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Mechanical recycling of polylactide, upgrading trends and combination of valorization techniques

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ABSTRACT

The upcoming introduction of polylactides in the fractions of polymer waste encourages technologists to ascertain its valorization at the best quality conditions. Mechanical recycling of PLA represents one of the most cost-effective methodologies, but the recycled materials are usually directed to downgraded applications, due to the inherent thermo-mechanical degradation affecting its mechanical, thermal and rheological performance. In this review, the current state of mechanical recycling of PLA is reported, with special emphasis on a multi-scale comparison among different studies. Additionally, the applications of physical and chemical upgrading strategies, as well as the chances to blend and/or composite recycled PLA are considered. Moreover, the different valorization techniques that can be combined to optimize the value of PLA goods along its life cycle are discussed. Finally, a list of different opportunities to nurture the background of the mechanical recycling of PLA is proposed, in order to contribute to the correct waste management of PLA wastes.

1. Framework of the review

Short-time applications from bio-based and biodegradable [1] plastics have attracted much interest [2] in different industrial, social and economic sectors ranging from biomedical applications for their use in surgery [3], as sutures, tissues or scaffolds; pharmacology [4] as drug carriers [5], and packaging, as containers [6] for drinkable liquids [7] or cosmetics. One of the

Abbreviations: $[LA_C]_n$, cyclic PLA oligomer; $[LA_L]_n$, linear PLA oligomer; Δh_{CC}, specific cold-crystallization enthalpy; AFM, Atomic Force Microscopy; D, fragility parameter; DETA, Dielectric Thermal Analysis; DMTA, Dynamic Mechanical-Thermal Analysis; DSC, Differential Scanning Calorimetry; EOL, End of Life; FT-IR, Fourier-Transform InfraRed Scpectroscopy; GC, Gas Chromatography; GPC, Gel Permeation Chromatography (see also SEC); GWP, Global Warming Potential; HDT, Heat Deflection Temperature; HPLC, High Performance Liquid Chromatography; LCA, Life Cycle Assessment; LMWC, low molecular weight compounds; MALDI, Matrix-Assisted Laser Desorption/Ionization; MFR, Melt-Mass Flow Rate; Mn, average molar mass in number; MS, Mass Spectrometry; MV, viscous molar mass; NMR, Nuclear Magnetic Resonance; OIT, Oxidation Induction Time; OT, Oxygen Transport; PE, polyethylene; PET, poly(ethylene terephthalate); PHA, poly(hydroxyalcanoate); PLA, polylactide or poly(lactic acid); POM, Polarized Optical Microscopy; PS, polystyrene; PVC, poly(vynil chloride); Py, pyrolysis; Ri, reprocessing cycle number "i"; RPLA-i, PLA reprocessed "i" times; RWF, Recycled Wood Fiber; SEC, Size Exclusion Chromatography (see also GPC); SEM, Scanning Electron Microscopy; σ_B, stress at break; σ_T, tensile strength; T_{CC}, cold-crystallization temperature; TDB, Thermal Decomposition Behaviour; TEM, Transmission Electron Microscopy; T_g, glass transition temperature; tg(δ), tangent of delta, from DMTA; TGA, Thermogravimetric Analysis; T_M, melting temperature; TOF, Time-of-Flight; T_{OX}, Temperature of Oxidation; UV, ultra-violet; V, virgin; VFTH, Vogel-Fulcher-Tamann-Hesse; VPLA, virgin PLA; WVT, water vapour transport; X_C, crystallinity degree; ZDT, Zero-Decomposition Temperature.

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key reasons driving this growing interest is the incompatibility of the non-renewable polymeric waste with the environment where they are disposed after their use. The efforts have been therefore focused on the development of novel biodegradable polymers satisfying the requirement of degradability, compatibility with the disposal environment and the release of low-toxicity degradation products [8]. In fact, a trend to derive more carbon from the renewable resources to preserve the ecosystem can be found, moving from the petrochemical industry to fermentation and genetic engineering options, in a cost-effective and ecologically sustainable framework [8]. However, after the evaluation of the sustainability of bio-based plastics, it is generally concluded that none of those currently in commercial use or under development are fully sustainable. Some bio-based plastics are preferable from a health and safety perspective and others from an environmental perspective. In general, polymers such as polylactides (PLA)s, poly(hydroxyalcanoate)s (PHA)s or starch-based polymers are commonly chosen over other bio-based polymers [9].

Polylactides (PLA) are thermoplastic polyesters obtained from the ring-opening polymerization of lactide, which may be derived from the fermentation of sugar feedstocks at competitive prices compared to those previously achievable from petrochemical derived products [10,11]. PLAs have numerous interesting properties including good processability, mechanical properties, thermal stability and low environmental impact [12]. In particular, PLA stands out as an alternative to substitute commodities in well-established sectors. Such could be the case of the replacement of poly(ethylene terephthalate) (PET) bottles in the packaging industry [13]. Actually, a comparative assessment of the environmental profile of PLA and PET for drinking water bottles from a Life Cycle Assessment (LCA) perspective showed that the environmental performance of PLA bottles was better than that of PET bottles in terms of Global Warming Potential (GWP), reduction of dependency on fossil energy, and decrease of human toxicity [14]. The End of Life (EoL) is not always considered in LCA, nevertheless, those reports that included it described much higher GWP results than those which limited the scope to the stage of the production of resins or pellets. Including EoL in the LCA provides more comprehensive results for bio-based polymers, but simultaneously introduces greater amounts of uncertainty and variability. Although there is little LCA data available on the impacts of different manners of disposal, it has been argued that it would be critical for future sustainability assessments [15].

The necessary implementation of unit operations during the dismantling process, new separation technologies, and the logistics of handling additional streams of material will require further studies, developments, and monitoring, in order to develop more robust and effective recovery methods [16]. As well, it is known that bio-based materials are suitable for biological waste treatment trough composting, thus having a great potential to contribute to the reduction of the amount of waste sent to landfill and generating valuable soil improvers, which is of great importance for industries, governments and consumers [17]. However, the presumably high amount of bio-based plastic waste surpassing the capability of composting facilities has to be taken into account [13]. In this sense, to explore the chances of enhancing the valorization of PLA goods, by means of material/mechanical or chemical/energy methods would be advisable, thus strengthening the possibilities of extending their service lives and or obtain an added value before finally discarding them into bio-disposal facilities [18].

Previous reviews have been focused on the different possibilities of general recycling of plastic waste [18] and bioplastics, their blends and biocomposites by means of mechanical and chemical methods [19]. In this review, a deep focus is given to the mechanical recycling of polylactide, blends, and composites thereof, with emphasis on the connection between molecular-level variations and macroscopic performance of recyclates. In addition, the different valorization techniques that can be combined to optimize the value of PLA goods along its life-cycle are discussed. Finally, a list of different opportunities to nurture the background of the mechanical recycling of PLA is proposed, in order to contribute to the correct waste management of future PLA wastes.

2. Mechanical recycling

Mechanical recycling represents one of the most successful processes and has received considerable attention due to its main advantages, since it is relatively simple, requires low investment, and its technological parameters are controlled [20].

The assessment of the degradation mechanism is necessary to determine the quality of recycled polymers and guarantee their further performance in second-market applications. The quality of recycled polymers has been defined as the combination between the degree of mixing, the degree of degradation and the presence of low molecular weight compounds [21]. It is known that polymers are subjected to the influence of degrading agents such as oxygen, light, mechanical stresses, temperature and water, which, separately or in combination, during its material loop (synthesis - processing - service life - discarding - recovery), results in chemical and physical changes that alter their stabilization mechanisms and long-term properties [21]. The degradation makes physical properties and functional quality of a polymer worse, hence reprocessed products of high confidence are difficult to obtain. In particular, top quality is crucial in the case of thin films, for which optical and barrier properties, among other issues, play an important role [22]. These degradation processes may modify the structure and composition of the polymers and consequently change the thermal, viscoelastic and mechanical performance of the recyclates [21].

It is therefore necessary to implement experimental protocols to simulate the environmental conditions that plastics are subjected to during mechanical recycling. A multi-level scheme in which the different stages of assessment of mechanical recycling performed in lab-scale facilities are represented is shown in Fig. 1, along with the analytical techniques commonly used to test the performance and/or degradation state of the resulting material.