Effects of process conditions on the effectiveness of solid-state polymerization in the recycling of poly(lactic acid) waste.

F.R. Beltrán[1,3], M.U. de la Orden[2,3], E. Climent[1], J. Martínez Urreaga[1,3]

[1]Dpto. Ingeniería Química Industrial y del Medio Ambiente, E.T.S.I. Industriales, Universidad Politécnica de Madrid, C7 José Gutiérrez Abascal - 2, 28006 - Madrid, Spain.
[2]Dpto. de Química Orgánica I, Facultad de Óptica y Optometría, Universidad Complutense de Madrid, C/ Arcos de Jalón – s/n, 28037 - Madrid, Spain.
[3]Grupo de Investigación: Polímeros, Caracterización y Aplicaciones (POLCA)
Keywords: solid-state polymerization; bioplastic waste; poly(lactic acid); mechanical recycling
Presenting author email: joaquin.martinez@upm.es

Poly(lactic acid), PLA, is one of the most important bioplastics in the market. Its good processability, optical and mechanical properties, along with its relatively low cost, have made this plastic one of the most interesting alternatives to fossil-fuel based polymers, such as polystyrene (PS) and poly(ethylene terephthalate) (PET), in several applications, among which food packaging stands out. The growing interest in PLA is leading to an increase in the production and consumption of this plastic, going from a global production capacity of $2·10^5$ t in 2014 to an expected capacity of $5·10^5$ t in 2021 (Aeschelmann and Carus, 2017).

Despite the low environmental impact of PLA, its massive use could generate some social and environmental problems, especially if the generated wastes are not adequately managed. Among the alternatives proposed for the management of PLA wastes is mechanical recycling, which would allow the valorization of PLA wastes, while reducing the consumption of raw materials and energy. However, previous studies conducted in our research group point out that, depending on the process conditions, mechanical recycling can cause a significant degradation on PLA, along with a reduction of the mechanical and gas barrier properties of the polymer, as it is shown in Table 1 (Beltrán et al., In press, Beltrán et al., 2017).

Table1. Intrinsic viscosity, mechanical and gas barrier properties of PLA submitted to different recycling processes

Sample	**Intrinsic Viscosity (mL/g)**	**Vickers Hardness (MPa)**	**Permeability coefficient against O_2 (Barrer)**
Virgin PLA	132 ± 1	174 ± 4	1.29
Recycled PLA	124 ± 4	157 ± 6	1.46
Recycled and washed PLA	104 ± 4	154 ± 2	1.57

The decrease of performance of mechanically recycled PLA might discourage plastic manufacturers from using recycled PLA in high-value applications, threatening its low environmental impact. Therefore, it is necessary to find methods that allow to recover the properties, or upgrading, of mechanically recycled PLA, in a cost-effective and environmentally friendly manner. Among the potential alternatives for upgrading mechanically recycled PLA is solid-state polymerization (SSP).

SSP consists in heating a solid polymer (or prepolymer) of relatively low molecular weight to a temperature between glass transition (Tg) and melting (Tm), to improve the mobility of the end groups and increase their reactivity. This process may or may not include the use of catalyst. The byproducts of the polymerization are continuously removed either by evaporation under reduced pressure or by passing inert gas through the system (Vouyiouka et al., 2005). It is worth to note that SSP does not require any solvents, making it very interesting from an environmental point of view. SSP has been studied as a method to increase molecular weight in different polymers such as PET or PLA. However, no information regarding the feasibility of this process to improve the performance of mechanically recycled PLA is currently available.

The effectiveness of SSP depends on several variables, which include time and temperature, atmosphere (vacuum or inert gas flow), reactor design and use of catalyst. Consequently, the main aim of this work is to study the effects of these variables on the molecular weight and the properties of mechanically recycled PLA. To achieve this, a commercial grade of PLA has been subjected to a mechanical recycling process including a first extrusion and compression molding process, an accelerated aging (consisting in photochemical, thermal and hygrothermal aging), a demanding washing step and, finally, a second melt processing step. The obtained material was introduced, with and without a tin octoate catalyst, in a reactor under vacuum pressure/N_2 atmosphere at different temperature and residence time conditions. The resulting material was then characterized using several experimental techniques such as solution viscosimetry, FTIR spectroscopy and differential scanning calorimetry.

The first results obtained indicate that significant increases in the values of the intrinsic viscosity of the recycled plastic can be achieved by this method.

Acknowledgements
The authors acknowledge financial support of MINECO-SPAIN (Project CTM2017-88989-P) and UPM (Project RP160543006).

References

Aeschelmann F, Carus M (2017). Biobased Building Blocks and Polymers: Global Capacities and Trends 2016-2021, Hürth, Germany, nova-Institüt.

Beltrán FR, Ortega E, Solvoll AM, Lorenzo V, de la Orden MU & Martínez Urreaga J (2017) Effects of Aging and Different Mechanical Recycling Processes on the Structure and Properties of Poly(lactic acid)-clay Nanocomposites. Journal of Polymers and the Environment .

Beltrán FR, Lorenzo V, Acosta J, de la Orden MU & Martínez Urreaga J (In press) Effect of simulated mechanical recycling processes on the properties of poly(lactic acid). J Environ Manag .

Vouyiouka, S.N., Karakatsani, E.K., Papaspyrides, C.D., 2005. Solid state polymerization. Progress in Polymer Science 30, 10-37.