

Communication

# Sustainable Bio-Composites Obtained from Recycling Post-Industrial PLA and Fillers Derived from Coffee Production

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**Abstract:** Bio-composites have been formulated by exploiting post-industrial PLA derived from thin film production and silver skin, a by-product of the coffee's roasting process. The mix design for the compounds exploits the effects of regrading and toughening agents. The mechanical properties of the materials have been investigated as well as the thermal and physical ones. The recycled material mixed with the regrading additive shows good mechanical properties. The filler addition increases the elastic modulus of PLA up to a 20% but decreases the mechanical properties (about 20% on tensile strength), leading to a brittle behavior (minus 35% of impact strength). The use of a toughening agent restores the plastic deformation ability of the matrix.

**Keywords:** PLA; biocomposites; agro-waste; mechanical properties; microstructure



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## 1. Introduction

The future progressive withdrawal from oil exploitation drives the industry towards the use of polymers deriving from renewable sources. Polylactide (PLA) is presently the most commercialized one, all over the world [1]. According to the large volumes of PLA commodities produced, mainly for packaging [2,3], PLA waste recycling is becoming an important issue. Although tertiary recycling, either chemical [4] or enzymatic [5], can be a possible route [6], mechanical recycling offers many advantages [7]. One of these is the possibility to obtain composites through a single step extrusion process. In the new material, the recycled polymer acts as a matrix filled by a second phase. If this second phase is another waste, the overall price of the material is lowered and a further positive environmental benefit is obtained [8]. The decrease of the mechanical properties of the derived composites, caused both by the polymer degradation and the scanty filler-matrix interaction, can be a drawback for subsequent applications [9–11]. Since the decrease of the mechanical properties of the degraded matrix derives from the reduction in the value of the average molecular weight, during the extrusion process the addition of regrading molecules [12–14] can restore the value. Moreover, to increase the polymer filler interaction, the use of a compatibilizer, a modified polymer [15–17] having affinity with both phases, can instead improve the mechanical properties. When the extreme brittleness of the material becomes the limiting factor to the final application, the microstructural modification through the insertion of a toughening phase [18–22] can be performed. In the present research the production of composites based on post-industrial PLA and a filler deriving from the roasting process of coffee beans has been investigated. The amount of silver skin deriving from the roasting process is remarkable, since it is estimated that it makes up a 4% weight of the bean [23]. Coffee silver skin has consequently attracted a lot of interest in the production of bio-composites due to its widespread availability and to its composition that contains antioxidant and UV radiation absorbing molecules such as phenols and Maillard reaction products [24,25]. In order to overcome possible problems deriving from the reduced mechanical properties of the composites, a mix design of the investigated materials including also a regrading chain extender and a toughening phase is proposed.

The effect on the mechanical properties of the different composition has been evaluated in view of a possible reuse in the formulation of packaging items.

## 2. Experimental

### 2.1. Materials

Post-industrial PLA, deriving from films production, kindly supplied by Taghleef (Como, Italy).

Coffee silver skins (hereafter defined as CSS) deriving from a mixture (80/20 wt%) of *Arabica* and *Robusta* variety have been ball milled to obtain powders with a dimension lower than 200  $\mu\text{m}$ . In details, the filler had a D10 value of 7  $\mu\text{m}$ , a D50 of 34  $\mu\text{m}$  and a D90 value of 107  $\mu\text{m}$ .

Chain extender: Chain extender (hereafter referred to as CE) is Jonkryl ADR 4368-C (BASF).

Toughening additive (hereafter referred to as T) is a thermoplastic polyurethane Elastollan N65A12P (BASF)

### 2.2. Compounding

Before compounding, all components were kept in dynamic vacuum at 60 °C for 12 h to eliminate moisture. A twin screw extruder (Coperion ZSK-18) was used, having an output of 5 kg/h and a round die (4mm diameter). The complete screw profile is reported in Figure 1.

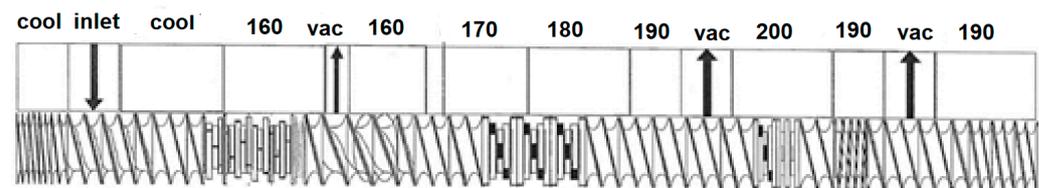


Figure 1. Screw profile.

As to the extrusion parameters, a temperature profile of 160, 170, 180, 190, 200, 190 and 190 °C in the extruder was applied and the rotational speed of the screw was 250 rpm. The obtained pellets were dried and afterwards used to prepare suitable samples for the subsequent characterizations by injection molding by means of a Negri Bossi, VE70 injection machine. The process conditions were the following: temperature 140–160–180–190 (last is nozzle temp), max injection pressure 800 bar. Holding pressure: 100 bar for 4 s, mold cooled at 25 °C, cycle time 50 s.

In Table 1 the composition (wt%) of the investigated materials is reported as well as the codes that will be used henceforth in the paper.

Table 1. Compositions (wt%) and codes of the investigated compounds.

Sample	PLA	CE	CSS	T
PLA	99.5	0.5	0	0
PLA_CSS	79.5	0.5	20	0
PLA_CSS_T	59.5	0.5	20	20

Figure 2 shows the specimens derived by injection molding to be submitted to the mechanical characterization.



**Figure 2.** Specimens derived by injection molding (reported composition is of PLA\_CSS).

### 2.3. Tests

Thermal analysis was performed by DSC (Q10, TA Instruments) from 0 to 170 °C in nitrogen flux (40 mL/min). Three scans were performed. The first one from 30 to 170, followed by an isothermal treatment at the highest temperature, erased the previous polymer history. Afterwards, a cooling scan to 0 °C at 15 °C/min was performed, followed by a third heating scan at 15 °C/min to 170 °C. The amount of crystalline phase was calculated according to the following expression:

$$\chi_c(\%) = \frac{\Delta H_m}{\Delta H_m^0 \times f_w} \times 100$$

where  $\Delta H_m^0$  is the melting enthalpy of the fully crystallized material  $\Delta H_m$  is the calculated enthalpy of the investigated sample and  $f_w$  is the PLA amount in the sample.

The thermal stability was studied by TGA (Perkin Elmer) from 40 to 700 °C in nitrogen flux (50 mL/min).

Tensile mechanical tests were performed by an INSTRON 5966 series instrument with a 10 kN load cell operating at test speed of 5 mm/min on the dog bone specimens reported in Figure 2. The laboratory temperature was  $22 \pm 1$  °C and a  $60 \pm 10\%$  relative humidity. The average of five different test for each material was obtained. Impact strength was determined in the Charpy configuration on unnotched samples in the previous laboratory conditions. Charpy tests were performed by using a Ceast Resil 5.5 Impact Strength Machine (CEAST S.p.a., Torino, Italy) according to ISO 179 on specimens of  $4 \times 10 \times 80$  mm derived from the injection moulded dog-bone ones (Figure 2).

The surfaces of the composite specimens fractured in the Charpy test, were observed by scanning electron microscopy (SEM, FEI XL20) after gold metallization (Quorum 150R ES).

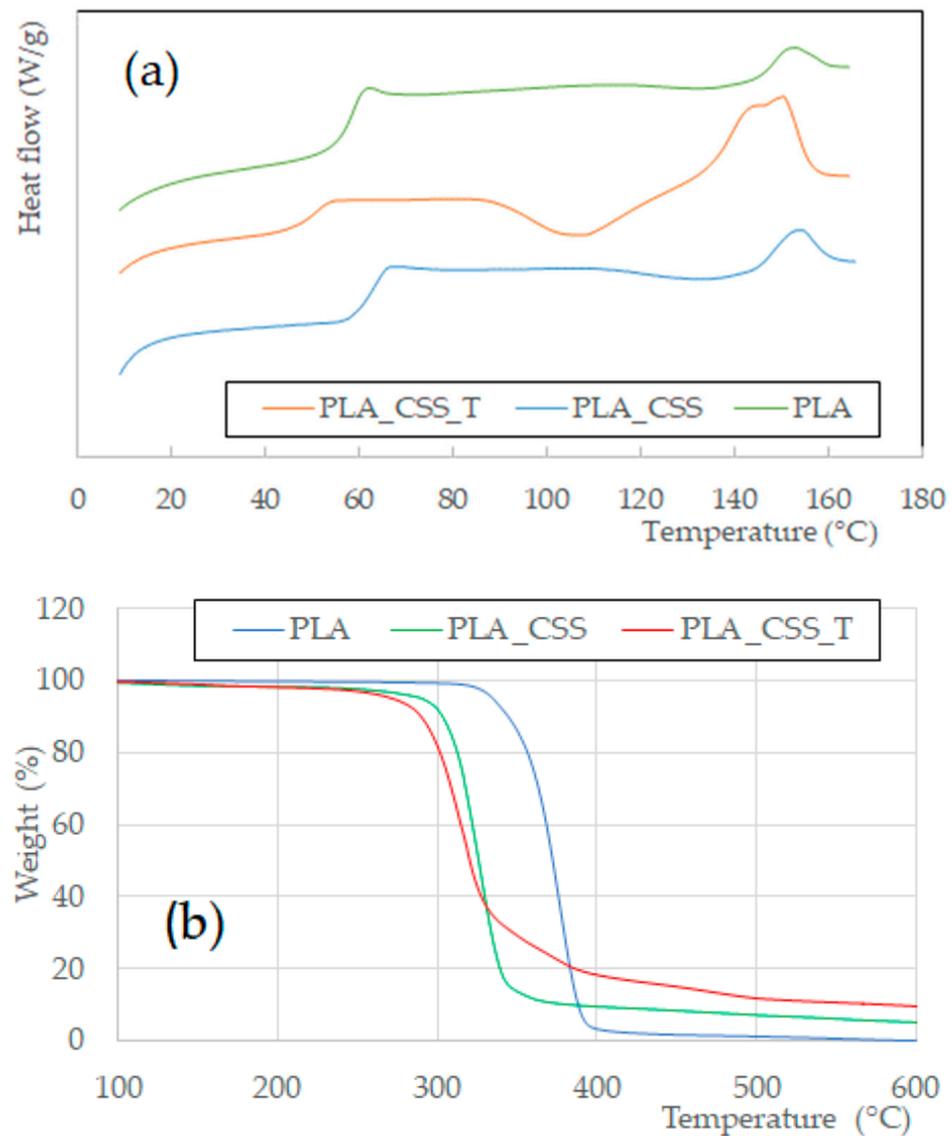
## 3. Results

Table 2 summarizes the results from the DSC analysis derived by the thermograms of Figure 3a.

**Table 2.** Thermal analysis results of the investigated materials <sup>1</sup>.

Sample	Tg (°C) <sup>1</sup>	Tm (°C) <sup>1</sup>	ΔHf (J/g) <sup>1</sup>	χc %
PLA	49	152.0	3.7	4.0
PLA_CSS	51	152.8	1.1	1.5
PLA_CSS_T	46	151.3	5.1	8.9

<sup>1</sup> The first column refers to the second scan, the others to the third one.



**Figure 3.** (a) thermograms derived by DSC; (b) TGA analysis.

All the investigated materials have close values of glass transition and melting temperatures. Only a small fraction of the regraded PLA is crystallized. CSS addition seems to hinder the development of the ordered phase, while the presence of the polyurethane acts possibly as a nucleating agent, creating crystals of different sizes as evidenced by the melting peak broadening. This leads to a higher fraction of crystallinity, as can be seen from the normalized percentage value in Table 2. The selected melting enthalpy value for the fully crystalline PLA phase is of 93 J/g, as reported in [26].

In Table 3, the results of the TGA analysis derived from Figure 3b are summarized. The onset temperature of decomposition ( $T_{onset}$ ) of the polymer is decreased by the presence of the filler as well as by the presence of the polyurethane. Nevertheless, in all cases the onset decomposition temperature is always above the highest compounding one (i.e., 200 °C) and consequently the possible degrading reactions taking place during compounding, should be comparable in all the samples. The same trend is recorded for the temperature of the maximum degradation rate.

**Table 3.** Thermogravimetric analysis results of the investigated materials.

Sample	Tonset (°C)	Tmax (°C)	Residue (%) <sup>1</sup>
PLA	354	376	0.0
PLA_CSS	302	323	1.1
PLA_CSS_T	290	317	6

<sup>1</sup> at 700 °C.

The average values, as well as the standard deviations, of the tensile properties and of the impact strength (IS) are summarized in Table 4.

**Table 4.** Mechanical properties, from the tensile tests, of the investigated materials.

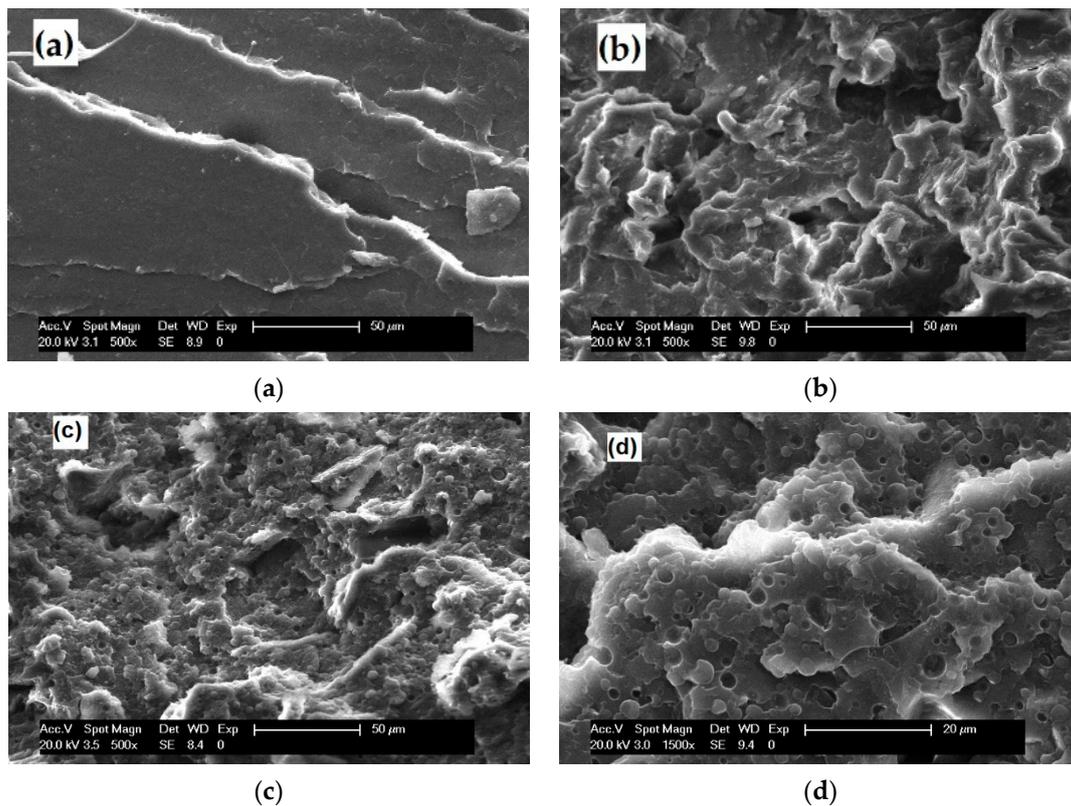
Sample	E (MPa)	$\sigma_{max}$ (MPa)	$\epsilon_{break}$ (%)	IS (kJ/m <sup>2</sup> )
PLA	3600	63.6	13.6	17.1
	50 *	3.2 *	1.8 *	1.7 *
PLA_CSS	4400	49.5	2.1	10.9
	100 *	1.9 *	0.2 *	0.7 *
PLA_CSS_T	3300	33.0	12.2	15.9
	50 *	0.4 *	3.6 *	0.8 *

\* Standard deviations are reported below the average values.

The filler strongly increases the value of the modulus (about 20%) but at the same time induces a more brittle behavior of the composite and negatively affects the values of the tensile strength. This feature is common to other types of organic fillers such as vine and grapes, potato pulp, wood flour, hemp hurd powder and alfalfa [11,27–29]. The effect derives from the weak adhesion between the filler and PLA, a feature that could be modified by adding a compatibilizer or by the surface modification of the filler [30]. These procedures would however affect the cost of the process. Although being reduced by the CSS addition, the mechanical properties of the composites are however still eligible for many packaging applications.

The results of the impact strength tests are summarized in Table 4. The bare matrix still shows good mechanical properties, a feature that possibly underlines the positive effect of the chain extender during the processing step. As can be seen, the presence of the filler causes an embrittlement of the polymer, as a 50% decrease in the IS value takes place. The use of the toughening additive, however restores almost completely the matrix behavior.

The microstructure of the composites, as well as the one of the plain matrix, is shown in Figure 4, where the fracture surfaces of the samples deriving from the Charpy test are reported. The filler presence leads to a rougher surface than the one of PLA (a). CSS modification creates a rougher fracture surface than the one of the bare matrix. The compounding process manages to evenly disperse the CSS particles inside the matrix leading to a homogeneous microstructure without the presence of CSS clusters or agglomeration. Both in micrograph (b) and (c) the silver skin particles are well enclosed inside the matrix without visible porosities at the interphase. The presence of the toughening phase leads to an even rougher surface, where this second phase appears as homogeneously dispersed in the PLA matrix, as highlighted in Figure 4d. The average dimension of this second phase is of about 3  $\mu\text{m}$ .



**Figure 4.** Fracture surface of PLA (a), PLA-CSS (b), PLA\_CSS\_T (c), and PLA\_CSS\_T (d) at higher magnification.

#### 4. Conclusions

Although a deeper understanding of the effects of the compounding process on the PLA characteristics is required, the present experimental work forecasts the possibility to recycle post-industrial PLA for the production composite materials, where an agro-waste can be used as a filler. In the present research the filler has been used without any chemical treatments that could have improved its interaction with the biopolymer. However, these treatments necessarily imply an economical drawback affecting the whole process. This feature on one side promotes the concepts of circular economy, on the other side allows to reduce the overall amount of biopolymer used thus decreasing the final material cost. Moreover, it could allow the recovery of at least a fraction of the large volume of coffee silver skin produced all over the world. The filler decreases the impact and tensile strength of the composites but on the other side it increases the value of the elastic modulus. The behavior of the plain PLA can be restored by properly modifying the composite microstructure by adding on a single mixing step a further toughening phase in the formulation.

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