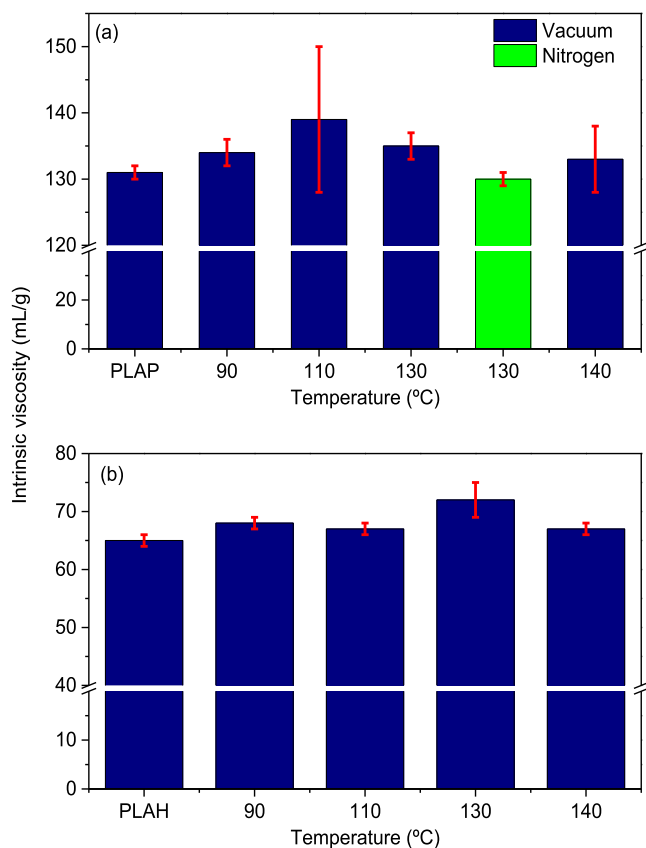


Fig. 1. Intrinsic viscosity values post-consumer (a) and hydrolyzed (b) PLA treated for 8 h.

Besides the slightly better results obtained using vacuum conditions, it is worth to note that, at industrial level, vacuum conditions are more easily attainable than an adequately conditioned carrier gas supply. Therefore, this work will be focused on the results obtained in vacuum conditions.

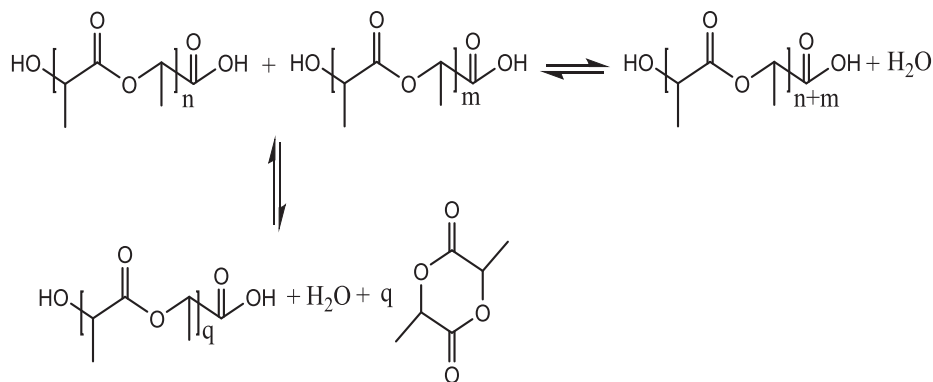
Regarding the behavior of the hydrolyzed PLA samples, Fig. 1b shows that even in these severely degraded materials it is possible to increase the intrinsic viscosity by means of thermal treatments in the adequate conditions. Results showed in Fig. 1 suggest that there is an optimal temperature for the thermal treatments, which depends on the level of degradation of the starting material (near 110 °C for PLAP and near 130 °C for PLAH).

### 3.2. Effect of reprocessing on the viscosity and structure of treated samples

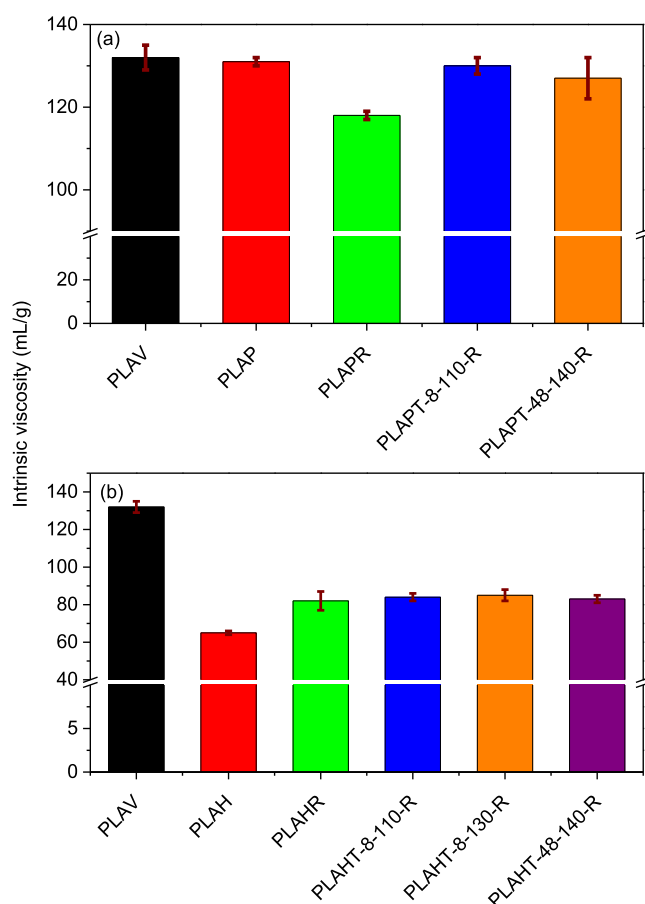
Once the positive effect of the thermal treatments on the intrinsic viscosity of post-consumer and hydrolyzed PLA have been analyzed, it is necessary to determine if the thermal treatments lead to an improvement of the aged samples after a reprocessing step including melt compounding and compression molding. Fig. 2a shows the intrinsic viscosity values of the reprocessed post-consumer samples. It can be seen that both treated samples present higher viscosity values than the untreated recycled plastic, PLAPR. These results could be explained considering the reactions of the carboxyl and hydroxyl end groups present in postconsumer PLA, which take place at high temperatures (Scheme 2). It is known that at low  $M_w$  values, the solid state polymerization (SSP) at temperatures between  $T_g$  and  $T_m$  results in the formation of larger polymer chains and causes an increase of the average molecular weight [18,24]. At relatively high  $M_w$ , such is the case of post-consumer PLA, SSP is less probable due to the reduced mobility of the molecular segments. However, some of the carboxyl end groups might react, reducing their autocatalytic effect on the degradation of PLA during reprocessing.

Regarding the behavior of the hydrolyzed PLA samples, Fig. 2b shows that the extrusion and compression molding process lead to an increase of approximately 25% of the intrinsic viscosity of hydrolyzed PLA, in both treated and untreated samples. This result points out that part of the decrease of the intrinsic viscosity resulting from the hydrolytic degradation could be partially recovered just by melt processing in adequate conditions. This behavior is rather unexpected, since PLA is susceptible to thermo-mechanical degradation during processing, which should have caused a decrease of the intrinsic viscosity, as it was seen in post-consumer PLA. To explain such behavior, one should consider that at temperatures higher than  $T_m$ , polycondensation reactions could compete with degradation reactions. The increase of the viscosity in PLAH samples suggests that the high temperature and shear produced inside the extruder, in the absence of oxygen, favored the polycondensation reactions and the formation of longer polymer chains. Besides that, Fig. 2b also shows that the thermal treatments do not seem to affect the intrinsic viscosity values of PLAH. Despite the increase of the intrinsic viscosity, it is important to mention that the values are still below of that of PLAV, suggesting that the severely degraded PLA samples might not be suitable for demanding applications.

Additional information about the changes in the chemical structure of PLA can be obtained analyzing the molecular weight distribution of the samples, which was obtained by means of GPC. Fig. 3a shows the molecular weight distribution of the virgin and selected reprocessed post-consumer PLA samples. It can be seen that ageing and reprocessing steps caused a displacement of the distribution towards lower values of  $M_w$  (up to 20% lower when compared with PLAV). This result confirms that shorter polymer

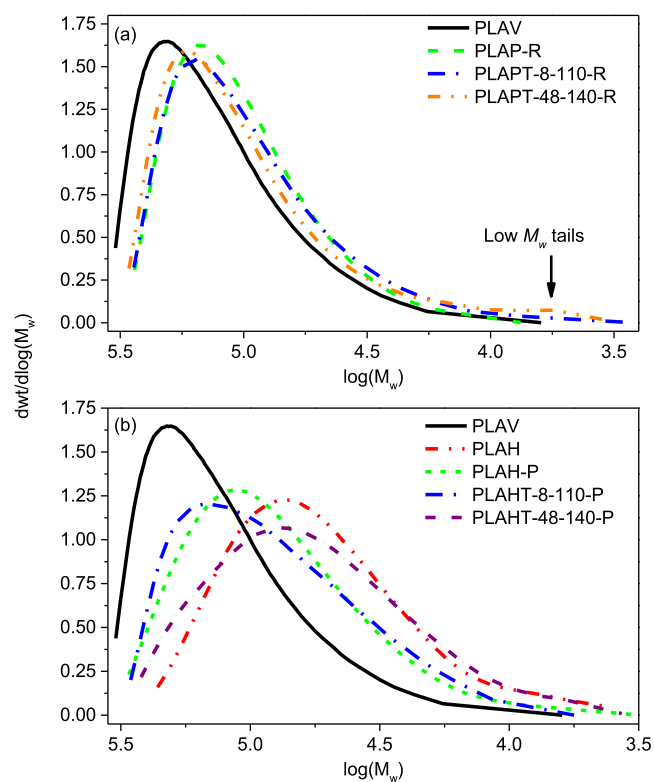


**Scheme 2.** Hydrolysis/condensation and ring/chain equilibria in PLA polycondensation [23].



**Fig. 2.** Intrinsic viscosity of reprocessed post-consumer (a) and hydrolyzed (b) PLA submitted to different thermal treatments.

chains are generated during the ageing and recycling processes. Regarding the effect of the thermal treatments, Fig. 3a shows that they cause a small shift of the distribution towards higher values of  $M_w$ . This result is in good agreement with those of intrinsic viscosity and point out that the thermal treatments result in a material with longer chains. However, the thermal treatments also produce an increase on the polydispersity of PLA, as it can be seen in Table 1, going from 1.5 in PLAPR to 1.9 in PLAPT-8-110-R. This behavior suggests that beside the longer polymer chains, some low molecular weight tails are formed in the treated materials. In fact, it can



**Fig. 3.** Molecular weight distribution of virgin and post-consumer (a) and hydrolyzed (b) PLA samples.

**Table 1**

GPC results of the different samples. The error associated with  $M_n$  and  $M_w$  is less than 2%.

Sample	$M_n$ (kDa)	$M_w$ (kDa)	Polydispersity
PLAV	97	153	1.6
PLAP	71	144	2.0
PLAP-R	82	121	1.5
PLAPT-8-110-R	63	118	1.9
PLAPT-48-140-R	58	125	2.2
PLAH	35	71	2.0
PLAH-P	57	104	1.8
PLAHT-8-110-P	59	106	1.8
PLAHT-8-130-P	51	101	2.0
PLAHT-48-140-P	39	79	2.1

be seen on Fig. 3a that the sample treated at 140 °C presents a small peak at low  $M_w$  values, which corresponds to the presence of the aforementioned low molecular weight tails. These results suggest that special care has to be taken when determining the conditions of thermal treatments for moderately degraded PLA samples. More severe treatments (high temperatures and residence times) could produce larger polymer chains, but they could also increase the amount of undesirable short polymer chains, which could be pernicious in a subsequent melt processing stage.

Regarding the GPC results of the hydrolyzed samples, Fig. 3b and Table 1 show that PLAH has a lower average molecular weight than PLAV (32% lower in  $M_w$  and 64% lower in  $M_n$ ), in good agreement with the results of the intrinsic viscosity measurements. It could also be seen that the processed hydrolyzed samples present higher average molecular weight than PLAH. This result confirms that melt compounding of severely degraded PLA samples promotes polycondensation reactions, thus leading to significant increases in the average molecular weight of the polymer. It is also worth to note that the molecular weight distribution of the hydrolyzed sample treated for 48h and 140 °C shows shoulders at  $\log(M_w) = 3.75$ , which indicates the formation of long and short polymer chains. This result highlights the relevance of the condition of the thermal treatments. As it was previously mentioned in the case of PLAP, if the treatment is too severe undesirable degradation reactions could take place, resulting in reduced average molecular weight and a worst overall performance of the material.

The changes caused by the reprocessing on the chemical structure of the treated PLA samples was also studied by means of FTIR spectroscopy. Fig. 4a shows the 1800–1700  $\text{cm}^{-1}$  region of the FTIR spectra of virgin PLA, post-consumer recycled PLA and a post-consumer thermally treated (8h at 110 °C) and reprocessed PLA

samples. The band centered at 1755  $\text{cm}^{-1}$  corresponds to the C=O stretching vibrations of the ester groups of PLA and can be used as an indicator of degradation of the polymer. It can be seen that the spectrum of PLAPR presents a small displacement of the C=O band toward lower wavenumbers. This result points out that –COOH groups are generated during both ageing and reprocessing steps. These groups absorb energy at lower wavenumbers and form hydrogen bonds, thus causing the observed displacement of the C=O absorption band. This result agrees with those of intrinsic viscosity and GPC measurements, which indicate that the ageing and reprocessing cause the degradation of PLA, generating –COOH and –OH terminal groups.

Regarding the effect of the thermal treatments, Fig. 4a show that the thermal treatment at 110 °C for 8h caused a displacement of the C=O band toward higher wavenumbers, suggesting that the treated material has a lower amount of –COOH groups than the untreated post-consumer sample. This behavior, which is in good agreement with the trends observed in intrinsic viscosity and molecular weight distributions is consequence of the polycondensation reactions that take place in the amorphous regions of PLA. Those reduce the amount of terminal –COOH groups present in the treated postconsumer PLA samples.

Fig. 4b shows the behavior of hydrolyzed PLA samples. As in PLAP, the hydrolysis process led to a displacement of the C=O stretching band toward lower energies, due to the severe hydrolytic degradation of PLA. The melt compounding of both the untreated and the thermally treated samples causes a shift of the C=O band toward higher wavenumbers, getting closer to the spectra of PLAV, due to the partial disappearance of –COOH groups in the hydrolyzed samples. These results highlight the relevance of the polycondensation reactions that take place at  $T > T_m$ , in absence of oxygen.

### 3.3. Effect of the reprocessing on the properties of thermally treated samples

The thermally treated samples seem to adequately withstand the second melt compounding step, at least from a point of view based on intrinsic viscosity and molecular weight measurements. However, it is important to study the effect of the reprocessing on the optical, mechanical and thermal properties of the treated samples, because the performance of the recycled materials is one of the main drivers of the demand for recycled plastics.

The optical clarity is a very important property in food packaging applications. UV–Vis spectroscopy was used to determine the visible light transmission rate of the post-consumer and hydrolyzed PLA samples. Results are summarized in Table 2. It can be seen that neither the degradation processes nor the thermal treatments significantly affect the optical clarity of PLA samples, since in all cases the light transmission rate is close to 90%. This result might indicate that the thermally treated PLA could be used in applications in which a good optical clarity is needed.

Table 2 also shows the Vickers hardness and Young Modulus values of untreated and thermally treated samples after reprocessing. The observed differences are small. This could be due to the presence of several counteracting effects on both hardness and Young modulus. On the one hand, the generation of shorter polymer chains, as it was observed by means of GPC, leads to a decrease of the mechanical properties. On the other hand, the generation of polar groups (namely –COOH) increases the interaction between the polymer chains, which along with the increase of the intrinsic viscosity could result in an increase of the hardness and Young modulus. The presence of these opposing effects results in an overall small change of the mechanical properties. However, it is worth to note that Table 2 shows that, in general, the samples

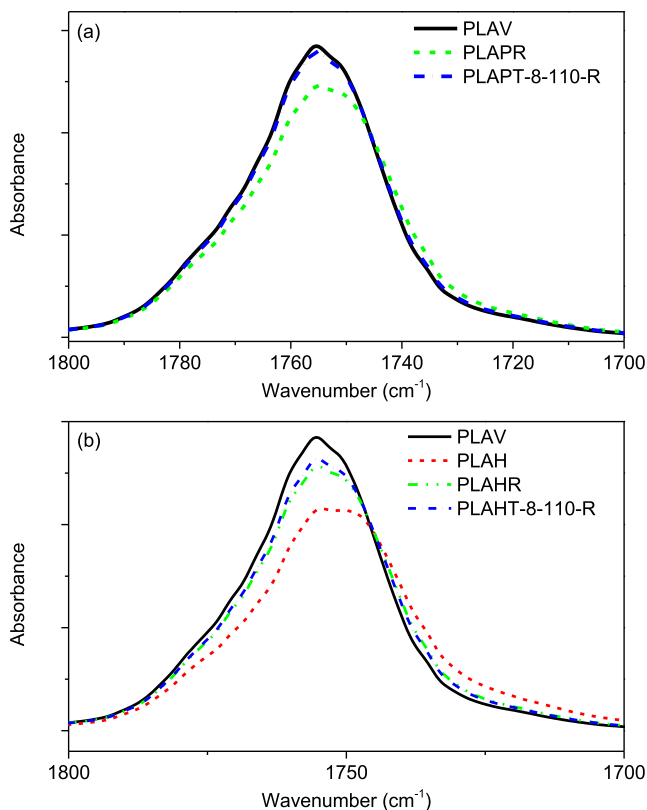


Fig. 4. FTIR-ATR spectra of post-consumer (a) and hydrolyzed (b) PLA samples in the C=O stretching region.

**Table 2**Optical, mechanical and thermal properties of post-consumer and hydrolyzed samples. The error associated with  $T_{10}$  and  $T_{max}$  is less than 2%.

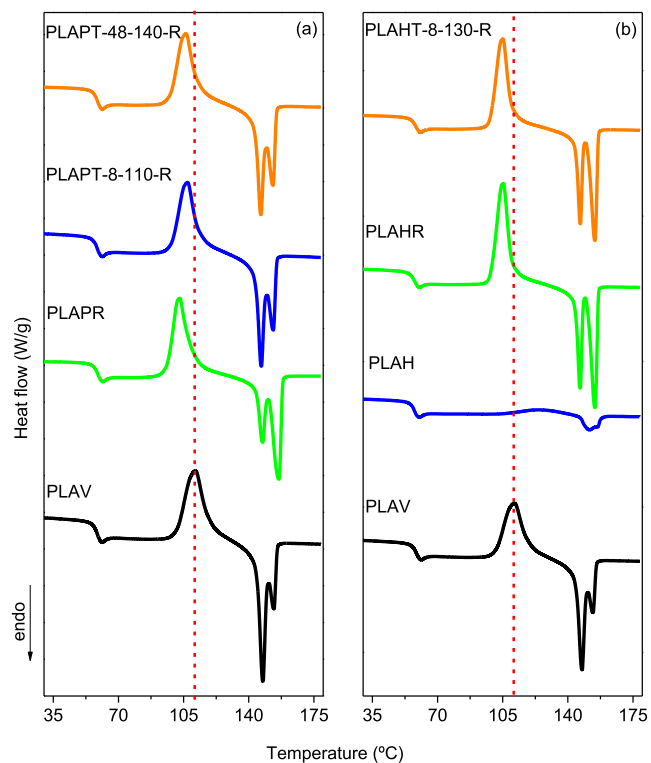
Sample	Light transmission (%)	Vickers hardness (MPa)	Young Modulus (GPa)	$T_{10}$ (°C)	$T_{max}$ (°C)
PLAV	90.3 ± 0.2	154 ± 3	3.29 ± 0.09	344	376
PLAPR	89.7 ± 0.2	146 ± 5	3.25 ± 0.05	321	357
PLAPT-8-110-R	90.7 ± 0.1	152 ± 4	3.31 ± 0.04	333	368
PLAPT-48-140-R	90.9 ± 0.1	145 ± 6	3.32 ± 0.02	332	367
PLAHR	89.8 ± 0.2	141 ± 5	3.31 ± 0.02	333	371
PLAHT-8-110-R	89.3 ± 0.2	149 ± 3	3.38 ± 0.06	336	370
PLAHT-8-130-R	89.5 ± 0.2	140 ± 4	3.30 ± 0.03	334	369
PLAHT-48-140-R	88.4 ± 0.2	153 ± 3	2.90 ± 0.03	335	370

treated at 110 °C present slightly higher hardness values than their untreated counterparts. These results point out that the positive effect of the increase of the viscosity prevails over the generation of some shorter polymer chains. Table 2 also shows that the samples treated at higher temperatures present, overall, lower values of both Young modulus and Vickers hardness (with the unexplained exception of PLAHT-48-140-R). This decrease might indicate that the negative effect of the generation of shorter polymer chains prevails in the samples treated at more severe conditions.

The thermal properties of the different samples were analyzed using TGA and DSC. Table 2 shows the  $T_{10}$  (temperature at which 10% of the mass is lost) and  $T_{max}$  (temperature of maximum decomposition rate) values for post-consumer and hydrolyzed PLA samples. These values are commonly used as a reference for thermal stability. First of all, it can be seen that the mechanical recycling process led to a decrease of the thermal stability of PLA. This behavior has been reported in previous works, and it is attributed to the degradation of the polymer, as the shorter polymer chains generated during the ageing, washing and reprocessing step decompose at lower temperatures [16]. Table 2 also shows that the thermal treatments resulted in increase of  $T_{10}$  values of the post-consumer samples, although they are still lower than that of PLAV. This behavior could be explained by the previously observed increase of the intrinsic viscosity, since longer polymer chains decompose at higher temperatures.

The behavior of the severely hydrolyzed PLA samples is different. The hydrolytic degradation of PLA leads to a reduction of the thermal stability, due to the formation of shorter polymer chains. However, PLAH presents similar  $T_{10}$  and  $T_{max}$  values than those of the treated and processed samples, despite having a lower intrinsic viscosity. In order to explain this result, it must be considered that besides chain length, there are other factors that play a very important role on the thermal stability, such as the nature of the interactions between the polymer chains. PLAH presents a large amount of -COOH and -OH terminal groups, as a result of the hydrolytic degradation. These groups make the interactions between the polymer chains more intense, thus increasing the thermal stability of PLAH. In the case of the treated and processed samples, the amount of these terminal groups has decreased (as it was seen in FTIR spectroscopy), thus weakening the interactions between chains, and counteracting the effect of the increase of the molecular weight.

Fig. 5a and Table 3 show the effects of the different thermal treatments on the structure and thermal transitions of recycled PLA. Virgin PLA and materials obtained from the post-consumer plastic have a similar thermal behavior, with  $T_g$  near 60 °C, an exothermic peak between 100 and 120 °C, which is attributed to the cold crystallization of the polymer and, finally, a double endothermic peak, which corresponds to the melting of the crystalline structures, between 147 and 156 °C. This multiple melting behavior has been previously studied by Di Lorenzo et al. [25], and it was related to a melt recrystallization mechanism, which consists on

**Fig. 5.** Second heating scans of post-consumer (a) and hydrolyzed (b) PLA samples.

the melting of the less perfect crystals at lower temperatures, their rearrangement in more perfect crystals and their melting at higher temperatures.

However, Fig. 5a and Table 3 also reveal some differences. Mechanical recycling caused a slight decrease of the cold crystallization temperature of PLA. This behavior could be attributed to the presence of shorter polymer chains, generated during the ageing, washing and reprocessing steps. These shorter polymer chains have higher mobility and crystallize at lower temperatures. In the thermally treated post-consumer samples the cold crystallization temperature is slightly higher than in PLAPR. This behavior is in good agreement with the increase of the intrinsic viscosity previously observed, since the longer polymer chains present in the treated samples have more difficulties to crystallize. Fig. 5a also shows that the high temperature melting peak is more relevant in the post-consumer samples than in the virgin material. This result could also be attributed to the degradation of the polymer during recycling, since the shorter polymer chains are able to form more stable structures during the cold crystallization and melt recrystallization processes, hence increasing the relevance of high temperature melting peak [26]. In the case of the thermally treated

**Table 3**  
DSC results (second heating) of the post-consumer and hydrolyzed PLA samples. The error associated with the different temperatures and enthalpies is less than 2%.

Sample	$T_g$ (°C)	$T_{cc}$ (°C)	$T_{m1}-T_{m2}$ (°C)	$\Delta H_{cc}$ (J/g)	$\Delta H_m$ (J/g)	$X_c$ (%)
PLAV	58	111	148–154	29.1	29.1	0
PLAPR	59	103	148–156	27.6	27.8	0
PLAPT-8-110-R	58	107	147–153	26.2	27.2	1
PLAPT-48-140-R	59	106	147–153	27.0	27.6	1
PLAH	58	124	152	4.9	5.1	0
PLAHR	58	105	147–155	34.6	35.1	1
PLAHT-8-110-R	58	105	147–155	30.5	31.0	1
PLAHT-8-130-R	59	105	147–155	31.8	32.3	1
PLAHT-48-140-R	58	105	147–155	36.1	36.2	0

samples, the presence of longer polymer chains causes the decrease of the relevance of the high temperature melting peak, but without reaching the behavior of PLAV.

Regarding the crystallization and melting of the different samples, no important variations can be observed between the untreated and treated samples. This result indicates that the thermal treatment did not affect the ability of PLA chains to form crystalline structures, which is important since crystallinity affects the optical, thermal, mechanical and gas barrier properties of PLA.

The DSC curves (second heating scans) of the hydrolyzed PLA samples are shown in Fig. 5b. It can be seen that the unprocessed hydrolyzed PLA shows very small cold crystallization and melting peaks. This result might seem surprising, since the shorter polymer chains present in PLAH should crystallize more easily; however, similar results were observed by Fukushima et al. [27] and Badía et al. [28] in previous studies with hydrolyzed PLA. This behavior could be attributed to the  $-\text{COOH}$  and  $-\text{OH}$  terminal groups generated during the hydrolytic degradation. The presence of these groups increases the interaction between the polymer chains, reducing their mobility and hindering the crystallization.

Fig. 5b and Table 3 also show that samples obtained by reprocessing hydrolyzed PLA samples, whether they were thermally treated or not, are able to form crystalline structures by means of a cold crystallization mechanism during the heating. This could be explained by the reduction of the amount of terminal  $-\text{COOH}$  groups during processing, which would decrease the interactions between the polymer chains and facilitate the crystallization of the polymer. Nevertheless, only the crystalline structures formed during the cold crystallization are melted at  $T_m$ , as it is indicated by the small differences between  $\Delta H_{cc}$  and  $\Delta H_m$ .

The above results show that the thermal treatments of the PLA residues can contribute to obtain recycled PLA with structure and properties very similar to those of virgin plastic (PLAV). Considering that thermal treatments are technically simple processes and that neither reagents nor solvents are used, this can be an economical and environmentally friendly way to improve the recycling of PLA.

#### 4. Conclusions

The effect of different thermal treatments in the structure and properties of recycled PLA was studied. Two different accelerated ageing protocols were applied to a commercially available PLA grade to simulate residues with different levels of degradation. The different ageing steps and the reprocessing lead to the degradation of the PLA samples, which translates in an increased amount of carboxyl end groups and reduced intrinsic viscosity and thermal stability.

Thermal treatments of aged PLA promote polycondensation reactions that lead to the elimination of carboxyl end groups and increases in average molecular weight. It is necessary to choose the adequate process conditions because the treatments also cause

degradation reactions, which can negate the positive effects when too high temperatures or residence times are used. The results also depend on the level of degradation of the aged plastic. When severely degraded residues are considered, the thermal treatments are not enough to recover the structure and properties of the starting material. However, when the aged PLA is only moderately degraded, a thermal treatment at 110 °C for 8 h leads to the partial recovering of the initial intrinsic viscosity and the obtainment of recycled materials with structure, thermal stability, Vickers hardness and thermal behavior very similar to those of virgin plastic, using heat treatments that are technically simple, cost-effective and environmentally sound.

#### Author contribution

Freddys R. Beltrán: Investigation, Conceptualization, Formal analysis, Writing - original draft, Visualization.

Esteban Climent-Pascual: Investigation, Conceptualization, Formal analysis, Resources, Writing - review & editing.

María U. de la Orden: Investigation, Conceptualization, Formal analysis, Writing - review & editing, Project administration.

Joaquín Martínez Urreaga: Conceptualization, Methodology, Formal analysis, Writing - review & editing, Project administration.

#### Declaration of competing interestCOI

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

The raw data required to reproduce these findings are available from the authors upon reasonable request.

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