Use of nanoclays for the valorization of poly(lactic acid) wastes

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Poly(lactic acid) (PLA) is one of the best positioned bioplastics in the market. Its good optical and mechanical properties, along with its biodegradability, biocompatibility and safety in food contact have made PLA an alternative, with lower environmental impact, to fossil fuel-based polymers in several applications, such as food packaging (Auras et al., 2010). This interest is leading to a continuous growth in the production of PLA, which is projected to grow by 60% between 2018 and 2023 (European Bioplastics, 2019). Despite the low environmental impact of PLA, a massive consumption and the inadequate management of the derived wastes could lead to social and environmental problems, making it necessary to propose methods to valorize PLA wastes. Among the alternatives posed for the valorization of PLA wastes, mechanical recycling plays a prominent role, since it allows to reduce the amount of raw materials and energy used in PLA production (Beltrán et al., 2018a).

Despite the advantages of mechanical recycling, previous studies conducted in our research group report that mechanical recycling leads to a decrease on the molecular weight and some important properties for packaging applications (Beltrán et al., 2018a). However, there are several methods to overcome, at least partially, the decrease of the performance of recycled PLA, such as the addition of organic fillers and nanofillers, the reactive extrusion using chain extenders and/or peroxides (Beltrán et al., 2019) or the addition of functionalized clays. Recently, it has been shown that the additions of small amounts of amino-modified halloysite allows improving some properties of recycled PLA (Beltrán et al., 2018b). Following this research project, the main aim of this work is to study the use of different organically-modified nanoclays to improve the properties of mechanically recycled PLA, in order to increase the attractiveness of recycled PLA in demanding applications.

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. During this second processing step, halloysite nanotubes modified with (3-glycidyloxypropyl)trimethoxysilane (GPTS) and a polyethylenimine (PEI) (M_w = 800 g/mol) were added to PLA to obtain nanocomposites. The resulting materials were characterized using intrinsic viscosity measurements, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR) and microhardness measurements.

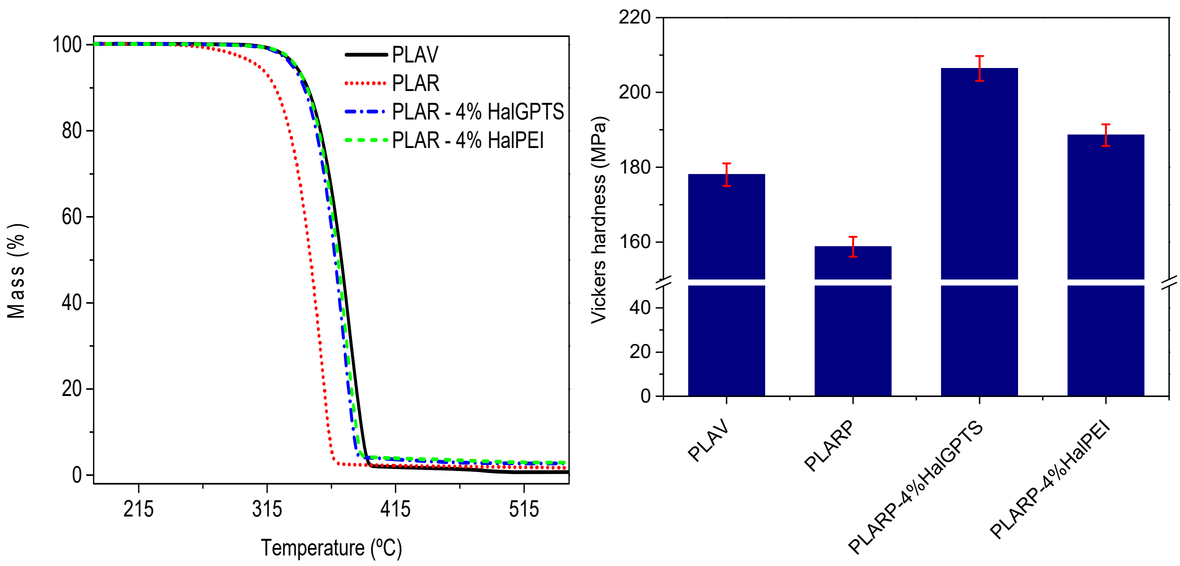

Figure 1. TGA curves (left) and Vickers hardness (right) of PLA with functionalized halloysite.

Figure 1 shows the results of TGA and microhardness measurements for the virgin (PLAV), recycled (PLAR) and PLAR-halloysite nanocomposites. TGA curves show that mechanical recycling leads to a decrease of the thermal stability of PLA. This result is in good agreement with those obtained in previous studies (Beltrán et al., 2018a), and it can be explained by the chain scission reactions that take place during the ageing, washing and reprocessing steps. The shorter polymer chains decompose at a lower temperature, hence decreasing the thermal stability of the material. However, most of the thermal stability can be recovered with the addition of 4% functionalized halloysite. Both GPTS (PLAR-4%HalGPTS) and PEI (PLAR-4%HalPEI) functionalized halloysite nanocomposites show a thermal stability close to that of PLAV. To explain this behaviour two factors could be considered. Firstly, the halloysite nanotubes could interact with some of the carboxyl end groups present in aged PLA, reducing the catalytic effect these have on PLA degradation and thus reducing the decrease of molecular weight of PLA (Beltrán et al., 2018b). Secondly, halloysite nanotubes could act as a barrier, delaying the liberation of decomposition products of PLA, and thus increasing the thermal stability of the material.

Regarding the mechanical properties of the samples, figure 1 shows that degradation during mechanical recycling leads to a decrease of the hardness of PLA. Figure 1 also that the addition of functionalized clays also causes an important improvement of the mechanical properties of PLA, even exceeding those of PLAV. These results can be explained considering that the modified clays reduce the degradation of PLA during the reprocessing step and that the clay nanotubes reinforce the recycled PLA matrix.

Summarizing, the above results indicate that the utilization of functionalized nanoclays could lead to an improvement of the performance of recycled PLA, compensating the degradation of the plastic during recycling, thus increasing its recyclability.

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Reference

Auras, R., Lim, L., Selke, S.E.M., Tsuji, H., 2010. Poly(Lactic Acid): Synthesis, Structures, Properties, Processing, and Applications. John Wiley & Sons, New Jersey

Beltrán, F.R., Lorenzo, V., Acosta, J., de la Orden, M.U., Martínez Urreaga, J., 2018a. Effect of simulated mechanical recycling processes on the structure and properties of poly(lactic acid). J. Environ. Manag. 216, 25-31

Beltrán, F.R., de la Orden, M.U., Martínez Urreaga, J., 2018b. Amino-Modified Halloysite Nanotubes to Reduce Polymer Degradation and Improve the Performance of Mechanically Recycled Poly(lactic acid). J. Polym. Environ. 26, 4046-4055

Beltrán, F.R., Infante, C., de la Orden, M.U., Martínez Urreaga, J., 2019. Mechanical recycling of poly(lactic acid): evaluation of a chain extender and a peroxide as additives for upgrading the recycled plastic. J. Clean. Prod. https://doi.org/10.1016/j.jclepro.2019.01.206

European Bioplastics. https://www.european-bioplastics.org/market/ visited on 01/31/2019