Improving the Mechanical Ductility and Toughness of Injection-molded Polylactide Pieces by the Dual Incorporation of Liquor Waste Derived Spent Coffee Grounds and Oligomers of Lactic Acid

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Abstract

This work puts the Circular Bioeconomy’s concept into action, originally valorizing residues from the beverage liquor coffee industry into reinforcing fillers for green composites of polylactide (PLA). The as-received spent coffee grains derived from liquor waste were first milled to obtain the so-called spent coffee grounds (SCGs), which were then incorporated at 20 wt.% into PLA by extrusion. With the aim of improving the compatibility between the biopolyester and the lignocellulosic particles, two oligomers of lactic acid (OLAs), namely OLA2 and OLA2_{mal}, being the latter functionalized with maleic anhydride (MAH), were both added during the extrusion process at 10 wt.%. The resultant compounded pellets were finally shaped into pieces by injection molding for characterization. Results showed that, as opposite to most claims published in the literature of PLA composites based on lignocellulosic fillers derived from soluble coffee wastes, the incorporation of liquor waste derived SCGs increased the ductility of the pieces by nearly 280% due to their high coffee oil content. The incorporation of OLA2 and OLA2_{mal} contributed to improve the impact strength of the pieces by approximately 6% and 12.6%, respectively. The higher performance of OLA2_{mal} was ascribed to a reduction of crystallinity in the green composite due to the chemical interaction by the MAH groups. However, the incorporation of SCGs into PLA slightly reduced the thermal stability and yielded a dark-to-brown color, whereas it also delayed the disintegration rate of the pieces in controlled compost soil. Therefore, the results attained herein open up novel opportunities for the development of green composites of PLA with higher ductility and toughness through the valorization of liquor coffee wastes.

Statement Of Novelty

The successful transition in the packaging industry of linear economies to circular and more sustainable bioeconomies requires the development of high-performance materials derived from biomass and wastes. The novelty of this study lies on the valorization, for the first time, of liquor coffee waste to yield fillers able to produce compostable green composites of with improved ductility.

Introduction

In recent years, society is becoming more aware about the environmental issues produced by the extensive use of petroleum derived and non-compostable or recyclable e materials. This has promoted the development of environmentally friendly polymer materials with high performance that could potentially replace conventional polymers [1]. Among these materials, green composites are particularly interesting since they are formed by a biopolymer matrix and a natural filler [2-4]. Furthermore, green composite materials can strongly contribute to the development of the so-called Circular Bioeconomy as these are obtained from natural resources or, more sustainably, wastes and can be fully biodisintegrated under different composting conditions [5]. In the area of biodegradable polymers, polylactide (PLA) has made a large contribution since this biopolyester is both fully bio-based, obtained from starch-rich materials, and compostable in controlled industrial facilities [6, 7]. PLA is a linear thermoplastic that shows high mechanical resistance and thermal stability, good transparency, and water-barrier
performance, by which it can potentially substitute some polymer commodities, such as polypropylene (PP) or polystyrene (PS), in several applications, ranging from food packaging [8-10] to automotive [11], biomedicine [12], or electronics [13]. In spite of this, the use of PLA-based articles is currently limited by its poor toughness and brittle behavior, low thermomechanical resistance, and relatively high cost [14].

In a Circular Bioeconomy context, lignocellulosic materials obtained from processing by-products and wastes of the food and agroforestry industries are also gaining more attention as cost-effective fillers due to their natural origin and favored biodegradability [15]. Several agro-food waste derived fillers have been reported in recent years, for example, almond shell [16], peanut skin [17, 18], argan nut shell [19, 20], pineapple flour [21], coconut fibers [22], etc. In this regard, huge quantities of by-products and wastes are generated during the ‘fruit-to-cup’ transformation of coffee beans, including not only leaf, flower, and cherry, but also coffee husks, coffee silver skin (CSS), and spent coffee grounds (SCGs) [23, 24]. SCG is the resultant dark colored residual material obtained during the treatment of coffee powder with hot water or steam for the instant (or hydrosoluble) coffee preparation. It is considered that nearly 50% of the worldwide coffee production is processed for soluble coffee preparation, whereas 0.33—0.45 kg of instant coffee is obtained in the soluble coffee industry from 1 kg of green coffee beans [25]. As a result, this process generates 550—670 g of SCG per kg of coffee beans, that is, 6 million tons of SCG per year. Polysaccharides are the most abundant components in SCG (12.4 wt.% cellulose, 39.1 wt.% hemicellulose, 23.8 wt.% lignin), followed by proteins (17.4 wt.%), lipids (2.3 wt.%), and ashes (1.3 wt., mainly potassium minerals), which varies depending on both the variety of coffee beans and extraction process [26]. The industry of coffee liquor, however, is not so common due to it is quite specific from certain geographical areas. In this industry, Arabian coffee grounds are naturally roasted and then macerated with alcohol to obtain the alcoholic beverage. Furthermore, different than the instant coffee, which uses pressurized hot water (175 ºC) to extract all the soluble solids and volatile compounds [23], the coffee used for the liqueur industry is not subjected to any drastic temperature or extraction processes. As a result, the resultant SCGs can retain their natural compositions in proteins and lipids.

Potential uses of SCGs include biodiesel production [27], elements to increase compost quality [28], water purification of pharmaceutic products [29], or used as a biofuel by its own [30]. Nevertheless, SCGs can also be used as reinforcing filler in the development of green composites [31-33]. Moreover, SCG also contains polyphenols and free radicals that can offer antioxidant and anti-tumor activities [34]. However, one of the main drawbacks of lignocellulosic fillers when incorporated into polymer matrices, such as SCGs and PLA, respectively, is their poor filler-matrix interfacial adhesion, which increases the probability of particle aggregate formation. This low compatibility is based on the their poor chemical affinity since PLA and other biopolymesters are highly hydrophobic, while lignocellulosic fillers show a more hydrophilic character [35]. As a result of this poor affinity, the thermal stability and mechanical ductility of these green composites tend to decrease. In this regard, the use of plasticizers or compatibilizers can be very useful for improving the interfacial adhesion between the lignocellulosic fillers and polymer matrices [16, 36]. In green composites, compatibilization is achieved through a melt-grafting process of the natural fillers onto the polymer chains during extrusion using multi-functional additives, that is, with multiple
reactive groups or sites [37]. Normally, these reactive compatibilizers are low-molecular weight (M<sub>W</sub>) polymers or oligomers containing multiple epoxy or maleic anhydride (MAH) groups [38, 39]. During the so-called reactive extrusion (REX), some of the oxygen-based groups of the compatibilizer form new ester bonds with the terminal hydroxyl (—OH) or carbonyl (—COOH) groups of the biopolyester while, at the same time, other groups can react with the —OH groups present on the surface of the lignocellulosic filler, thus improving compatibility by the formation of covalent bonds [16, 40]. In PLA formulations, oligomers of lactic acid (OLAs) habitually provide this kind of compatibility through plasticization of the biopolyester matrix, taking advantage of their similar chemical structure. In particular, 20 wt.% of OLA has been reported to reduce PLA’s glass transition temperature (T<sub>g</sub>) by 13 ºC [41] as well as to improve its mechanical ductile properties [42]. Moreover, it is possible to chemically modify OLAs, incorporating reactive functional groups into their structure. For example, Lowe et. al. [43] reported the development of controlled M<sub>W</sub> telechelic lactic acid oligomers with acrylate functionalities by transesterification. Additionally, the work of Grosse et. al. [44] reported the addition of functional MAH groups into the structure of OLA.

This work reports the preparation and characterization of injection-molded pieces of PLA/SCG green composites with the objective of developing a sustainable and cost-efficient material for packaging and other industrial applications. To improve the compatibility between the PLA matrix and the SCG filler and, then, the performance of the green composite, two novel OLAs were originally tested, namely OLA2 and OLA2<sub>mal</sub>. Whereas OLA2 is based on the typical structure of OLA, OLA2<sub>mal</sub> is a novel grade that presents several reactive MAH groups distributed along its chains.

**Materials And Methods**

**Materials**

PLA, PURAPOL L130 grade, with 99% L-isomer, was provided by Corbion (Amsterdam, Netherlands). It shows a density of 1.24 g·cm<sup>-3</sup> and a melt flow rate (MFR) of 16 g/10 min (210 ºC and 2.16 kg). This PLA grade has the food contact status, whereas it is suitable for both injection molding and fiber spinning and in compliance with the compostability EN-13432 standard.

SCGs were supplied by Licores Sinc. S.A. (Alcoy, Spain), which is obtained as a by-product from a liquor drink production process. In this process, the coffee grains are first naturally roasted and then macerated for 10 days in alcohol to obtain the drink, called coffee liquor. The resultant biomass was washed with clean water and, thereafter, dried in a dehumidifying stove (MCP Vacuum Casting System, Lubeck, Germany) for 48 h at 40 ºC to remove any residual moisture. Finally, to obtain the so-called SCGs, the grains were milled in a ZM 200 centrifugal mill from Retsch (Düsseldorf, Germany) at a speed of 12,000 rpm and sieved with a 250-µm mesh filter. Figure 1 shows the images of the as-received liquor waste derived spent coffee grains and the resultant SCG particles.
Glyplast OLA2 y OLA2$_{\text{mal}}$ were gently obtained from Condensia Química Inc. (Barcelona, Spain). Glyplast OLA2 is a liquid oligomer of lactic acid with a molecular weight comprised between 500–600 g mol$^{-1}$. It has a viscosity of 90 mPa s at 40 °C and an ester content >99% as indicated in the technical datasheet. Its density is 1.10 g cm$^{-3}$; it has a maximum acid number of 2.5 mg KOH g$^{-1}$, and a maximum water content of 0.1 wt%. With regard to Glyplast OLA2$_{\text{mal}}$, it is an OLA2 derivative grafted with maleic anhydride to increase reactivity. The maleic anhydride content is comprised between 3-4 wt%. Figure 2 depicts the chemical structure of both oligomers.

**Preparation of PLA/SCG Composites**

PLA, OLA2, OLA2$_{\text{mal}}$, and SCG were initially dried at 40 °C for 48 h in a dehumidifying dryer MDEO to remove any residual moisture prior to processing. Then, the corresponding weight fraction (wt.%) of each component was mixed and pre-homogenized in a zipper bag. The corresponding formulations, shown in Table 1, were compounded in a twin-screw extruder from Construcciones Mecánicas Dupra, S.L. (Alicante, Spain). This extruder has a 25 mm diameter with a length-to-diameter ratio (L/D) of 24. The extrusion process was carried out at a rate of 22 rpm, using the following temperature profile (from hopper to die): 180–185–190–195 °C. The compounded materials were pelletized using an air-knife unit. In all cases, the residence time was approximately 1 min.

**Table 1.** Summary of compositions according to the weight content (wt.%) of polylactic (PLA), spent coffee ground (SCG), and the oligomers of lactic acid (OLAs).

| Piece           | PLA (wt.%) | SCG (wt.%) | OLA2 (wt.%) | OLA2$_{\text{mal}}$ (wt.%) |
|-----------------|------------|------------|-------------|----------------------------|
| PLA             | 100        | 0          | 0           | 0                          |
| PLA+SCG         | 80         | 20         | 0           | 0                          |
| PLA+OLA2        | 90         | 0          | 10          | 0                          |
| PLA+OLA2$_{\text{mal}}$ | 90     | 0          | 0           | 10                         |
| PLA+OLA2+SCG    | 70         | 20         | 10          | 0                          |
| PLA+OLA2$_{\text{mal}}$+SCG | 70     | 20         | 0           | 10                         |

The pellets were shaped into standard samples in a Meteor 270/75 injector from Mateu & Solé (Barcelona, Spain). The temperature profile in the injection molding unit was 185 °C (hopper), 190 °C, 195 °C, and 200 °C (injection nozzle). A clamping force of 75 tons was applied, while the cavity filling and cooling times were set to 1 and 10 s, respectively. Standard samples, with an average thickness of 4 mm, were obtained for characterization.

**Characterization of PLA/SCG Composite Pieces**
Morphological Characterization

The morphology of the SCG particles and the fractured samples obtained from the Charpy tests were studied by field emission scanning electron microscopy (FESEM) in a ZEISS ULTRA 55 microscope from Oxford Instruments (Abingdon, United Kingdom). Prior to observation, the samples were sputtered with a gold-palladium alloy in an EMITECH sputter coating SC7620 model from Quorum Technologies, Ltd. (East Sussex, UK). The FESEM measurements were carried out using an acceleration voltage of 2 kV.

Mechanical Characterization

Tensile properties of PLA/SCG pieces sizing 150 mm x 10 mm x 4 mm were obtained in a universal testing machine ELIB 50 from S.A.E. Ibertest (Madrid, Spain), as recommended by ISO 527-1:2012. A 5-kN load cell was used and the cross-head speed was set to 5 mm min⁻¹. Shore hardness was measured in a 676-D durometer, from J. Bot Instruments (Barcelona, Spain), using the D-scale on rectangular samples with dimensions 80 mm x 10 mm x 4 mm, according to ISO 868:2003. The impact strength was also studied by means of injection-molded rectangular samples with dimensions of 80 mm x 10 mm x 4 mm in a Charpy pendulum (1-J) from Metrotec S.A. (San Sebastián, Spain) on notched samples (0.25 mm radius V-notch), following the specifications of ISO 179-1:2010. All mechanical tests were performed at room temperature and, at least, 6 samples of each material were tested and the corresponding values were averaged.

Thermal Analysis

The most relevant thermal transitions of PLA/SCG green composites were obtained by differential scanning calorimetry (DSC) in a Mettler-Toledo 821 calorimeter (Schwerzenbach, Switzerland). Samples with an average weight of 6–7 mg were subjected to a thermal program divided into three stages: a first heating from 25 to 180 °C, followed by a cooling to 0 °C, and a second heating to 300 °C. All the heating and cooling rates were set to 10 °C/min and tests were run in nitrogen atmosphere with a flow-rate of 66 mL/min using standard sealed aluminum crucibles with a capacity of 40 μL. The percentage of crystallinity (Xₖ) and maximum crystallinity (Xₖ_max) was calculated using the following equations:

\[
X_c = \left[ \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^0 \cdot (1 - w)} \right] \cdot 100
\]

\[
X_{c,\text{max}} = \left[ \frac{\Delta H_m}{\Delta H_m^0 \cdot (1 - w)} \right] \cdot 100
\]

Where \( \Delta H_m^0 = 93.7 \) J/g is the theoretical enthalpy of a 100% crystalline PLA sample [45], the term \( 1-w \) corresponds to the PLA weight fraction in the blend, \( \Delta H_m \) and \( \Delta H_{cc} \) are respectively related to the melting and cold crystallization enthalpies.
Thermal degradation of the PLA/SCG pieces was assessed by thermogravimetric analysis (TGA) in a LINSEIS TGA 1000 (Selb, Germany). Samples with a weight of 15–17 mg were placed in 70-µl alumina crucibles and subjected to a dynamic heating program from 40 to 700 °C at a heating rate of 10 °C min⁻¹ in air atmosphere. The first derivative thermogravimetric (DTG) curves were also determined. All the thermal tests were carried out in triplicate in order to obtain reliable results.

**Thermomechanical Characterization**

Dynamical mechanical thermal analysis (DMTA) was carried out in a DMA1 dynamic analyzer from Mettler-Toledo (Schwerzenbach, Switzerland), working in single cantilever flexural conditions. Rectangular samples with dimensions 20 mm x 6 mm x 2.7 mm were subjected to a dynamic temperature sweep from 30 to 140 °C at a constant heating rate of 2 °C min⁻¹. The selected frequency was 1 Hz and the maximum flexural deformation or cantilever deflection was set to 10 µm. All the thermomechanical tests were also performed in triplicate.

**Color and Wetting Characterization**

A Konica CM-3600d Colorflex-DIFF2, from Hunter Associates Laboratory, Inc. (Reston, Virginia, USA) was used for the color measurement. Color coordinates (L*a*b*) were measured with the illuminant D65 and observer 10° according to the following criteria: L* = 0, darkness; L* = 100, lightness; a* represents the green (a*<0) to red (a*>0); b* stands for the blue (b*<0) to yellow (b*>0) coordinate.

Contact angle measurements were carried out with an EasyDrop Standard goniometer model FM140 (KRÜSS GmbH, Hamburg, Deutschland), which was equipped with a video capture kit and analysis software (Drop Shape Analysis SW21; DSA1). Double distilled water was used as the test liquid. Tests were performed at least 10 times.

**Water Absorption Test**

The water absorption capacity of the PLA/SCG pieces was evaluated by the water uptake method [36]. Samples sizing 80 mm x 10 mm x 4 mm were first weighted in a balance and then put inside a beaker filled with distilled water, being wrapped with a metal grid. Thereafter, the samples were taken out of the beaker and weighed in different time intervals for up to 14 weeks. In every measurement, the superficial moisture of the samples was removed with tissue paper. Three samples of each formulation were tested.

**Biodisintegration Test**

The biodegradability of the samples was evaluated using a disintegration test in controlled compost conditions according to the guidelines of the ISO 20200 standard at the conditions of 58 °C and a relative humidity (RH) of 55%. Injection-molded samples with dimensions 30 mm x 30 mm x 1 mm were placed in a carrier bag and buried in a soil with the following controlled composition: sawdust (40 wt.%), rabbit-feed (30 wt.%), ripe compost (10 wt.%), com starch (10 wt.%), saccharose (5 wt.%), com seed oil (4 wt.%), and urea (1 wt.%). To monitor the biodisintegration process, samples were periodically unburied, washed
with distilled water, dried, and weighed in an analytical balance. Pictures were also taken at each weight measurement with the objective of visually evaluate the biodisintegration process. The weight loss due to disintegration in the controlled compost soil was calculated by means of the following expression:

\[
\text{Weight loss (\%) = } \left( \frac{W_t - W_0}{W_0} \right) \cdot 100
\]

Where \( W_t \) is the weight of the sample after certain time into the controlled compost soil and \( W_0 \) is the initial dry weight of the sample. All tests were triplicated in order to ensure reliability in results.

\textbf{Results And Discussion}

\textbf{Morphology of SCGs}

Particle interlocking is an essential mechanism in polymer composites. Figure 3 shows the morphology of the SCG particles observed by FESEM and their respective length and diameter histograms. One can observe in Figure 3a that the lignocellulosic particles displayed a round-like morphology with a rough surface, which can be ascribed to the milling process effect on particles with high hardness. These particles also displayed high porosity on their surface, which can be beneficial towards interactions with the biopolymer matrix by acting as anchoring points. In this regard, Mendes et. al. [46] observed a very similar structure for SCG powder when studying composites with high-density polyethylene (HDPE). It was also reported that SCG particles tend to form small aggregates due to their hydrophilic characteristic. In this regard, Garcia-Garcia et al. [33] described that, while individual particle size is in the 15–20 µm range, these form aggregates sizing 60–80 µm. Figures 3b and 3c gather the particle histograms in terms of length and diameter, respectively. The particles presented an average length of approximately 42.5 µm, whereas the average diameter was around 40 µm. In both cases, the dimensions were defined by a classical monomodal distribution. This particle morphology is based on a relatively low size, which can offer a positive effect on the overall properties. For instance, Crespo et. al. [47] observed that considerably larger lignocellulosic particles, with diameter sizes over 150 µm, led to an impairment and certain heterogeneity in composites of vinyl plastisols.

\textbf{Optical Properties of PLA/SCG Composites}

The visual appearance is essential in terms of the impression that an end-product makes on the consumer. In this sense, Figure 4 shows the visual appearance of the pieces of PLA and its composites and blends with SCGs and OLAs obtained by injection molding. It can be observed that the neat PLA piece and the pieces of PLA with any of the OLAs showed contact transparency. The loss of transparency in PLA is due to the semicrystalline nature of PLA [48], in which the amorphous and crystalline regions have different light refraction indexes. While the addition of OLA2 and OLA2mal kept the original appearance of PLA, the samples with SCG developed a dark brown-to-black tonality due to the intrinsic characteristic color of these particles (see previous Figure 1), making the samples also completely opaque.
Table 2 gathers the L*a*b* color coordinates obtained for these injection-molded pieces. Luminance (L*) is indicative of the brightness or lightness of the color of a sample. In this sense, the injection-molded PLA piece and the PLA/OLA2 and PLA/OLA2\textsubscript{mal} pieces exhibited very similar L* values, in the range 45.6–48. This was expected due to the very similar nature and miscibility between the biopolymer and its oligomers. In the case of the green composite pieces, which were filled with SCGs, these presented significantly lower and very similar L* values, in the range of 25.8–26.6. Furthermore, the color coordinate a*, which is representative of green (negative) or red color (positive), showed values in the range -0.23–0.14 for the pieces of PLA, PLA/OLA2, and PLA/OLA2\textsubscript{mal}. In the case of b*, which indicates blue (negative) or yellow (positive) color, all the unfilled pieces presented similar positive values between 1.25 and 1.89. Therefore, these pieces tend to show a slight yellow pale, showing no significant differences among them. On the contrary, all the SCG-containing pieces showed very positive a* values, in the range 0.74–1.10, whereas the b* values were high, that is, 4.9 and 5.56 for the green composite pieces with PLA/OLA2 and PLA/OLA2\textsubscript{mal}, respectively. The combination of red and yellow colors quantified the above-qualified dark brown aspect of the green composite pieces. A similar color change was reported by Suaduang et. al. [31] for PLA/SCG composites containing up to 10 wt.% SCG, showing a* and b* values from -0.9 to 7.5 and from -4.4 to 16.5, respectively.

Table 2. Luminance and color coordinates (L*a*b*) of the injection-molded pieces of polylactide (PLA)/spent coffee ground (SCG) containing the oligomers of lactic acid (OLAs).

| Piece                  | L*         | a*         | b*         |
|------------------------|------------|------------|------------|
| PLA                    | 48.0 ± 0.5 | -0.23 ± 0.02 | 1.89 ± 0.08 |
| PLA+SCG                | 26.6 ± 0.1 | 1.10 ± 0.13 | 5.42 ± 0.19 |
| PLA+OLA2               | 45.6 ± 0.1 | 0.13 ± 0.02 | 1.25 ± 0.08 |
| PLA+OLA2\textsubscript{mal} | 47.4 ± 0.2 | -0.14 ± 0.02 | 1.68 ± 0.09 |
| PLA+OLA2+SCG           | 26.3 ± 0.1 | 0.74 ± 0.02 | 4.91 ± 0.06 |
| PLA+OLA2\textsubscript{mal}+SCG | 25.8 ± 0.1 | 0.75 ± 0.04 | 5.56 ± 0.11 |

\(^{a-f}\) Different letters in the same column indicate a significant difference among the samples (p < 0.05).

Mechanical Properties of PLA/SCG Composites

Table 3 gathers the results obtained in the mechanical characterization of the PLA/SCG pieces. These results are of great interest to evaluate the effect of both SCGs and OLA2 and OLA2\textsubscript{mal} on PLA in terms of mechanical resistance and ductile properties, which can be relevant for several applications, as well as to ascertain the compatibility attained between the biopolymer matrix with the lignocellulosic fillers. It can be observed that the neat PLA piece showed a Young modulus (E) of 2913 MPa, a maximum tensile
strength ($\sigma_{\text{max}}$) of 52.43 MPa, and an elongation at break ($\varepsilon_b$) of 10.36 %. These values agree with those reported previously, for instance by Agüero et. al. [49], which are indicative of a rigid material with low ductility, particularly when compared with other biopolymer pieces such as those of bio-based high-density polyethylene (bio-HDPE) [50] or polyethylene terephthalate (bio-PET) [51], showing values nearly 500%. The incorporation of the SCG particles into PLA decreased all the mechanical resistance properties, that is, the E and $\sigma_{\text{max}}$ values were reduced down to 2367 MPa and 13.85 MPa, respectively, which indicates that a poor dispersion of the lignocellulosic fillers in the biopolyester matrix was attained [32]. However, contrary to most claims published in the literature of PLA composites based on lignocellulosic fillers derived from soluble coffee wastes [52], the ductility properties were improved. In particular, the $\varepsilon_b$ value significantly increased up to 39.56%, which corresponds to a 280% increase in relation to neat PLA. This ductility improvement suggests that the PLA matrix was plasticized by the SCG particles since this waste biomass can contain water and, more importantly, large amounts of lipids [53]. Among lipids, the main plasticizing molecules correspond to organic compounds containing oxygen-based groups such as fatty acids [54]. Furthermore, since water was removed during drying prior to processing the samples by extrusion to avoid hydrolysis, plasticization can be then mainly ascribed to the presence of fatty acids. In this regard, it has been reported that the coffee oil content in SCG is 10.98 wt.%, from which approximately 46% corresponds to linoleic acid [55]. In this sense, the work of Battegazzore et. al. [56] reported the presence of several plasticizing compounds in natural fillers, such as hazelnut skin or cocoa by-products, which were also used to increase the ductility of PLA.

Table 3. Mechanical properties of the injection-molded pieces of polylactide (PLA)/spent coffee ground (SCG) containing the oligomers of lactic acid (OLAs) in terms of tensile modulus (E), maximum tensile strength ($\sigma_{\text{max}}$), elongation at break ($\varepsilon_b$), Shore D hardness, and impact strength.
| Piece               | E (MPa)          | $\sigma_{\text{max}}$ (MPa) | $\varepsilon_{b}$ (%) | Shore D hardness | Impact strength (kJ·m$^{-2}$) |
|---------------------|------------------|-----------------------------|----------------------|-----------------|-------------------------------|
| PLA                 | 2913 ± 84        | 52.43 ± 3.09                | 10.36 ± 0.84         | 82.0 ± 0.5      | 27.7 ± 2.3                    |
| PLA+SCG             | 2367 ± 61        | 13.85 ± 0.67                | 39.56 ± 1.98         | 80.6 ± 0.9      | 18.6 ± 1.9                    |
| PLA+OLA2            | 2835 ± 49        | 35.28 ± 3.88                | 6.05 ± 0.39          | 76.8 ± 1.3      | 29.3 ± 3.6                    |
| PLA+OLA2$_{\text{mal}}$ | 3002 ± 172      | 24.03 ± 3.65                | 4.30 ± 0.60          | 82.8 ± 0.8      | 31.2 ± 2.1                    |
| PLA+OLA2+SCG        | 2042 ± 43        | 18.89 ± 1.30                | 33.35 ± 2.95         | 81.4 ± 1.1      | 20.6 ± 2.2                    |
| PLA+OLA2$_{\text{mal}}$+SCG | 2291 ± 96     | 22.19 ± 0.92                | 20.65 ± 2.34         | 81.8 ± 1.1      | 18.6 ± 2.4                    |

Different letters in the same column indicate a significant difference among the samples ($p < 0.05$).

From the above, it can be considered that coffee wastes derived from the liquor industry seems to possess a higher lipidic content than traditional soluble coffee due to its processing technology that, as described above, does not imply the use of high temperature or extraction steps, apart from natural roasting of the coffee grains. This result agrees with the findings from Suaduang et. al. [31], who showed that SCG contents of 7.5 and 10 wt.% derived from the coffee beans roasting process, not then used yet for soluble or liquor coffee, resulted in a slight increase of PLA films. In particular, $\varepsilon_{b}$ increased from 4.18% and 5.04% in transversal (TD) and machine direction (MD), to 4.24% and 5.31% and 5.33% and 6.63% for 7.5 and 10 wt.% loadings of SGCs, respectively. The higher improvement observed herein can be then related to the higher SCG content used in the green composite but, more importantly, in addition to potential differences in the high fatty acid content due to the particular production process of the liquor industry. Indeed, other more conventional polymer composites based on SCGs derived from the soluble coffee industry showed that increasing the filler content reduced the ductility of the polymer. For instance, the work of Mendes et. al. [46] reported a decrease in $\varepsilon_{b}$ of HDPE of approximately 50%, in relation to neat HDPE, for a 30 wt.% SCG content.

In relation to the two tested OLAs, the addition of OLA2 and OLA2$_{\text{mal}}$ clearly decreased the $\sigma_{\text{max}}$ value of PLA down to 35.28 MPa and 24.03 MPa, respectively, which is in agreement with previous studies [41, 57], whereas the E values remained nearly unaltered. However, the $\varepsilon_{b}$ value also decreased down to 6.05% and 4.3% for PLA+OLA2 and PLA+OLA2$_{\text{mal}}$, respectively. This result could be due to the fact that both OLAs reduce the macromolecular PLA chains cohesion, as they increase chain mobility based on
their plasticizing effect. In this regard, Burgos et. al. [57] reported that the E values of PLA decreased with the content of OLA from 2500 MPa for neat PLA to 250 MPa for a 25% OLA content. Therefore, intermediate values were obtained when OLA2 and OLA2\textsubscript{mal} were added to the green composite. In particular, the OLA2-containing piece showed the lowest resistant properties, as the E value highly decreased down to 2042 MPa, while $\sigma_{\text{max}}$ slightly increased up to 18.89 MPa in relation to the green composite sample. However, it also showed enhanced ductile properties, with a $\varepsilon_b$ value of 33.35%. For the green composite piece with OLA2\textsubscript{mal}, one can observe that it presented better mechanical resistant properties, showing values of E and $\sigma_{\text{max}}$ of 2291 MPa and 20.65 MPa, respectively, but $\varepsilon_b$ still resulted in a value of 20.65%. This difference observed in the mechanical response of the green composite pieces with the two OLAs tested herein can be ascribed to the MAH content of OLA2\textsubscript{mal}, which makes it more reactive and leads to better chain-to-chain PLA interactions [58]. In particular, the multiple MAH groups can provide certain grafting for the cellulose materials onto the backbone of PLA and, thus, acting an interfacial compatibility agent with the SCG particles [32]. All in all, the combination of the three materials, namely SCG and OLA2 and OLA2\textsubscript{mal} successfully provided PLA pieces with varying mechanical performance in terms of rigidity and ductility, whereas the mechanical resistance was reduced for all the formulations tested.

Regarding Shore D hardness, it can be observed that most of the PLA and its green composite pieces developed herein showed values in the 82–80 range, being in most cases slightly lower than neat PLA, which agrees with the results obtained by Lascano et al. [41]. This supports the fact that SCGs, despite being a hard lignocellulosic filler [36], yields an overall softening effect on the PLA material due to its high lipidic content. The only noticeable change was observed for the green composite containing PLA+OLA2, in which hardness decreased down to 76.8, due to the plasticizing effect exerted by this type of OLA, which seems to give more mobility to the PLA chains. Concerning impact strength, the neat PLA piece showed a value of 27.7 kJ/m\textsuperscript{2}, which is a relative low value and characteristic of a brittle material [41]. The addition of SCGs at 20 wt.% further reduced this value significantly, down to 18.6 kJ/m\textsuperscript{2}, which could be attributed to the presence of SCG aggregates that embrittled the PLA matrix by creating local tensions [59]. In this regard, Da Silva et al. [60] also reported a toughness decrease in PLA of 6% for contents of SCGs above 15 wt.%. Impact strength of the PLA and the green composite pieces successfully increased after the addition of both OLAs. In the case of neat PLA, without SCGs, OLA2 increased impact strength by approximately 6%, while OLA2\textsubscript{mal} increased it by 12.6%. This slight but significant energy absorption enhancement during impact can be ascribed to the high solubility of OLA in PLA that enables inhibition of microcrack formation and growth. However, it is also worth noting that the combination of SCG with OLA2 and OLA2\textsubscript{mal} did not improve the overall impact strength of the injection-molded pieces, by which it can be inferred that these OLAs exert no effect on the dispersion and interaction of these lignocellulosic particles with PLA.

**Morphology of PLA/SCG Composites**
In order to better ascertain the effect of the SCG particles and the two tested OLAs on PLA, the morphology of the fracture surfaces of the injection-molded pieces obtained after the impact tests were observed by FESEM and the resultant micrographs are gathered in Figure 5. As it can be observed in Figure 5a, the neat PLA piece displays the characteristic morphology of a polymer with a brittle behavior due to the formation of a smooth fracture surface with the presence of microcracks (see white arrows). A similar morphology was reported by Quiles-Carrillo et al. [61], confirming the aforementioned mechanical properties in relation to its low impact strength and ductility. As opposite, in Figure 5b, the fracture surface changed to a rougher morphology due to the increase in ductility and the presence of the SCG fillers. From this FESEM micrograph it can also be inferred a good dispersion of SCG particles along the PLA matrix. However, the existence of some holes (identified in the image by white circles) corroborates the lack of compatibility between the PLA matrix and SCGs, since these voids correspond to lignocellulosic particles that were detached after impact [16]. The poor SCG-to-PLA adhesion can be therefore responsible for the reduced mechanical resistance, as shown above during the mechanical analysis.

Figures 5c and 5d show the micrographs of the fracture surface for both PLA+OLA2 and PLA+OLA2\textsubscript{mal} pieces, respectively, which yielded very similar structures. In contrast with the fracture surface of the neat PLA piece, which showed some microcracks, one can observe the formation of several macrocracks along the biopolyester matrix. This feature, which was observed by Lascano et al. [41] when studying the effect of different OLA concentrations on PLA, can be appreciated especially in the PLA+OLA2\textsubscript{mal} piece. Therefore, OLA2 and, more noticeably, OLA2\textsubscript{mal}, led to a rougher surface that corresponds to a fracture with a major energy absorption, which agree with the mechanical properties reported above in terms of toughness. Interestingly, it is also worth mentioning that phase separation was not noticeable due to the great chemical affinity between PLA and OLA. Finally, Figures 5e and 5f show the FESEM micrographs corresponding to the fracture surfaces of the PLA+OLA2+SCG and PLA+OLA2\textsubscript{mal}+SCG pieces, respectively. It can be observed that, in both cases, the interfacial adhesion of the SCG particles with the surrounding PLA matrix was noticeably improved due to the decrease in the void density. Furthermore, SCGs seem to be more imbedded into the biopolyester since the gap between the edge of the particles (see white arrows) and the PLA matrix is very narrow. Thus, both OLAs can potentially increase the affinity of the SCG particles in PLA, especially OLA2\textsubscript{mal}, due to the presence of the multiple MAH groups that could interact with both the backbone ester (R—COO—R) groups of PLA and —OH groups of SCGs [54]. This visual effect was more intense in the PLA+OLA2\textsubscript{mal}+SCG sample since the particle-matrix gap was almost imperceptible, which correlates better with the mechanical properties reported above.

**Thermal Properties of PLA/SCG Composites**

In order to study the thermal properties of the green composites, the DSC thermograms corresponding to the cooling and second heating steps were analyzed. Figure 6 shows the results of the cooling (Figure 6a) and heating scans (Figure 6b), whereas Table 4 gathers the main thermal parameters obtained from these thermograms. First of all, one can observe that the neat PLA sample showed a glass transition
temperature (T\text{g}) of 62.8 °C, being noticeable by a change in the baseline of the heating thermogram. A very similar result was observed by Lascano et. al. [41], who reported a T\text{g} value of PLA of 63 °C. In this case, however, cold crystallization was not observed probably due to the slow cooling step carried out prior to heating, at 10 °C/min, in which the PLA molecules could crystallize from the melt during the previous cooling step showing a crystallization temperature (T\text{c}) of 103.7 °C. The melting of the biopolymer thereafter occurred at a temperature of 173.3 °C, which is also close to the melting temperature (T\text{m}) value obtained previously [41]. The addition of SCGs to PLA reduced the value of T\text{g}, from 62.8 to 61.1 °C, confirming the plasticizing effect exerted by the coffee oil on the biopolyester amorphous regions. In this case, cold crystallization was observed and identified by a peak located at 99.3 °C, corresponding to the cold crystallization temperature (T\text{CC}). This finding points out to the fact that the presence of SCGs also impaired crystallization of the PLA molecules from the melt. Finally, the T\text{m} value of PLA was hardly affected by the presence of SCGs, showing no significant difference. In relation to crystallinity, the neat PLA sample showed a X\text{C} value of nearly 20%, which is very similar to that obtained by Rojas-Lema et. al. [62], whereas the single addition of SCGs increased crystallinity up to approximately 36%. In the case of the maximum crystallization degree (X\text{C}\text{max}), which does not consider the crystals formed during heating and provides more accurate information about the effect of a given additive on polymer crystallinity, this increase was higher, up to nearly 54%. This result indicates that, even though the lignocellulosic fillers delayed the crystallization process, they also acted as heterogeneous nuclei during the subsequent formation of crystals. This phenomenon has been previously described by da Silva et. al. [60], who also observed an increase in the PLA crystallinity by means of SCGs obtained as a waste from instant coffee preparation. Authors reported an increase in crystallinity of PLA from 9.10 to 12.7% for a 5 wt.% content of SCGs in the green composite.

**Table 4.** Glass transition temperature (T\text{g}), crystallization temperature (T\text{C}), cold crystallization temperature (T\text{CC}), melting temperature (T\text{m}), crystallinity (X\text{C}), and maximum crystallinity (X\text{C}\text{max}) of the injection-molded pieces of polylactide (PLA)/spent coffee ground (SCG) containing the oligomers of lactic acid (OLAs).
In terms of the effect of the OLAs, it can be observed that OLA2 and OLA2\textsubscript{mal} provoked a significant decrease in $T_g$, reducing it down to 55.4 and 45.33 °C, respectively. This reduction has been previously attributed to the plasticizing effect exerted by both OLAs, as it has been reported by other studies [42, 58]. Similar to the case of SCGs, for the samples containing OLA2 and OLA2\textsubscript{mal}, cold crystallization also appeared, showing $T_{cc}$ values of 103.7 and 112.9 °C, respectively. This finding could indicate that these OLAs also impaired crystallization from the melt due to their high solubility and interaction with the PLA molecules [60]. In terms of melting, the slightly lower $T_m$ value attained in the OLA2\textsubscript{mal}-containing sample, which was reduced to 171 °C, confirms its higher interaction with the PLA matrix, and the imperfection effect provided by this additive on the crystals. However, although the crystallinity degree, that is, $X_C$, was slightly reduced after the addition of both OLAs, one can observe that maximum crystallinity degree, that is, $X_{C_{max}}$, increased to 50.87 and 41.98%, for OLA2 and OLA2\textsubscript{mal}, respectively. In this regard, other previous studies have reported that OLAs can act as heterogeneous nucleating agents and facilitate crystal formation in PLA since they are still present in the form of thin solids with a melting point higher than the $T_c$ value of PLA [63].

With regard to the combined additions of SCGs and the two tested OLAs, one can observe that $T_g$ suffered a considerable decrease due to the plasticization of PLA by both coffee oil and the presence of the oligomers. The $T_{cc}$ values also decreased further down to 91.9 and 93.7 °C, for PLA+OLA2+SCG and PLA+OLA2\textsubscript{mal}+SCG, respectively, which can be ascribed to the facilitated mobility of the amorphous phase. However, even though the PLA matrix was highly plasticized, the absence of crystallization from the melt also indicates impairment during crystal formation yielded by the presence of these additives. In all cases, and similar to the PLA+SCG and PLA+OLA2 and PLA+OLA2\textsubscript{mal} samples, the green composites

| Piece | $T_g$ (°C) | $T_c$ (°C) | $T_{cc}$ (°C) | $T_m$ (°C) | $X_C$ (%) | $X_{C_{max}}$ (%) |
|-------|-----------|------------|---------------|------------|-----------|-----------------|
| PLA   | 62.8 ± 0.2\textsuperscript{a} | 103.7 ± 0.1\textsuperscript{a} | - | 173.3 ± 1.9\textsuperscript{a} | 19.96 ± 0.3\textsuperscript{a} | 19.96 ± 0.3\textsuperscript{a} |
| PLA+SCG | 61.1 ± 0.3\textsuperscript{a} | 95.6 ± 1.0\textsuperscript{b} | 99.3 ± 0.9\textsuperscript{a} | 173.6 ± 2.0\textsuperscript{a} | 36.42 ± 0.7\textsuperscript{b} | 53.90 ± 0.6\textsuperscript{b} |
| PLA+OLA2 | 55.4 ± 0.2\textsuperscript{b} | 96.7 ± 0.5\textsuperscript{b} | 103.7 ± 1.2\textsuperscript{a} | 173.3 ± 1.9\textsuperscript{a} | 7.59 ± 0.5\textsuperscript{c} | 50.87 ± 0.5\textsuperscript{c} |
| PLA+OLA2\textsubscript{mal} | 45.3 ± 0.4\textsuperscript{c} | 94.9 ± 0.2\textsuperscript{b} | 112.9 ± 1.5\textsuperscript{b} | 171.0 ± 2.4\textsuperscript{a} | 3.91 ± 0.4\textsuperscript{d} | 41.98 ± 0.3\textsuperscript{d} |
| PLA+OLA2+SCG | 47.3 ± 0.3\textsuperscript{c} | 90.7 ± 0.3\textsuperscript{b} | 91.9 ± 1.1\textsuperscript{c} | 170.2 ± 2.5\textsuperscript{a} | 21.04 ± 0.3\textsuperscript{e} | 54.28 ± 0.1\textsuperscript{e} |
| PLA+OLA2\textsubscript{mal}+SCG | 48.4 ± 0.2\textsuperscript{c} | 100.7 ± 0.4\textsuperscript{c} | 93.7 ± 1.0\textsuperscript{c} | 170.1 ± 2.2\textsuperscript{a} | 23.02 ± 0.2\textsuperscript{f} | 61.44 ± 0.2\textsuperscript{f} |

\textsuperscript{a-f} Different letters in the same column indicate a significant difference among the samples ($p < 0.05$).
containing both additives showed significantly higher values of $X_{C_{\text{max}}}$, with values of approximately 54% and 61% for PLA+OLA2+SCG and PLA+OLA2_{mal}+SCG, respectively.

Regarding thermogravimetric characterization, Figure 7 shows the variation of mass with temperature (Figure 7a) and the first derivative versus temperature (Figure 7b) to evaluate the degradation processes of each sample. Moreover, Table 5 gathers the most relevant parameters related to the degradation processes. In this sense, it can be observed that neat PLA exhibited a single step degradation process, showing slightly superior thermal stability than the composites with SCGs and blends with OLAs. In particular, PLA presented values of $T_{5\%}$ and $T_{\text{deg}}$ of 319.3 and 361.3 °C, showing a mass loss at $T_{\text{deg}}$ of 57.18%. A very similar degradation profile was observed for PLA by Rojas-Lema et al. [62]. The addition of SCGs reduced the thermal stability of PLA and generated a low-intense second degradation step at high temperatures. The first and main weight loss initiated at approximately 305 °C, which means a reduction of 14 °C with respect to neat PLA, which is related to the degradation of low-$M_W$ components present in the lignocellulosic residue, such as hemicellulose [64]. The second step appeared at the 370–500 °C range, it was less pronounced and it is ascribed to the thermal degradation of lignin and cellulose from SCGs [65]. The maximum degradation peak, represented by $T_{\text{deg}}$ also decreased by approximately 2 °C versus the neat PLA, although it does not mean a significant change. A similar reduction in thermal stability was also observed by Mendes et. al. [46] when studying the thermal properties of HDPE/SCG composites. The incorporation of OLA2 and OLA2_{mal} into PLA also decreased the onset degradation, that is, $T_{5\%}$, down to 287.7 and 289 °C, respectively. In the case of $T_{\text{deg}}$, a reduction to values of 354.3 and 356.7 °C was respectively observed, meaning a not significant loss in thermal stability. In this context, several studies have reported the inherently poorer thermal stability of OLA [41, 62] in comparison with PLA. Particularly, OLA2_{mal} yielded a slightly higher thermal stability than OLA2. This fact could be ascribed to the presence of MA groups in this OLA grade that, similar to other properties, resulted in a higher interaction with the PLA matrix by forming a more stable macromolecule in which the chain-scission process at high temperature was delayed [58]. The combined systems of PLA+OLA2+SCG and PLA+OLA2_{mal}+SCG also showed the characteristic two-step degradation process of green composite due to the presence of the lignocellulosic filler. Thermal degradation occurred more rapidly at the start of the process, showing $T_{5\%}$ values of 275 and 282 °C, respectively, but $T_{\text{deg}}$ values were not significantly different than that of neat PLA (361.3 °C), being slightly higher than those of the green composite without OLA and the OLA-containing PLA samples. Finally, the residual mass, in all cases, was below 1 wt.%. This suggests a good synergetic effect between the SCG and the OLA, which was previously observed during the morphology analysis. In general terms, therefore, one can consider that the combined addition of SCGs derived from the liquor industry and OLAs lead to materials with relatively similar thermal stability than PLA, which result adequate for applications that deal with temperatures of up to nearly 270 °C.

**Table 5.** Main thermal degradation parameters of the injection-molded pieces of polylactide (PLA)/spent coffee ground (SCG) containing the oligomers of lactic acid (OLAs) in terms of the onset degradation temperature at a mass loss of 5 wt.% ($T_{5\%}$), maximum degradation rate (peak) temperature ($T_{\text{deg}}$), and residual mass at 700 °C.
| Piece                        | T_{5\%} (°C) | T_{deg} (°C) | Mass loss at T_{deg} (%) | Residual weight (%) |
|------------------------------|--------------|--------------|--------------------------|---------------------|
| PLA                          | 319.3 ± 0.8^a| 361.3 ± 2.4^a| 57.18 ± 0.9^a            | 0.1 ± 0.1^a         |
| PLA+SCG                      | 305.3 ± 1.1^a| 359.0 ± 1.3^a| 51.36 ± 1.1^b            | 0.2 ± 0.1^b         |
| PLA+OLA2                     | 287.7 ± 1.4^b| 354.3 ± 1.8^a| 49.87 ± 1.0^b            | 0.4 ± 0.2^c         |
| PLA+OLA2_{mal}               | 289.0 ± 0.5^b| 356.7 ± 2.2^a| 57.3 ± 0.8^c             | 0.6 ± 0.2^d         |
| PLA+OLA2+SCG                 | 275.0 ± 1.2^c| 361.3 ± 1.0^a| 61.71 ± 1.0^d            | 0.2 ± 0.1^e         |
| PLA+OLA2_{mal}+SCG           | 282.0 ± 0.7^c| 361.3 ± 1.5^a| 57.26 ± 0.7^e            | 0.3 ± 0.1^f         |

Different letters in the same column indicate a significant difference among the samples (p < 0.05).

**Thermomechanical Properties of PLA/SCG Composites**

DMTA allows to obtain mechanical properties in dynamic conditions through the application of a sinusoidal stress as a function of temperature. **Figure 8** shows the DMTA curves for all the PLA/SCG composites, while **Table 6** gathers the most relevant thermomechanical parameters. In **Figure 8a** one can observe the evolution of the storage modulus as a function of temperature. Regarding the neat PLA piece, the storage modulus suffered a pronounced drop between 50 and 70 °C, which is indicative of the α-relaxation process of the PLA chains when surpassing the glass transition region [41]. This can be seen in the difference between the 1263 MPa value at 35 °C and the 43 MPa value at 100 °C. Another important feature is the change in the 90–100 °C range, which corresponds to the cold crystallization process [36] and provokes a rearrangement of the PLA chains into a more ordered structure with higher thermomechanical resistance. The addition of SCGs to PLA decreased the storage modulus of the biopolyester down to 1150 MPa at 35 °C as a result of the plasticization process by the remaining coffee oil. However, it made the cold crystallization process to occur at lower temperatures than the neat PLA (80–90 °C range). This confirms that the SCG particles acted as nucleating agents during the crystallization process of PLA, as previously described during the DSC analysis, resulting in a storage modulus of approximately 80 MPa at 100 °C. A similar behavior was observed by Quiles-Carrillo et al. [36] when PLA was reinforced with almond shell flour (ASF), a lignocellulosic filler. With the incorporation of OLA2 into the PLA matrix, the storage modulus showed a value of 1210 MPa at 35 °C, being slightly lower than for the neat PLA piece and with a value of 53 MPa at 100 °C. Furthermore, the storage modulus values were lower along the whole temperature range in comparison with neat PLA, which confirms that OLA2 reduces the stiffness of PLA due to its role as a plasticizing agent, as it has been aforementioned during the mechanical analysis. A similar behavior was observed in the OLA2_{mal} sample, but with a more emphasized effect, reducing the storage modulus down to 1130 MPa at 35 °C. It should be noted that both OLAs reduced the temperature at which cold crystallization phenomenon
occurs. This is representative for the nucleating effect provided by the short-length OLA molecules, which were able to facilitate packing of the PLA macromolecular structure [63]. The combination of OLA2 and OLA2\textsubscript{mal} with SCG also led to a decrease in the storage modulus in all the temperature range, mainly ascribed to the plasticizing effect of both the coffee oil and oligomers. The cold crystallization temperature was also reduced, as a result of the combined nucleating effect of SCG and OLA2 or OLA2\textsubscript{mal}. In this sense, OLA2\textsubscript{mal} seems to exert a higher nucleating effect, as it decreases the crystallization process down to the 70–80 °C temperature range.

**Figure 8b** shows the evolution of the dynamic damping factor (\(\tan \delta\)) with temperature. This allows to identify the \(\alpha\)-relaxation of PLA, which is related to its \(T_g\), seen as the maximum peaks. Neat PLA showed a \(\tan \delta\) peak at 73.1 °C, which agrees with values reported by other authors [36, 41]. The presence of SCGs in the PLA matrix decreased the \(\tan \delta\) peak down to 63.1 °C due to the aforementioned described plasticization process by the coffee oil, providing it with improved chain mobility and free volume. It can be observed that OLA2 and OLA2\textsubscript{mal} also reduced the \(\tan \delta\) peaks, down to 64.9 and 54.4 °C, respectively, which correlate with the \(T_g\) values attained in the DSC results shown above. Thus, the combined additions of OLA2 and OLA2\textsubscript{mal} with SCGs followed the same tendency that the single ones with OLA2 and OLA2\textsubscript{mal}, showing the PLA+OLA2\textsubscript{mal}+SCG sample a very similar \(\tan \delta\) peak value than the OLA2\textsubscript{mal} sample (53.5 vs 54.4 °C, respectively) while the PLA+OLA2+SCG and PLA+OLA2 pieces presented values over 60 °C (63.2 vs 66.5 °C). Interestingly, all the green composite samples presented a lower maximum damping factor, approximately 15% lower than the unfilled PLA samples. This reduction is ascribed to the replacement in the injection-molded piece of the biopolymer with an amorphous regions with a hard lignocellulosic filler, by which the material shows lower energy dissipation and reduced toughness [35].

**Table 6.** Dynamic-mechanical properties of the injection-molded pieces of polylactide (PLA)/spent coffee ground (SCG) containing the oligomers of lactic acid (OLAs) in terms of storage modulus at 35, 80, and 100 °C and dynamic damping factor (\(\tan \delta\)) peak.
| Piece                        | Storage modulus at 35 °C (MPa) | Storage modulus at 80 °C (MPa) | Storage modulus at 100 °C (MPa) | tan δ peak (°C) |
|-----------------------------|--------------------------------|--------------------------------|---------------------------------|-----------------|
| PLA                         | 1263 ± 30<sup>a</sup>         | 1.5 ± 0.1<sup>a</sup>         | 43 ± 5<sup>a</sup>              | 73.1 ± 1.2<sup>a</sup> |
| PLA+SCG                     | 1150 ± 25<sup>b</sup>         | 4.0 ± 0.2<sup>b</sup>         | 80 ± 10<sup>b</sup>             | 63.1 ± 1.4<sup>b</sup> |
| PLA+OLA2                    | 1210 ± 39<sup>c</sup>         | 1.3 ± 0.2<sup>c</sup>         | 53 ± 7<sup>c</sup>              | 64.9 ± 2.5<sup>b</sup> |
| PLA+OLA2<sub>mal</sub>      | 1130 ± 31<sup>d</sup>         | 58.0 ± 2.0<sup>d</sup>        | 62 ± 4<sup>d</sup>              | 54.4 ± 3.1<sup>c</sup> |
| PLA+OLA2+SCG                | 1037 ± 37<sup>e</sup>         | 3.8 ± 0.3<sup>e</sup>         | 80 ± 8<sup>e</sup>              | 63.2 ± 1.7<sup>d</sup> |
| PLA+OLA2<sub>mal</sub>+SCG  | 1115 ± 40<sup>f</sup>         | 57.1 ± 2.5<sup>f</sup>        | 51 ± 3<sup>f</sup>              | 53.5 ± 1.6<sup>e</sup> |

<sup>a-f</sup> Different letters in the same column indicate a significant difference among the samples (<i>p</i> < 0.05)

**Thermomechanical Properties of PLA/SCG Composites**

Water contact angle measurements were carried out in order to obtain information about the hydrophilic behavior of the sample pieces and to evaluate the effect of the additives on the material surface. Figure 9 shows the water drops and their respective contact angles with the surface of the PLA pieces. It can be observed that all samples presented hydrophilicity since their contact angle was less than 90°, which is characteristic of the hydrophobic behavior of PLA [66, 67]. In particular, the neat PLA piece showed a contact angle of 87.1°, which is almost in the 90° limit. The addition of OLA2 and OLA2mal reduced the water contact angle down to 83 and 81.8°, respectively and, therefore, made PLA more hydrophilic. This is due to the more hydrophilic nature of the lactic acid oligomers, which reduces the hydrophobicity of PLA, as reported by Darie-Niță et. al. [66] when studying different plasticizers for PLA film processing. In particular, authors showed a reduction of about 12.5% in the contact angle in relation to neat PLA for a 7 wt.% content of oligomer. Regarding the incorporation of SCG particles, one can observe that the hydrophilicity of PLA also increased, reducing the value of contact angle down to 82.5°. This reduction is related to the higher hydrophilicity of SCGs due to the high content –OH groups in the lignocellulosic particles. This effect was previously observed by Laaziz et. al. [67] when filling PLA with lignocellulosic almond particles. The combined additions that resulted in the PLA/OLA2/SCG and PLA/OLA2<sub>mal</sub>/SCG pieces further decreased the contact angle, down to 79° and 80.4°. This is indicative of a synergistic effect between SCGs and the OLAs, which both increase the polarity of PLA and its free volume.
Moreover, it should be noted that the differences observed for the OLA2- and OLA2\textsubscript{mal}-containing pieces is related to their composition. OLA2\textsubscript{mal} achieves a lower contact angle value due to its MAH content, which increases the polarity of the compound in a higher extent than OLA2, which does not possess MAH groups.

In addition to the contact angle measurements, the water uptake of the injection-molded pieces was evaluated through the water absorption test. Figure 10 shows the evolution of the water uptake of each sample after 14 weeks of immersion in distilled water. As expected, neat PLA exhibited the lowest water absorption during all the immersion time, with a saturation value of approximately 0.67 wt.\% at 14 weeks of immersion, due to the hydrophobic nature of PLA. In this regard, Balart et. al. [68] observed a very similar saturation content of water for PLA. The addition of SCGs to the PLA matrix significantly increased the water absorption capacity of the composite up to a saturation value of 5.38 wt.\%, which is more than 5 times the water absorption of neat PLA. This high increase is related to the hydrophilic nature of SCGs, as shown above during the water contact angle. In this sense, cellulose, hemicellulose, and lignin present in SCGs contain multiple –OH groups that can readily interact with water molecules, forming hydrogen bonds and allowing water to enter the PLA’s structure [68]. Similarly, Wu [32] reported high water absorption values for PLA/SCG composites, reaching about 12.5 wt.\% water absorption for a 20-wt.% filler content at 60 days of immersion in water. On the other hand, it is worthy to mention that the presence of OLA2 and OLA2\textsubscript{mal} in the PLA matrix slightly increase water uptake to values of 0.74 wt.\% and 0.98 wt.\%, respectively. This low increase may be related to the higher free volume attained in the PLA samples due to the plasticization by the oligomers, being higher for OLA2\textsubscript{mal} due to its higher interaction with the biopolymer matrix provided by the presence of MAH groups, which are highly hydrophilic. A similar behaviour was observed by Wu [32], who treated PLA with MAH and observed a water absorption about 4% superior to that of neat PLA. Finally, the combined additions in the PLA+OLA2+SCG and PLA+OLA2\textsubscript{mal}+SCG pieces yielded values of 5.33 and 5.55 wt.\%, respectively, which are very similar to the value obtained for the PLA+SCG piece. However, the water uptake kinetic was lower, particularly from week 2, which corroborates the above-reported morphological results that the OLAs were mainly located at the filler-to-matrix interface and, then, reduced the water absorption produced on the lignocellulosic particle surfaces.

**Disintegration in Controlled Compost Soil of PLA/SCG Composites**

Figure 11 shows the percentage of weight loss as a function of the elapsed time during disintegration in the controlled compost soil of the injection-molded pieces based on PLA, SCG, OLA2, and OLA2\textsubscript{mal}. It can be observed that only the PLA, PLA+OLA2 and PLA+OLA2\textsubscript{mal} samples fully disintegrated. Nonetheless, all the pieces achieved certain mass loss after 98 days in compost soil. Neat PLA presented a weight loss of 100% at 84 days due to a hydrolytic degradation process [68]. A similar disintegration profile was observed by Quiles-Carrillo et. al. [69] when studying the compostability of neat PLA, achieving a mass decomposition of 100 wt.\% after 56 days. One can observe that the addition of 20 wt.\% SCGs highly decreased the biodegradation rate in comparison with neat PLA, with a weight loss of approximately 48%
at 98 days. This delay in the biodegradation rate can be due to the higher crystallinity that PLA/SCG samples possess in relation to neat PLA, as shown in previous Table 4. Hydrolytic degradation occurs faster in the amorphous regions, so the higher the crystallinity, the lower the disintegration rate. Quiles-Carrillo et. al. [68] observed this effect in PLA/HSF composites, which delayed the disintegration of PLA in 7 days. The inclusion of OLA2 and OLA2\text{mal} into the PLA matrix increased its biodegradation rate during almost all the experiment, which could be ascribed to the fact that both oligomers reduced the crystallinity of PLA in the temperature range of this experiment, as it was also demonstrated during the thermal analysis. PLA/OLA2 and PLA/OLA2\text{mal} presented a mass loss at 49 days of 60 and 65%, respectively, in comparison with neat PLA, which degraded 55% at 49 days. Finally, the combined additions of PLA with SCGs and OLA2 and OLA2\text{mal} showed disintegration rates lower than that of neat PLA, presenting mass losses of about 65 and 60% at 98 days, respectively, not fully degrading. This is obviously ascribed to the higher crystallinity of these samples provided by SCG, as it has been aforementioned. Their disintegration was superior to that observed for PLA/SCG because their crystallinity was lower, as illustrated in previous Table 4 during thermal analysis.

Finally, Figure 12 shows the visual aspect of all the pieces studied herein during the disintegration test, providing more information about their compostability profile. From the visual appearance of these samples, it can be confirmed that three of them were not fully disintegrated after 98 days buried in compost soil. Regarding neat PLA, it lost its transparent appearance only after 7 days of incubation time in compost soil due to the hydrolysis process of the polyester [70]. At 14 days, PLA already started to develop a brown color, which is a significant evidence of biodegradation. It then started to fragment and present microcracks, until complete degradation at 98 days. The PLA+SCG piece did not present apparent biodegradation signs until day 28, when it showed a clear crack and it then started to fragment until day 98, it can be seen how its biodegradation was quite slower than that of PLA. With regard to the PLA+OLA2 and PLA+OLA2\text{mal} pieces, both of them started to show a dark brown color at day 14, both being quite fragmented at this time, which confirms the faster disintegration rate in comparison with neat PLA. This confirms the faster biodegradation profile observed in Figure 11, in which the two OLA-containing samples presented a higher disintegration rate than neat PLA, although the latter piece fully disintegrated earlier. Concerning the combined additions to produce the PLA+SCG+OLA2 and PLA+SCG+OLA2\text{mal} pieces, they yielded similar disintegrated samples. However, the PLA+SCG+OLA2\text{mal} piece started to fragment earlier (day 14), supporting the biodegradation profile shown above. These results suggest that, despite PLA being already a biodegradable polymer under compost soil conditions, the addition of these compatibilizers can improve the compostability profile. On the other hand, SCG highly delays the biodegradation of PLA, fact that is closely linked with the increase in crystallinity that this food waste derived lignocellulosic filler provides.

**Conclusions**

The results presented in this work demonstrate, for the first time, the high potential of manufacturing PLA-based green composites through the valorization of wastes derived from the liquor coffee industry,
the here so-called SCG. The use of these lignocellulosic fillers yield PLA materials with enhanced ductility and lower cost. Furthermore, the co-addition of OLAs, particularly that functionalized with multiple MAH groups, contributes to improve impact strength and interaction of the SCG fillers with the PLA matrix, narrowing the filler-to-matrix gaps. In both cases, a relative high thermal stability was attained whereas the visual appearance of the pieces showed a typical dark-brown color that can resemble natural materials based on wood. Therefore, it can be concluded that the use of liquor coffee waste is very promising for developing cost-effective green composites and it opens a new route towards the development of ductile PLA-based materials. Future works will be focused on further optimizing the amount of SCG, the development of other compatibilizers that lead improved performance, and also on the evaluation of other properties of the resultant composites, such as their antioxidant capacity for active food packaging applications.

**Declarations**

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**Author contributions**

All authors contributed to the study conception and design. Methodology, Software, Investigation, and Writing – original draft were performed by Enrique Terroba-Delicado, Jaume Gomez-Caturla, and Nestor Montanes. Stefano Fiori contributed to Conceptualization, Methodology, Validation, Formal analysis. The final version of the manuscript was written by Sergio Torres-Giner and it was supervised by Lourdes Sanchez-Nacher: All authors read and agreed to the published version of the manuscript.

**Declaration of competing interest**

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 datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.
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Figures
Figure 1
(a) As-received spent coffee grains from waste of the liquor industry; (b) Resultant spent coffee grounds (SCGs) obtained after washing, drying, and milling.

Glyplast OLA2
m = 6.9–8.3

Glyplast OLA2_{mal}
MAH content 3–4 wt.%

Figure 2
Chemical structures of the oligomers of lactic acid (OLAs): Glyplast OLA2 (left) and Glyplast OLA2_{mal} (right).
Figure 3

(a) Field emission scanning electron microscope (FESEM) image of spent coffee ground (SCG) particles. Image was taken with a magnification of 500x and a scale marker of 10 µm; (b) Histogram of the SCG length; (c) Histogram of the SCG diameter.
**Figure 4**

Visual appearance of the injection-molded pieces of polylactide (PLA)/spent coffee ground (SCG) containing the oligomers of lactic acid (OLAs): (a) PLA; (b) PLA+OLA2; (c) PLA+OLA2mal; (d) PLA+SCG; (e) PLA+OLA2+SCG; (f) PLA+OLA2mal+SCG.
Figure 5

Field emission scanning electron microscopy (FESEM) images, taken at 1000x and with scale markers of 10 µm, of the fracture surfaces of the injection-molded pieces of polylactide (PLA)/spent coffee ground (SCG) containing the oligomers of lactic acid (OLAs): (a) PLA; (b) PLA+SCG; (c) PLA+OLA2; (d) PLA+OLA2mal; (e) PLA+OLA2+SCG; (f) PLA+OLA2mal+SCG.

Figure 6

Differential scanning calorimetry (DSC) thermograms of the injection-molded pieces of polylactide (PLA)/spent coffee ground (SCG) containing the oligomers of lactic acid (OLAs) during cooling (a) and
second heating (b).

Figure 7
(a) Thermogravimetric analysis (TGA) curves and (b) first derivative (DTG) of the injection-molded pieces of polylactide (PLA)/spent coffee ground (SCG) containing the oligomers of lactic acid (OLAs).

Figure 8
Plot evolution of (a) the storage modulus and (b) the dynamic damping factor ($\tan \delta$) of the injection-molded pieces of polylactide (PLA)/spent coffee ground (SCG) containing the oligomers of lactic acid (OLAs).
Figure 9

Water contact angle of the injection-molded pieces of polylactide (PLA)/spent coffee ground (SCG) containing the oligomers of lactic acid (OLAs): (a) PLA; (b) PLA+OLA2; (c) PLA+OLA2mal; (d) PLA+SCG; (e) PLA+OLA2+SCG; (f) PLA+OLA2mal+SCG.
Figure 10

Water uptake of the injection-molded pieces of polylactide (PLA)/spent coffee ground (SCG) containing the oligomers of lactic acid (OLAs).
Figure 11

Evolution plot of the percentage of weight loss as a function of the elapsed time during disintegration in controlled compost soil of the injection-molded pieces of polylactide (PLA)/spent coffee ground (SCG) containing the oligomers of lactic acid (OLAs).
Figure 12

Visual aspect at selected disintegration times of the injection-molded pieces of polylactide (PLA)/spent coffee ground (SCG) containing the oligomers of lactic acid (OLAs).

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