Mechanical recycling of polylactide: improvement of the properties of the recycled material

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Abstract

Poly(lactic acid) (PLA) is one of the most promising alternatives to fossil-fuel based polymers in several applications. However, the production of PLA consumes large amounts of land, increasing the environmental impact of this plastic. Therefore, mechanical recycling has been proposed as an alternative for reducing the consumption of raw materials and thus lowering the environmental impact of PLA. Nevertheless, if the properties of the recycled material are not acceptable, the feasibility of the recycling process would be comprised. The main aim of this work is to study an alternative to improve the properties of the recycled PLA, in order to increase its recyclability. A commercial grade of PLA was subjected to a simulated mechanical recycling process, including photochemical, thermal and hygrothermal ageing steps and a demanding washing process. The obtained material was then melt compounded with virgin PLA, in a 50/50 ratio, and the resulting plastic was characterized. Results indicate that mechanical recycling caused the degradation of PLA, although the structure and optical properties of the recycled plastic were similar to those of the virgin PLA. Furthermore, the addition of 50% of virgin PLA led to an increase on the molecular weight of the polymer, so it could be an interesting alternative for upgrading the properties of the recycled plastic.

Keywords

Poly(lactic acid); Mechanical recycling; Optical properties; Thermal properties

1. Introduction

During the last years, there has been an increasing concern about the environmental issues derived from the massive usage of plastics. The accumulation of wastes has become a genuine problem, with plastics representing approximately 20% by volume of municipal solid waste. Furthermore, conventional plastics are produced from fossil fuels, which limit their sustainability and might even generate an economic problem in a long-term basis [1]. In response to these issues, bioplastics have generated a fair deal of interest over the past years. In fact, it is expected their global production to increase by almost 50% from 2016 to 2021 [2]. Among the most well-known bioplastics are poly(lactic acid) (PLA), polyhydroxyalkanoates (PHA), bio-based poly(ethylene terephthalate) (Bio-PET) and bio-based polyurethanes (Bio-PUR).

PLA is an aliphatic bio-based polyester, produced fundamentally from the fermentation of the glucose present in agricultural sources such as corn, sugar cane or potato [3]. PLA presents some interesting properties, such as: it is biocompatible, safe in food contact, processable with currently available technology

and it has good optical and mechanical properties, comparable to those polystyrene (PS) or PET. These features have made PLA one of the most interesting alternatives for the replacement of fossil-fuel based polymers in several applications, such as textile and packaging applications [4]. Due to this, PLA production and consumption is expected to grow in the coming years, going from 0.2 million tons in 2014 to 0.5 million tons in 2021 [2].

Despite the environmental advantages of using a bio-based plastic, such as PLA, the increase on the consumption of this plastic could generate several environmental and social issues. Firstly, there is the moral debate of using potential food sources (corn or potato) for the manufacture of plastics, while there are several countries experiencing famine problems [5]. Secondly, the massive use of PLA could generate an important accumulation of wastes, especially if the low degradation rate of the grades used in packaging applications is considered [6]. In fact, some studies, such as those conducted by Piemonte [7] and Rossi et al. [8], claim that mechanical recycling is, from an environmental point of view, the most interesting alternative for the valorization of PLA wastes coming from packaging applications.

Although mechanical recycling seems as an interesting valorization method for PLA wastes, it is worth to note that PLA is susceptible to thermo-mechanical degradation during melt processing, which might negatively affect its properties. Therefore, over the past years, several studies have tried to determine the effect of reprocessing and recycling on the performance of PLA. For example, Yarahmadi et al. found an 80% increase of the melt flow index (MFI) of PLA after six reprocessing steps [9]. Similarly, Brüster et al. reported that three reprocessing cycles caused an increase on the crystallization ability and a 30% decrease of the molecular weight [10]. On the same vein, Badía et al. [11], Pillin et al. [12] and Żenkiewicz et al. [13] noticed considerable molecular weight decreases and loss of mechanical properties after five, seven and ten reprocessing steps. Besides thermo-mechanical degradation, other stages of the mechanical recycling process could affect the performance of PLA. In this regard, previous studies performed in our research group point out that the presence of a washing step in the mechanical recycling cause a considerable decrease of the molecular weight, as well as in the gas barrier and mechanical properties of PLA [14,15].

The studies mentioned above demonstrate that mechanical recycling negatively affects the performance of PLA. This might compromise the obtainment of products with added value from recycled PLA, and thus, compromise its recyclability and even its low environmental impact [16]. Consequently, the main aim of this work is to study different alternatives for upgrading the properties of recycled PLA, thus improving the recyclability of the polymer.

2. Potential alternatives for the improvement of the properties of recycled PLA

There are several strategies for increasing the properties of recycled PLA. These strategies could include reactive extrusion with the use of additives, use of nanoparticles and blending of recycled PLA with other polymers [17]. Below, a brief summary of these potential alternatives is presented:

- Reactive extrusion: Several researchers have studied the use of additives for increasing the molecular weight of PLA. These additives might as well be used in the case of the recycled polymer, improving its properties and thus increasing the recyclability of PLA. For example, various peroxides, such as dicumyl peroxide (DCP), have been reported to cause an increase on the molecular weight of PLA [18]. Other studies, as those conducted by Meng et al. [19], Al-Itry et al. [20] and Jaszkiewicz et al. [21], reported that the addition of a multifunctional epoxide chain extender led to an increase of the molecular weight of PLA, with the consequent improvement of the properties of the polymer. Triphenyl phosphite (TPP) has also been studied as a chain extender for PLA, Meng et al. reported an increase of 57% of the molecular weight of PLA with the addition of 2% TPP, with a processing temperature of 180 ºC [22].
- Use of nanoparticles: Although PLA have good optical and mechanical properties, during the past years several reinforcements have been studied, in order to improve other properties of PLA, such as

gas barrier properties [4]. For example, several authors have obtained improvements of the mechanical and thermal properties of PLA by adding small amounts (up to 6%) of modified cellulose nanocrystals [23-26]. Clay nanoparticles have also been widely investigated as reinforcement agents for PLA. Some works point out that the addition, by melt compounding, of small amounts of organically modified montmorillonite (o-MMT) led to the improvement of the mechanical, thermal and gas barrier properties of a PLA matrix [27-31]. Another clay used for the improvements of the properties of PLA is halloysite. Various studies report that the incorporation of modified halloysite nanotubes into a PLA matrix causes an improvement of the mechanical, thermal and gas barrier properties of the polymer [32-34].

- Blending of recycled PLA with other polymers: Some authors, such as Hopmann et al. [35] and Chariyachotilert et al. [36] reported that virgin PLA with a content of up to 60 % of reprocessed or post-consumer PLA, presented acceptable mechanical, optical and thermal properties.

3. Material and methods

3.1. Materials

A commercial grade of PLA, Ingeo^{TM} 2003D, was supplied by Natureworks. It has a melt mass-flow rate of 6 g/10 min (2.16 kg at 210 °C) and a specific gravity of 1.24.

3.2. Recycling simulation

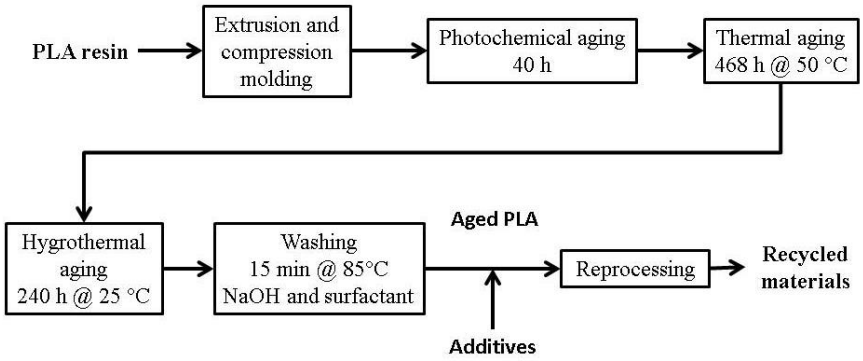

Fig. 1. Recyling process applied to PLA

Fig. 1 schematically shows the mechanical recycling process used in this study. The original resin was melt compounded in a Rondol Microlab twin-screw microcompounder, with L/D = 20 and a screw speed of 60 rpm. The temperature profile was 125, 160, 190, 190 and 180 °C for the feed zone, zones 1, 2, 3 and die, respectively. Then, the resulting material was transformed into films (200 ± 20 μm) in an IQAP-LAP hot-plate press, according to the following procedure: an initial melting without pressure for 5 minutes; a degasification step for 2 minutes; and, finally, a cooling step between cold plates, using a pressure of 14 MPa for 5 minutes.

Part of these films was then subjected to an accelerated ageing process, which included 40 h of photochemical ageing in an Atlas UVCON chamber with eight F40UVB lamps, 468 h of thermal degradation at 50 °C and 240 h of a hydrolytic ageing in water at 25 °C. The aged samples were then washed at 85 °C in a solution of NaOH (1.0 wt.%) and a surfactant (Triton X, 0.3 wt.%). After the washing process, the material was grounded and then reprocessed, by extrusion and compression molding. Table 1 summarizes the obtained materials. It is

worth to note that prior to processing, all PLA was crystallized at 100 °C for 20 minutes. Then, all the materials were dried in a vacuum oven at 85 °C for two hours

Table 1. Materials obtained during the mechanical recycling process.

Description	Abbreviated name
PLA subjected to the first extrusion and compression molding process	PLA-V
PLA subjected to different ageing steps and the washing process	PLA-AW
PLA subjected to the simulated mechanical recycling process	PLA-R
PLA recycled with 50 wt.% virgin PLA	PLA-RV

3.3. Characterization of the samples

Intrinsic viscosity measurements were performed using an Ubbelohde viscosimeter, at 25 °C and using chloroform as solvent. DSC scans were performed on TA Instruments Q20 calorimeter, under nitrogen atmosphere, using standard aluminum pans, a heating rate of 5 °C/min and samples of approximately 5 mg. The thermal program consisted in first heating scan from 30 to 180 °C, an isothermal step for three minutes, a cooling scan until 0 °C, and a second heating scan until 180 °C. FTIR was conducted between 650 and 4000 cm^{-1}, using 16 scans and with a resolution of 4 cm^{-1}, in a Nicolet iS10 spectrometer equipped with an Attenuated Total Reflectance accessory (ATR). The spectra were corrected using the software Omnic 9.2.41. UV-Vis spectra were recorded in a Shimadzu 2401 PC UV-Vis spectrophotometer equipped with a Shimadzu integrating sphere, using a scan speed of 200 nm/min. The overall transmittance in the visible light region was measured according to the ISO 13468 standard.

4. Results and discussion

PLA can undergo several chain scission processes (such as photochemical, hydrolytic and thermomechanical) during its service life and/or its mechanical recycling, which cause a decrease of the molecular weight of PLA, and might affect the performance of the material [15]. Table 2 shows the values of intrinsic viscosity of the different samples. On the one hand, it can be seen that mechanical recycling caused a 17% decrease on the intrinsic viscosity of PLA. Such decrease is related to the generation of shorter polymer chains as a result of the degradation of PLA during the photochemical, thermal and hydrothermal ageing of the polymer. However, the intrinsic viscosity values of PLA-V and PLA-AW are very close, suggesting that most of the chain scission processes take place during the melt reprocessing step. On the other hand, the sample with 50% virgin PLA presents a slightly higher value of intrinsic viscosity than the recycled material. This result was expected, since virgin PLA (which has not been subjected to any degradation process) has a higher molecular weight than PLA-R.

Table 2. Molecular weight and light transmission rate of the different samples.

Sample	Intrinsic viscosity (mL/g)	Light transmission (%)
PLA-V	132 ± 2	94 ± 1
PLA-AW	129 ± 7	78 ± 3
PLA-R	109 ± 4	95 ± 1
PLA-RV	115 ± 8	95 ± 1

The reduction of the molecular weight of PLA could also affect the chemical structure of the polymer; therefore, FTIR.-ATR spectra of all the samples were recorded. In general, there were no important differences between the samples. However, as it can be seen on Fig. 2, there is a significant difference between the PLA-AW and the rest of the materials between 1000 and 900 cm^{-1}. PLA-AW present an increased absorption band at 920 cm^{-1}, which is related to the formation of crystalline structures [37]. This absorption band disappears in the recycled sample. These results indicate that the ageing and washing processes cause the crystallization of the polymer; however, this crystalline structure is destroyed during the reprocessing step.

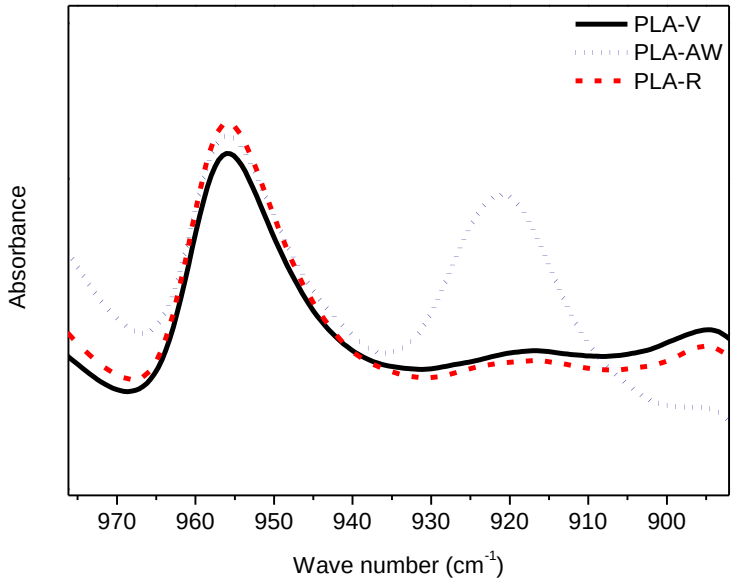

Fig. 2. Comparison of the band at 920 cm^{-1} of PLA-V, PLA-AW and PLA-R.

DSC scans were conducted on all the samples in order to study the effect of the mechanical recycling, and the posterior upgrading of the recycled material, on the structure and thermal properties of PLA. The results are summarized on Table 3 and Fig. 3. On the one hand, it can be seen that that PLA-AW does not show the characteristic cold crystallization peak of PLA. A similar behavior was reported by us for PLA immersed in a PBS solution at 58 °C, and it was attributed to the high crystallinity of the material, which inhibits the reorganization of the polymeric chains into crystalline structures during the heating [37]. Furthermore, Table 3 shows that PLA-AW present a crystallinity degree of 32 %, which agrees with the results seen by means of FTIR-ATR spectroscopy.

On the other hand, Fig. 3 shows the glass transition of PLA was affected neither by the recycling processes, nor by the blending of the recycled and virgin materials. Fig. 3 and Table 3 also show a decrease of the cold crystallization temperature (T_{CC}) of PLA-R in comparison with PLA-V. This difference is due to the degradation of PLA during the recycling processes, since shorter polymer chains crystallize at lower temperatures [15]. However, it can also be seen that the addition of 50% of virgin PLA caused a slight increase on T_{CC}, indicating that this material has longer polymer chains, as it was seen by means of solution viscosimetry. Finally, it can be noticed on Table 3 that the cold crystallization and melting enthalpies are very similar for PLA-V, PLA-R and PLA-RV, thus indicating that the mechanical recycling did not promoted the formation of crystalline structures in PLA.

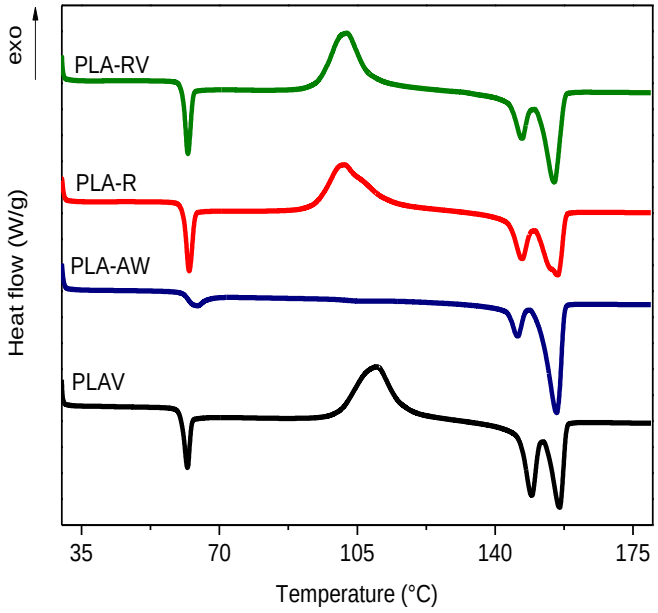

Fig. 3. First DSC heating scans of the different samples.

Table 3. DSC results obtained for the different materials.

Sample	First heating scan				
	T_{CC} (°C)	T_M (°C)	ΔH_{CC} (J/g)	ΔH_M (J/g)	Xc (%)
PLA-V	109.9	149.3-156.4	29.2	29.6	0
PLA-AW	-	145.8-155.6	0.0	29.4	32
PLA-R	101.8	146.9-156.0	27.2	27.8	0
PLA-RV	102.4	146.9-155.0	28.5	29.0	0

Mechanical recycling could affect some properties of PLA, such as the optical properties. UV-Vis spectra of all the samples are presented in Fig. 4. It can be noticed that the ageing and washing step cause an important decrease on the light transmission rate of PLA. This behavior could be explained by the high

crystallinity degree of PLA-AW, which was observed by means of DSC and FTIR-ATR, since crystalline structure could act as scattering agents for the visible light.

Regarding the optical properties of the recycled materials, there is a small difference between PLA-V, PLA-R and PLA-RV, concretely, the appearance of an absorption band around 280 nm in the recycled materials. This band has been previously reported in PLA subjected to washing processes [15,36], and could be attributed to the presence of carboxyl end groups, as a result of the degradation of the polymer during the different ageing and reprocessing steps. However, PLA-R present a slightly higher absorption than the material PLA-RV, indicating that the sample with 50% virgin PLA is less degraded than PLA-R, as it was seen by solution viscosimetry. It is also worth to note that Fig. 4 and Table 2 show that, despite the degradation of PLA, the light transmission on the visible region (i.e. between 400 and 800 nm), of PLA-V, PLA-R and PLA-RV is very similar. This result is very important since the optical clarity, which is directly related with the light transmission rate, plays a key role in food packaging applications.

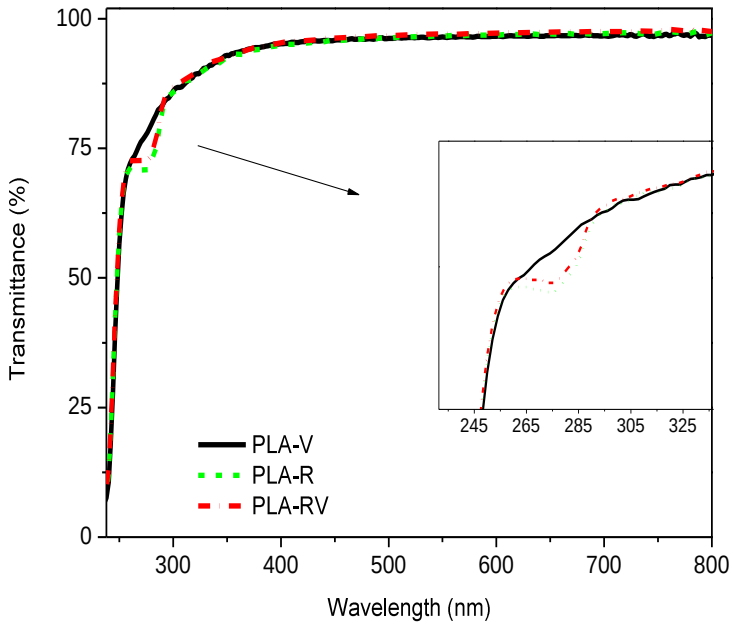

Fig. 4. UV-Vis spectra of PLA-V, PLA-R and PLA-RV

5. Conclusions

The preparation of blends, consisting in 50% virgin and 50% mechanically recycled PLA, as an alternative for the improvement of the properties of recycled PLA was studied. Intrinsic viscosity measurements and UV-Vis spectroscopy show that mechanical recycling caused a decrease of the molecular weight of PLA. Most of this degradation takes place during the reprocessing step. However, the addition of the virgin polymer resulted in an increase of the intrinsic viscosity of the material. DSC results point out that cold crystallization of recycled PLA takes place at lower temperatures than in the virgin polymer. Similarly to what was observed in the intrinsic viscosity values, the addition of the virgin polymer led to a displacement of the cold crystallization temperatures to higher values, thus confirming the higher molecular weight of the recycled material with 50% virgin PLA.

Despite these changes in the molecular weight, DSC results show no difference between the overall crystallinity degrees of the samples, being close to zero in all the cases. The amorphous nature of the material

contributed to the good optical properties, achieving a light transmission rate of approximately 95% in all the samples.

Summarizing, the ageing, washing and reprocessing steps resulted in the degradation of PLA, although the structure and the optical properties of the recycled material are similar to those of virgin PLA. The preparation of a blend with 50% virgin PLA led to an increase of the molecular weight of the material, which may indicate that the addition of virgin PLA is an interesting alternative for improving the properties of mechanically recycled PLA. Furthermore, other alternatives such as the addition of peroxides or nanoreinforcements could be studied in order to upgrade the performance of mechanically recycled PLA.

6. Acknowledgements

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