

Eco-sustainable systems based on
poly(lactic acid), diatomite and coffee grounds extract for food packaging

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Abstract

In the food packaging sector many efforts have been (and are) devoted to the development of new materials in order to reply to an urgent market demand for green and eco-sustainable products. Particularly a lot of attention is currently devoted both to the use of compostable and biobased polymers as innovative and promising alternative to the currently used petrochemical derived polymers, and to the re-use of waste materials coming from agriculture and food industry. In this work, multifunctional eco-sustainable systems, based on poly(lactic acid) (PLA) as biopolymeric matrix, diatomaceous earth as reinforcing filler and spent coffee ground extract as oxygen scavenger, were produced for the first time, in order to provide a simultaneous improvement of mechanical and gas barrier properties. The influence of the diatomite and the spent coffee ground extract on the microstructural, mechanical and oxygen barrier properties of the produced films was deeply investigated by means of X-Ray diffraction (XRD), infrared spectroscopy (FT-IR, ATR), scanning electron microscopy (SEM), uniaxial tensile tests, O₂ permeabilimetry measurements. An improvement of both mechanical and oxygen barrier properties was recorded for systems characterised by the co-presence of diatomite and coffee grounds extracts, suggesting a possible synergic effect of the two additives.

Keywords: Polylactic (acid); Diatomite; Spent coffee grounds extract; Microstructure; Mechanical properties; Thermal properties.

Introduction

In the food packaging sector the wide and indiscriminate use of non-biodegradable petrochemical-derived polymers (e.g., polystyrene (PS), polypropylene (PP) and polyethylene terephthalate (PET)) has led to serious and dramatic environmental and ecological problems. Thus, recently a lot of attention has been directed towards biodegradable and/or compostable polymers (biopolymers) as a promising alternative to the traditional petrochemical-derived polymers [1-3]. Among biopolymers (e.g. poly(lactic acid) (PLA), polyhydroxyalkanoates (PHA), polybutylene succinate (PBS), polybutylene-adipate-terephthalate (PBAT), chitosan, alginate, PLA is the most widely used, due to its outstanding properties [4-6], and to the fact that it has gained the CE and compostability marks, as well as the FDA approval. Nevertheless, a more extensive industrial employment of PLA is still limited and precluded in food packaging, due to its low mechanical performances and poor gas barrier properties, with respect to those shown by traditional petrochemical-derived polymers. Therefore, many efforts are currently being devoted to the development of new strategies to overcome the main biopolymers limits [7]. For the enhancement of the mechanical properties, nanoparticles are usually employed as fillers, such as lignocellulosic materials [8], calcium sulphate [6], cellulose nanocrystals [9], graphite [10], silica nanoparticles [11], calcium phosphates [12,13], and, mainly, nanoclays [14,15].

In order to improve the oxygen barrier properties, fundamental requirement in food packaging applications to maintain food freshness, and to enhance its shelf life, two approaches are usually followed: the use of antioxidant molecules with the role of oxygen scavengers and/or the addition of suitable fillers (fibers, platelets, particles) to the polymeric matrix, providing a physical barrier to oxygen permeation [16]. In fact it is well known that, in the presence of well dispersed particles within the polymeric matrix, the permeating molecules are forced to wiggle around them in a random walk, and hence diffuse through a tortuous pathway, with a consequent reduced oxygen transmission rate (OTR) and enhanced gas barrier properties.

In this study, we propose, for the first time, the fabrication of an innovative completely compostable films, based on PLA as polymeric matrix, diatomaceous earth as reinforcement fillers, and coffee grounds extract as oxygen scavenger, in order to provide an improvement of both mechanical and gas barrier properties. In details, binary systems (i.e. PLA loaded with diatomite or with coffee grounds extracts), as well as ternary ones (PLA loaded with diatomite and coffee grounds extracts), were prepared and tested. Both coffee grounds extracts and diatomite are waste materials, readily available in the market at low costs and in high amounts and, thus, their reuse perfectly fits an eco-sustainable and green approach. Indeed, coffee is one of the most consumed beverages worldwide, and its production and consumption are characterised by a remarkably progressive rise, leading to a

consequent increase in the coffee waste generation. Since waste coffee grounds come from coffee beans, it is expected that they have comparable properties and preserve some of the present antioxidants and fatty acids [17], despite most of them are brewed in the produced beverages. Pujol et al. demonstrated that the main components in the lipophilic extractives of coffee grounds are free fatty acids (>60%), whereas total polyphenols and tannins represent <6% and <4%, respectively [17]. Therefore, extracts from coffee grounds present potential applications in several fields, for example as a biosource of antioxidants, and are expected to be able to provide an increase of barrier properties, acting as oxygen scavengers.

Diatomite consists in a natural fossil siliceous flour, originated from the sedimentation and accumulation of the silica remains of dead diatoms (microscopic single-celled algae) in marine sediments. It is commonly used in the food sector and characterised by low density, hierarchical porous structure, high surface area, abrasiveness, insulating properties, inertness, absorptive capacity, brightness, and high silica content. It can be used as filter aid, functional additive, absorbent, natural insecticide, dental filling, roofing compound, adhesive, sealant... [18,19]. For these reasons, diatomite was chosen as inorganic filler, both to act as reinforcing agent and, additionally, to create a more tortuous diffusive path to gases, preventing their diffusion inside the container and increasing the time required for molecules flux within the package thickness.

All produced films were fully characterized in terms of mechanical (tensile) and thermal (DSC) properties, microstructure (SEM, XRD) and chemical structure (ATR), Moreover the gas barrier properties through Oxygen Transmission Rate (OTR) measurements, were investigated too.

Materials and Methods

Materials

Poly(lactic) acid (PLA 3052D, molecular weight (M_n) of ca. 6×10^4 g/mol) was supplied by *Nature Works*[®].

Coffee grounds, collected from automatic coffee machines, were gently provided by *Blucomb S.r.l.*, and they consist in a blend of arabica and robusta species. As a reference, caffeine powder was purchased from *Sigma-Aldrich*. The used diatomite (*SuperCel*[®]*fine*, PM= 1,495 g/mol, average dimension of 14 μm , *Sigma Aldrich*) consists in a calcined diatomaceous earth, characterised by the following composition: SiO₂ 91.1 %, Al₂O₃ 4.0 %, CaO 0.5 %, Fe₂O₃ 1.3 %, Na₂O + K₂O 1.1 %, in weight percentages.

Extraction from coffee grounds

Coffee grounds powder (1%w/v) was magnetically stirred in chloroform (CHCl_3 , *Sigma Aldrich*, $\geq 99\%$), using a flask, equipped with a refrigerating column, at $70\text{ }^\circ\text{C}$ for 2 hours. The obtained suspension was then vacuum filtered and the extracted solution was analysed to evaluate caffeine content, using an UV-Vis spectrophotometer (UV-Vis Spectrophotometer UV-2450, *Shimadzu*) in the wavelength range 200-500 nm. Caffeine concentration was evaluated from the absorbance at 276 nm. The caffeine molar extinction coefficient, according to Lambert-Beer law, was obtained from the slope of Lambert-Beer plot obtained using the UV-Vis absorbance values at 276 nm of five different known concentrations (range: $3 \cdot 10^{-5}\text{ M}$ - $1 \cdot 10^{-4}\text{ M}$) of commercial caffeine solutions in chloroform. GC-MS analysis was also performed, dissolving approximately 1 mg of analyte in 1 mL of dichloromethane (DCM, *Sigma Aldrich*). Analysis was done on 5 μL aliquots using a *Shimadzu GCMS QP2010 Ultra*, equipped with an AOi20 autosampler unit. A SLB-5 ms Capillary GC Column ($L \times \text{I.D. } 30\text{ m} \times 0.32\text{ mm}$, $df\ 0.50\ \mu\text{m}$) was used as stationary phase and He as the mobile phase in the following conditions: pressure 100 kPa, injection temperature $280\text{ }^\circ\text{C}$, interface temperature $200\text{ }^\circ\text{C}$. The following program was carried out: $50\text{ }^\circ\text{C}$ start temperature for 1 min, $5\text{ }^\circ\text{C min}^{-1}$ heating rate, $240\text{ }^\circ\text{C}$ final temperature for 15 min; mass analysis after electron ionization using ca. 70 eV, $200\text{ }^\circ\text{C}$ ion source temperature, solvent cut time 4 minutes. The obtained data were analysed using Shimadzu GCMS Solution software.

Film Preparation

Binary and ternary systems, based on PLA, diatomite and spent coffee ground derived extracts, were prepared by solvent casting technique.

Binary samples containing extracts from spent coffee grounds (PLA-E) were made, completely dissolving PLA pellets in the extracted chloroform based solution, in order to obtain a polymer concentration of 5 % wt/v.

In the case of binary samples containing diatomite (PLA-D), a dispersion of diatomite powder was prepared suspending the particles in CHCl_3 in a content of 5 wt/wt% with respect to PLA, and sonicating them for around 30-60 minutes in an ultrasound bath. Pellets of PLA were then added to the prepared suspension to obtain a PLA concentration of 5 wt/v%.

In the case of ternary systems containing both spent coffee grounds derived extracts and diatomite (PLA-DE), a dispersion of diatomite powder was prepared by suspending the particles in the extracted chloroform based solution in a content of 5 wt/wt% with respect to PLA, and sonicating them for around 30-60 minutes in an ultrasound bath. Pellets of PLA were added to the prepared suspension to obtain a PLA concentration of 5 wt/v%.

All the obtained solutions/suspensions were magnetically stirred at room temperature, up to complete polymer dissolution, then cast on teflon Petri dishes and maintained under fumehood up to 72 hours, until complete solvent evaporation.

As a reference, neat PLA film (5 %wt/v) was also prepared following the same procedure, using pure chloroform as solvent.

Characterization of the obtained films

The functional chemical groups of the obtained films were identified by the acquisition of infrared spectra in the region 600-4000 cm^{-1} (spectral resolution of 4 cm^{-1}), using a FT-IR instrument equipped with an attenuated total reflectance (ATR) cell (Jas.co, FT/IR-6600). Spectra were acquired by placing and pressing the samples into contact with the ATR cell. A total of 32 scans were collected for each sample. As a reference, FT-IR spectrum was also acquired on spent coffee ground extract (FTIR *Perkin Elmer*) in the following conditions: wavenumber range of 400-4000 cm^{-1} , spectral resolution of 4 cm^{-1} and scans number of 32.

X-ray diffraction (XRD) (Philips X'Pert 1710, Cu- K_{α} radiation $\lambda = 1.5405600 \text{ \AA}$, $2\theta = 5\text{--}80^{\circ}$, step size = 0.020 $^{\circ}$, time per step = 2 s, scan speed = 0.005 $^{\circ}/\text{s}$) measurements were performed on all samples, in order to investigate the influence of the added diatomite and of the presence of spent coffee ground extract on the crystallization of PLA.

Thermal properties of all samples were assessed by differential scanning calorimetry (DSC, *TA Instruments Q2000*) under the following conditions: sample weight ~5 mg, temperature range from 0 to 200 $^{\circ}\text{C}$, heating and cooling rates of 10 $^{\circ}\text{C}/\text{min}$, nitrogen flux 50 cc/min . Two thermal cycles, composed of one heating scan and one cooling scan, were carried out. Melting temperatures (T_{mI} and T_{mII}), cold crystallization temperatures (T_{ccI} and T_{ccII}), glass transition temperatures (T_{gI} and T_{gII}), melting enthalpies (ΔH_{mI} and ΔH_{mII}), cold crystallization enthalpies (ΔH_{ccI} and ΔH_{ccII}), crystallinity degrees (X_{mI} and X_{mII}), and also were determined from first and second heating scans. The crystallinity degree (χ) was evaluated according to the following equation:

$$\chi = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^{\infty} (1 - x)} \cdot 100$$

where ΔH_m and ΔH_m^{∞} are the scan-related melting enthalpy and the melting enthalpy associated to 100% crystalline PLA (i.e. 93 J/g [9,12, 20-22]), respectively, ΔH_{cc} is the scan related crystallization enthalpy, and x is the nominal diatomite weight fraction.

The oxygen permeability of the prepared films was evaluated according to the ASTM D-3985 standard using gas permeation instrument (MOCON OX-TRAN® 2/61), in the following conditions: constant temperature 23 °C, relative humidity 0% and gas flow 10 ml/min.

The mechanical behaviour of solvent cast films was evaluated by uniaxial tensile tests (*Lloyd LRX*, 50N load cell), at 1,2 mm/min on dog bone specimens (4.8 mm x 22.25 mm) according to ASTM D1708. ASTM D882 was used for the calculation of the elastic modulus. Four specimens were considered for each film type, at least. Fracture surface of the stress strained films was observed at field emission scanning electron microscopy (FE-SEM, *LEO Supra 35*), in order to investigate the fillers distribution within the polymeric matrix and evaluate the compatibility/wettability between the filler and the matrix.

Results and discussion

Chemical composition of spent ground coffee extract

The spent coffee grounds derived extract was analysed by both UV-Vis and GC-MS analyses in order to quantify the caffeine amount and to identify the present components, respectively.

From the related UV-Vis spectrum we were able to assess that the caffeine amount within the spent coffee ground extract was about 2 mg per gram of spent coffee. The evaluated content was lower with respect to that reported in literature (i.e. around 4,7 mg of caffeine per gram of spent coffee [23], suggesting that either the caffeine content within the used coffee grounds was lower with respect that of the analysed spent coffee in literature or, more probably, the followed extraction procedure was not completely efficient. In fact, it has been extensively reported that chemical composition of spent coffee grounds significantly differs on the basis of coffee species and beverage production methods [23]. For example, caffeine, chlorogenic acids and other molecules contents change between *Arabica* and *Robusta* species and distinct beverage production methods provide different extraction efficiency of the main antioxidant molecules present in coffee beans [24].

The GP-MS analysis evidenced that extracted solution contains many components (**Figure 1**), including some fatty acids, mainly C18, that are typical organic components present in coffee beans, coffee brews and spent coffee [25]. The retention times, molecular weights and percentages (according to total counts) of the identified fatty acids are reported, resulting the stearic acid about 53% of the total amount.

Microstructural features of PLA based films

In **Figure 2a-b** the FTIR-ATR spectra of PLA based films are compared. In addition to the typical PLA vibrational modes [26-29], some extra peaks can be evidenced in the case of the films containing the extract, including a double peak around 1750 cm^{-1} (precisely at 1746 cm^{-1} and at 1753 cm^{-1}) and the peaks at 2920 cm^{-1} , 2850 cm^{-1} and 737 cm^{-1} . These latter vibrational modes testified the presence of spent coffee ground extract within the polymeric matrix. In details, the peak at 1746 cm^{-1} (**Figure 2a**) can be ascribed to the carbonyl (C=O) vibration in triglycerides [30] or to aliphatic esters [31], whereas the peak at 737 cm^{-1} to C-O-C vibration in chlorogenic acids [17] (**Figure 2a**). Moreover, the two sharp peaks at 2920 cm^{-1} and 2850 cm^{-1} confirm the presence of methyl and methylene groups, being correlated to the asymmetric ($\nu_{\text{as}}\text{ C-H}$) and symmetric ($\nu_{\text{s}}\text{ C-H}$) stretching of C-H bonds in aliphatic chains, respectively (**Figure 2b**). These peaks can be attributed to the presence of both caffeine [32,33] and lipids [17]. It is interesting to evidence that these peaks were slightly shifted with respect to the related ones detected for the coffee ground extract (**Figure 2c**), suggesting a possible interaction between the polymer and the extract.

Similarly, the XRD patterns of the samples containing extracted coffee (i.e. PLA-E and PLA-DE) further confirmed the stearic acid presence, showing the diffraction peak typical of stearic acid crystalline phase around 22° (JCPDS #38-1923) (**Figure 3**), in addition to the PLA typical diffraction peak at around 18° [10]. It is interesting to highlight the remarkably increased intensity of PLA XRD peak in the case of PLA-E and PLA-DE samples, suggesting an influence of the spent coffee grounds derived extracts on the crystallization mechanism of the PLA chains and an interaction between this extract and the polymeric matrix.

Thermal properties of PLA based films

The influence of the added diatomite and coffee ground extract on the thermal properties and crystallinity of the prepared films was investigated by means of DSC measurements. The first and second heating scan DSC curves are compared in **Figures 4a** and **4b**, respectively. DSC data, in terms of glass transition (T_g), melting (T_m), cold crystallisation (T_{cc}) temperatures, melting (ΔH_m) and cold crystallization (ΔH_{cc}) enthalpies and crystallinity degree (χ), related to the first and the second heating scans, are listed in **Table 1**.

Concerning the data related to the first heating scan, as expected, the glass transition temperature was not affected by diatomite addition, being a micrometric filler and thus not able to directly interact with the polymeric chains. On the other hand, a significant increase of T_g value was recorded in the presence of the coffee ground extract, very probably due to the presence of stearic acid crystals and to an interaction between the extract components and the poly(lactic acid) chains, in agreement with

the ATR and XRD data. Indeed, the present stearic acid crystals, identified in the XRD pattern (**Figure 3**), limited and hindered the polymeric chains mobility, leading to an increased T_g value, associated to a higher crystallinity degree (33-34 % vs 27 % for PLA-E/PLA-DE and PLA samples, respectively), in agreement with previous works [34].

The exothermic peak at around 110-115 °C, very evident in the case of PLA and PLA-D samples, has to be ascribed to the PLA typical cold crystallization (T_{cc}), due to the reorganization of amorphous domains into crystalline regions owing to the increased macromolecular flexibility and mobility upon increasing temperature.

It is interesting to note that in the case of the films containing coffee grounds extract, T_{cc} peak is not clearly visible, suggesting that the rearrangement of PLA chains, with the formation of a more organized structure, was favoured by the presence of extract components, acting as crystallization nuclei, during the solvent casting process. In addition, it is possible to observe only one well defined melting peak, with a very broad and little shoulder, whereas in the case of PLA and PLA-D two well-defined individual melting peaks were detected, due to the coexistence of two PLA crystalline structures or because of the melting behaviour with melt recrystallization model [35,36] or due to the dual lamellae population [36].

It has been reported that the lower melting peak belongs to the crystals formed through a melt-recrystallization process during the heating scan (cold crystallization process), whereas the higher one is related to the melting of the original crystals derived from the sample preparation, on the basis of the melt recrystallization model [35,36]. Considering the second heating scans, a decrease of T_g values was recorded in the case of films containing the spent coffee grounds extract, suggesting a plasticizing action starting from the melt state. In fact, plasticizers are commonly added to a polymeric matrix in order to increase polymer chain mobility by decreasing intermolecular forces [37] and hydrogen bonding between polymer chains [38,39]. The plasticizers are able to enhance the polymeric chain flexibility, promoting and making easier the cold crystallization process, as testified by the lower T_{cc} values detected for PLA-E and PLA-DE films. Furthermore, a significant T_m decrease was detected for ground coffee extract containing films, particularly for PLA-DE, suggesting an interaction between diatomite and spent coffee ground extract and their synergic effect on PLA.

This experimental evidence could be ascribed to the presence of smaller sized crystals or more defects in the crystals, even if the crystallinity degree remained comparable [40].

Moreover, as expected, significantly lower crystallinity degree values were obtained in all cases, due to the elimination of the thermal history, particularly of the influence of the applied process for the production of the films.

Gas barrier properties of PLA based films

The Oxygen Transmission Rate (OTR) gas permeability values of PLA based films are measured. The oxygen permeability of PLA was around $62 \text{ cm}^3 \cdot \text{mm}/\text{m}^2 \cdot \text{day}$, higher with respect to that reported in previous works (e.g. $20 \text{ cm}^3 \cdot \text{mm}/\text{m}^2 \cdot \text{day} \cdot \text{atm}$) [41,42] and $18 \text{ cm}^3 \cdot \text{mm}/\text{m}^2 \cdot \text{day} \cdot \text{atm}$ [43]). However, it has to be underlined that the film oxygen permeability strongly depends on the used polymer grade, the obtained chain flexibility, the polymer physical state and the packing of its molecules. Thus it is difficult to compare data related to films prepared starting from a different polymer grade and using different production conditions, in terms of employed solvent, petri dishes kind and environmental conditions (temperature and humidity).

In the case of ternary system, a lower OTR was recorded (around $53 \text{ cm}^3 \cdot \text{mm}/\text{m}^2 \cdot \text{day}$), suggesting that the presence of diatomite is able to create a tortuous path to the oxygen flux, and the spent coffee ground extract to act as oxygen scavenger. Accordingly, it has been reported that also the addition of fatty acids, such as stearic acid, allows to decrease the gas transmission rate [44].

Moreover, the lower OTR value can be ascribed to the higher crystallinity of the films containing the spent coffee grounds extract, as evidenced by the XRD (**Figure 3**) and DSC (**Table 1**) data. Indeed, it is well known that polymers with higher crystallinity can lower sorption and increase the barrier for diffusion [45] and that amorphous regions in a film are characterised by large amount of free volume which facilitates the space for diffusion of oxygen [34,46,47].

Mechanical properties of PLA based films

Finally, the mechanical behaviour was investigated by means of tensile tests. The stress-strain curves of the neat PLA and PLA-D samples are compared in **Figure 5a**, whereas in **Figure 5b** those of PLA-E and PLA-DE films are shown.

In **Table 2** the data of the uniaxial tensile tests, in terms of ultimate tensile stress (σ_{max}), yield stress (σ_{ys}), Young's modulus (E) and elongation at break (ϵ_{max}), are collected.

From the comparison between the stress-strain curves of PLA and PLA-D (**Figure 5a**) and the data reported in **Table 2**, it is evident that PLA-D film shows a remarkably higher Young modulus with respect to neat PLA, with an increase of about 50 %. This experimental evidence suggests a good compatibility between the used filler and the polymeric matrix, as supported by the SEM observation of the stress-strained fracture surfaces which highlighted a good wettability filler/matrix (**Figures 6c-d and 6g-h**). Indeed, the diatomite appeared completely covered by PLA and still well anchored, after the tensile test (**Figure 6c, inset**) and it is possible to observe polymeric filaments outgoing from the diatomite porosities (**Figure 6d**), as an evidence of the good adhesion between the filler and the

polymeric matrix, with an intercalation of polymer within diatomite particles. This outstanding result can be also ascribed to the microstructure of the used powder: the diatomite powder is composed of particles of different shapes (e.g. rounded, elongated, ovoid) and dimensions (between 2 and 70-80 μm) [48] (**Figure 6b**). It is interesting to note that all particles present a hierarchical porosity, with pore dimension ranging from few micrometres down to few tens nanometres.

In **Figure 5b** a comparison between the σ - ϵ curves of binary and ternary samples containing extracted coffee (i.e. PLA-E and PLA-DE) evidences a significant decrease of the elongation at break of around one order of magnitude with respect to neat PLA. In fact, even if a decreased elongation at break value was also recorded in the case of PLA-D sample with respect to neat PLA (172 % vs 249 %, as average value, for PLA-D and PLA, respectively), this remarkable decrement for PLA-E and PLA-DE samples has to be ascribed to the presence of coffee ground extract. Since the elongation at break takes into account the possibility of chains to orientate in stress direction, it has to be concluded that the used extract is able to hamper such disposition, in agreement with XRD and DSC data which evidenced an enhanced crystallinity of the films containing the coffee ground extract. Moreover, the highest decrease of elongation at break (i.e. about 50 % with respect to PLA-E sample) was recorded in the case of PLA-DE sample, due to an interaction between the diatomite and spent coffee ground extract, in agreement with the other experimental evidences.

Finally, it is possible to hypothesise an interaction between the coffee ground extract and the PLA chains, as further corroborated by the SEM observation of stress strained fracture surface of PLA-E, showing a peculiar flake-like morphology (**Figure 6f**), not detected in the case of neat PLA sample (**Figure 6a**). Moreover, it is possible to observe the presence of cauliflower structures that can be associated to the coffee ground extract components (**Figure 6e**).

Conclusions

In this work multifunctional PLA, diatomite and spent coffee ground extract based films were successfully prepared by solvent casting technique. Diatomite was added in order to provide both a mechanical reinforcement and a physical barrier to oxygen permeation and spent coffee ground extract to act as oxygen scavenger, containing caffeine, chlorogenic acids and a lot of fatty acids, particularly stearic acid, as confirmed by GC-MS analysis.

The presence of spent coffee ground extract within the polymeric matrix was confirmed by both ATR and XRD analyses, showing the first one the spent coffee ground extract vibrational modes and the second one the diffraction peak typical of stearic acid crystalline phase.

It has been demonstrated that the presence of diatomite does not remarkably influence the crystallinity and the thermal behaviour of the PLA matrix, but it is able to induce a remarkable increase of both E

and σ_y values, indicating good adhesion between the filler and the polymeric matrix, with an intercalation of polymer within diatomite particles, as supported by the SEM observation of the stress-strained fracture surfaces. On the other hand, the addition of the spent coffee ground extract seems to promote the PLA crystallization during the solvent casting process, as confirmed by the XRD patterns and DSC data, with a consequent remarkable decrease of the elongation at break. These experimental evidences suggest an interaction between the coffee derived extracts and the PLA chains and an action of the present stearic acid crystals as crystallization nuclei. Furthermore, the co-presence of the diatomite and the coffee ground extract guarantees improved oxygen barrier properties, leading to a decreased OTR value.

Thus, the obtained systems could be considered an innovative promising and performing alternative to the non-biodegradable petrochemical-derived polymers, such as polystyrene (PS), polypropylene (PP) and polyethylene terephthalate (PET), widely and commonly used in food packaging applications, due to their good mechanical and oxygen barrier properties.

Conflict of interest

The authors declare no competing financial interest.

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Captions to Figures

Figure 1. GC-MS chromatogram of spent coffee grounds extract and assignment of the detected peaks at specific retention times to its components.

Figure 2. FTIR spectra of PLA films (a) between 700 and 1850 cm^{-1} and between (b) 2750 and 3050 cm^{-1} ; (c) FTIR spectrum of spent coffee grounds derived extract.

Figure 3. XRD diffraction patterns of the PLA based films.

Figure 4. DSC curves related to the first (a) and second (b) heating scans of all the prepared films.

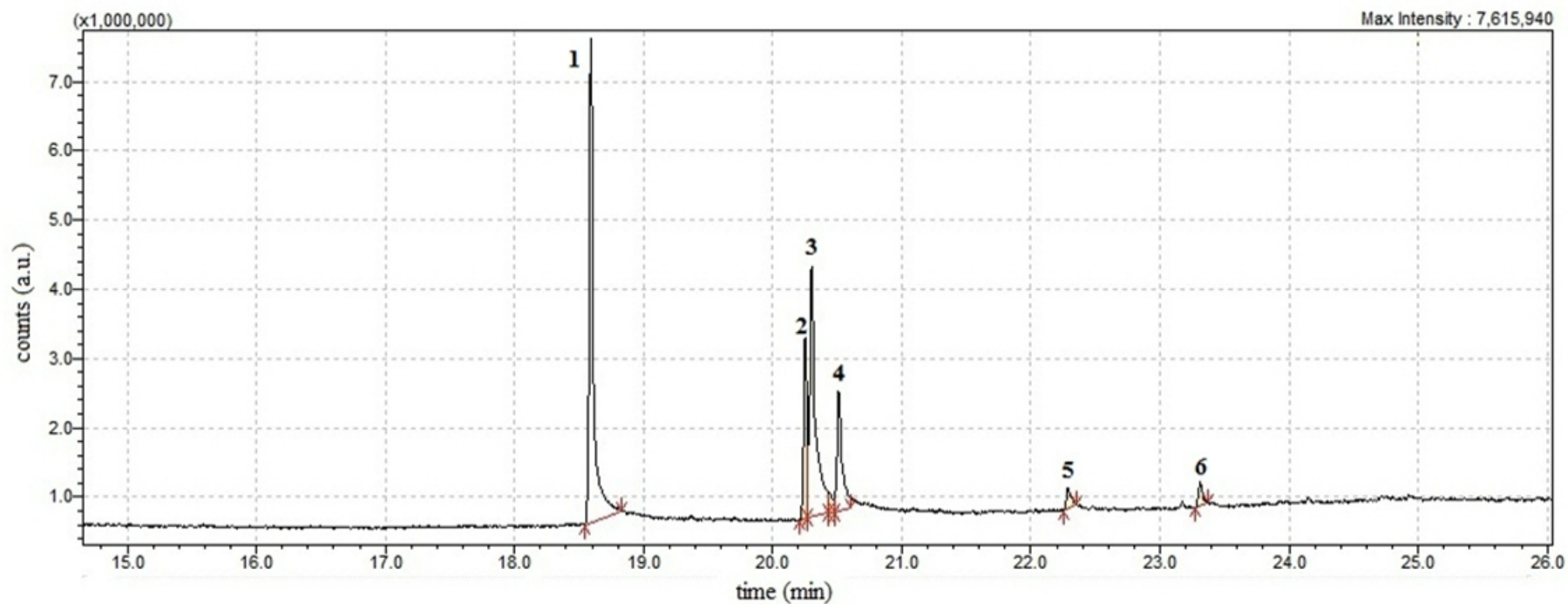
Figure 5. Stress-strain curves of PLA based on films: (a) PLA and PLA-D; (b) PLA-DE and PLA-E.

Figure 6. SEM micrographs of fracture surfaces of stress-strained PLA based films.

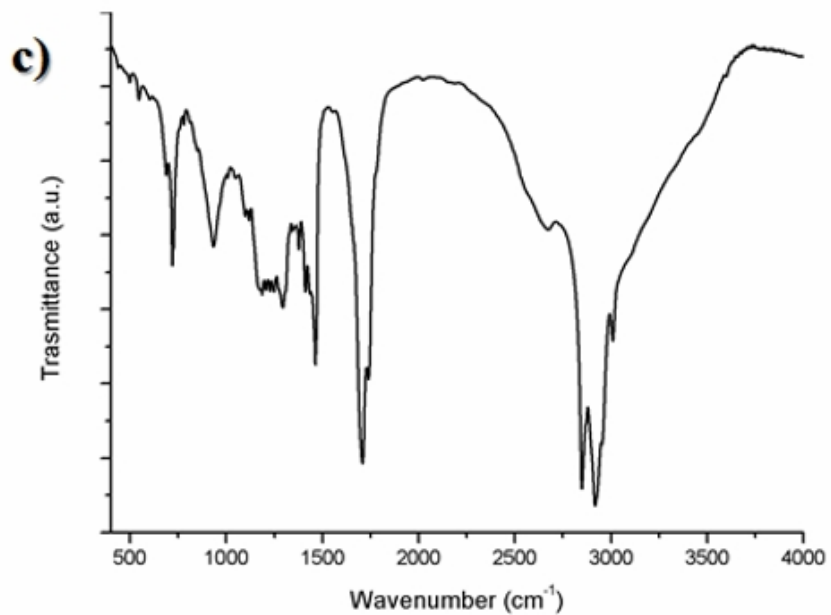
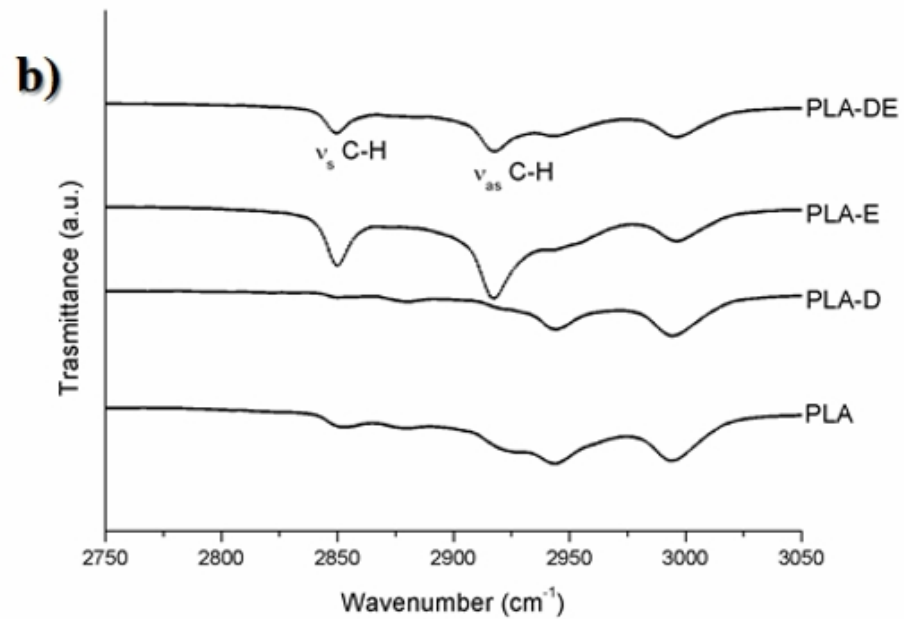
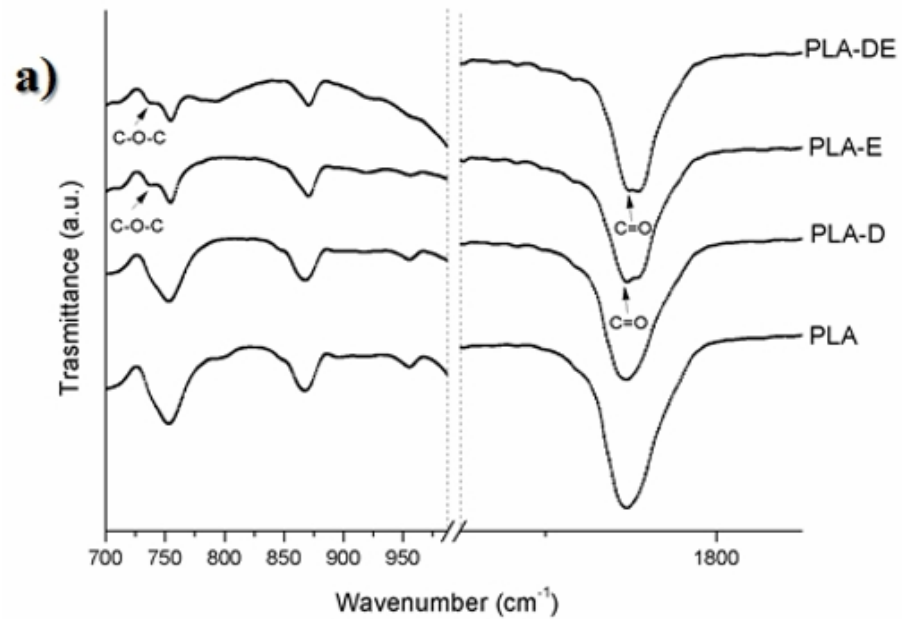
Captions to Tables

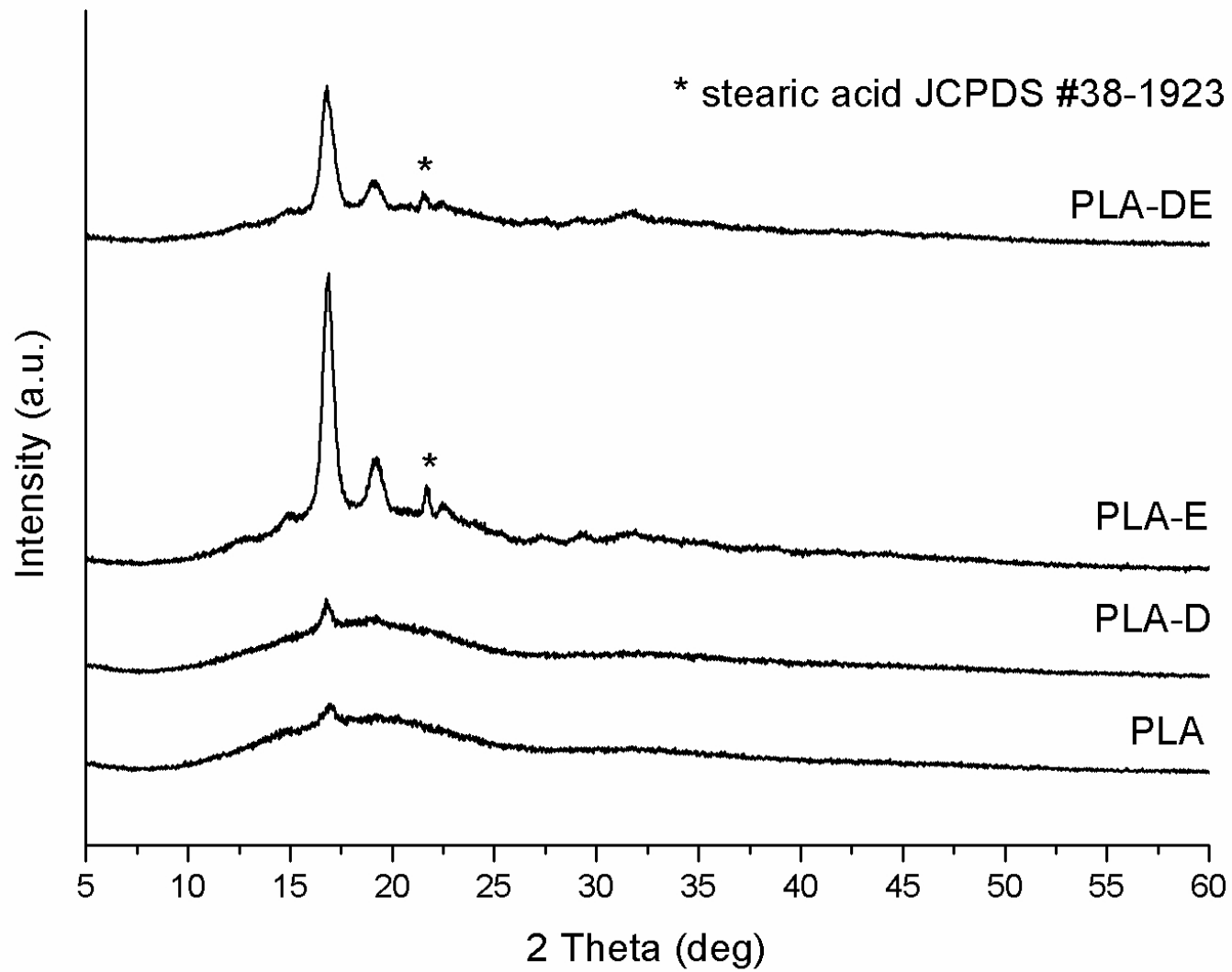
Table 1. Differential scanning calorimetry (DSC) data for PLA based films.

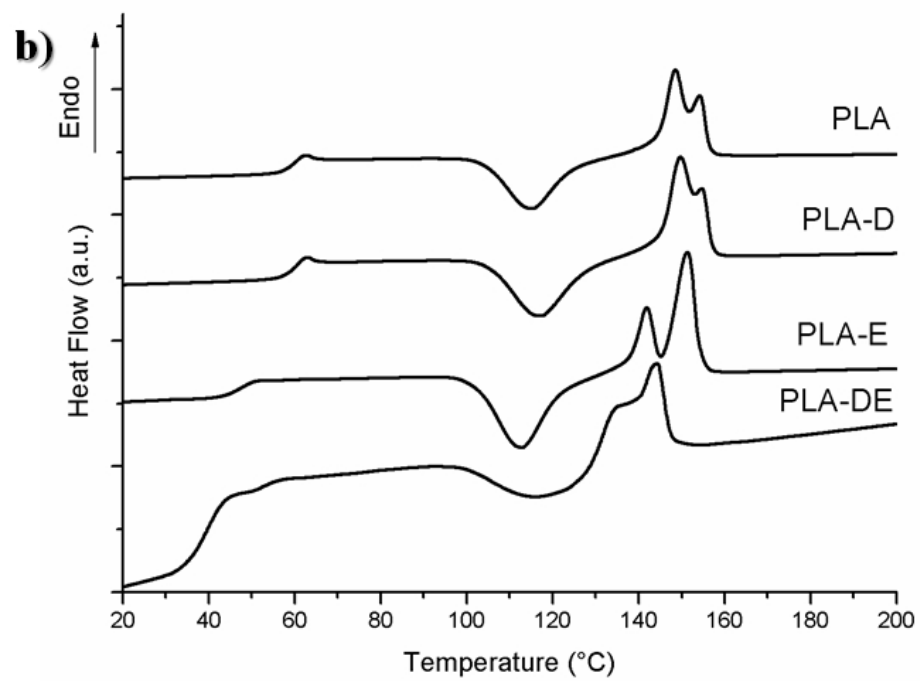
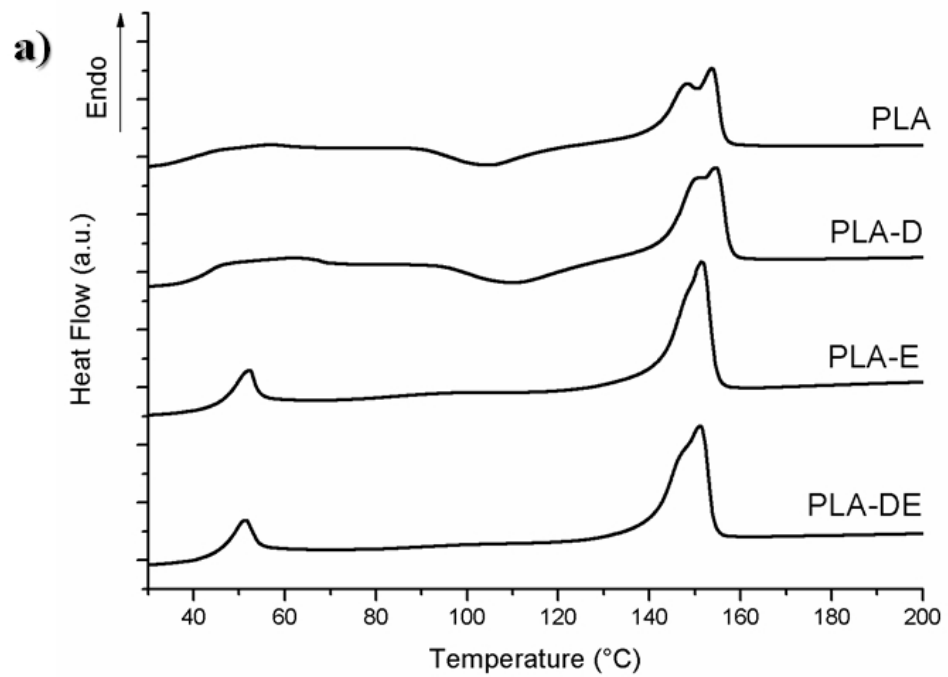
Table 2. Tensile modulus (E), ultimate tensile stress (σ_{\max}) and yield stress (σ_s) of PLA based films (all values are expressed as mean values \pm standard deviation (SD)).

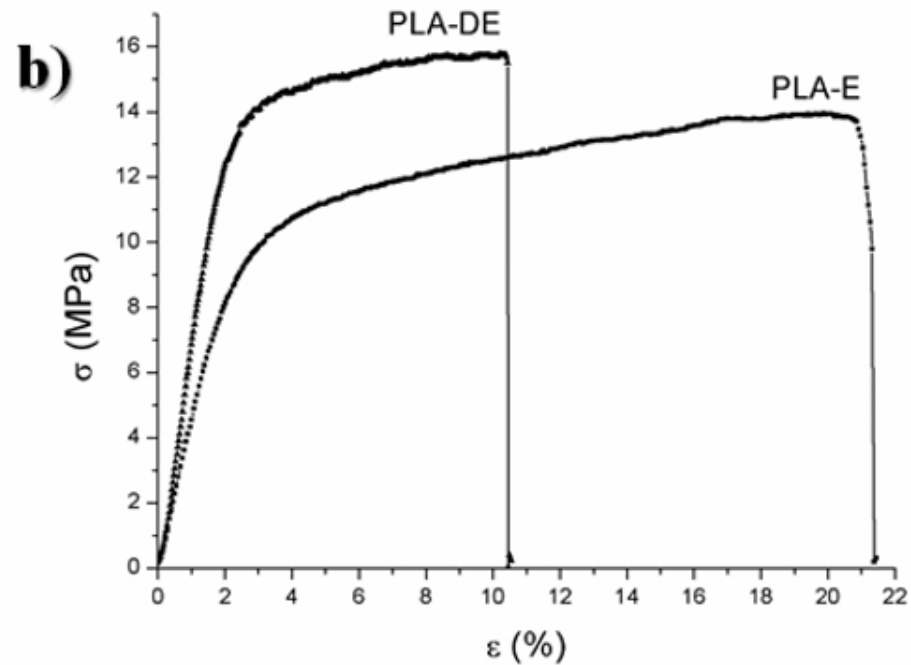
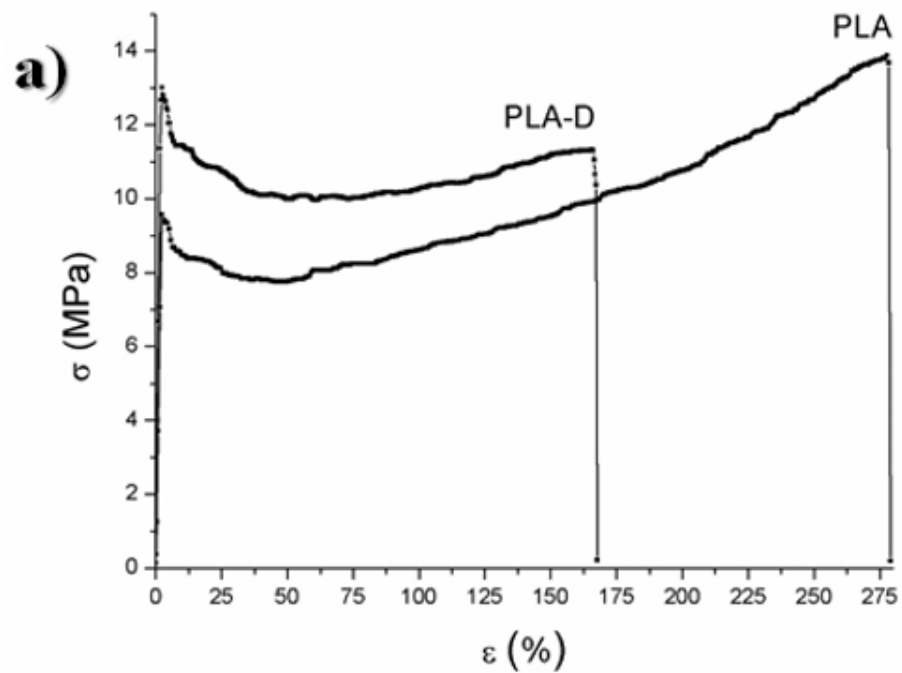


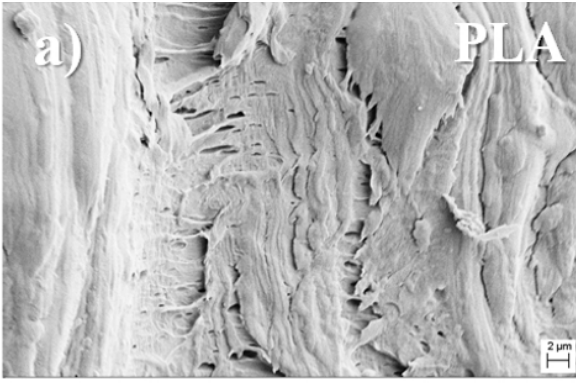
Peak#			Molecular weight (g/mol)	Retention time (min)	Intensity (%)
1	Stearic acid	$C_{18}H_{36}O_2$	284	18.6	42.99
2	Octadecadienoic acid	$C_{18}H_{32}O_2$	280	20.2	16.13
3	Oleic acid	$C_{18}H_{34}O_2$	282	20.3	22.31
4	Stearic acid	$C_{18}H_{36}O_2$	284	20.5	10.56
5	Nonadecanoic acid methyl ester	$C_{20}H_{40}O_2$	312	22.3	1.82
6	Eicosanoic acid	$C_{20}H_{40}O_2$	312	23.3	2.07
	Others (water,...)				4.12



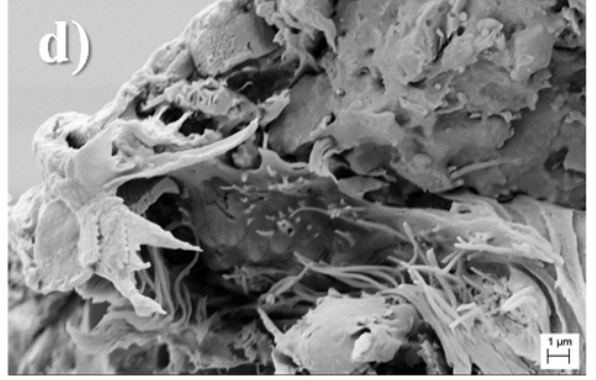
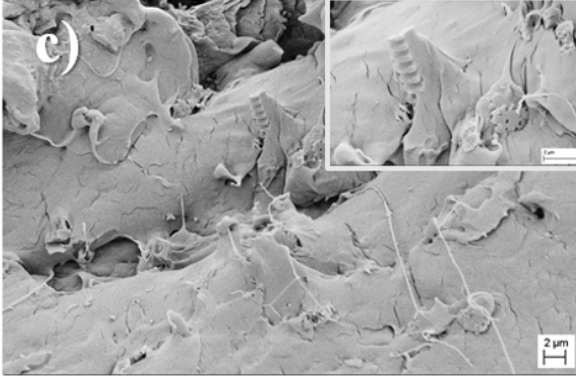




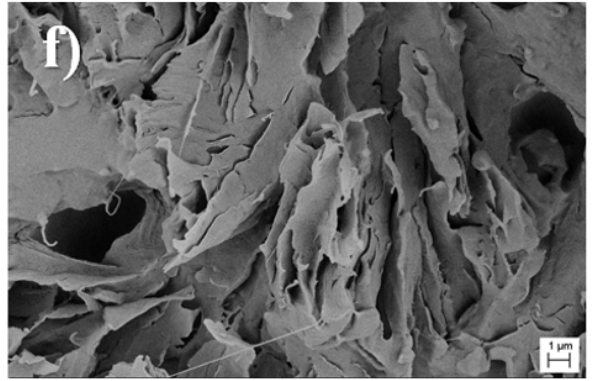
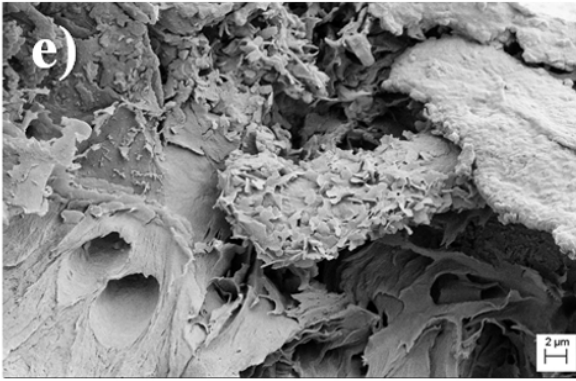




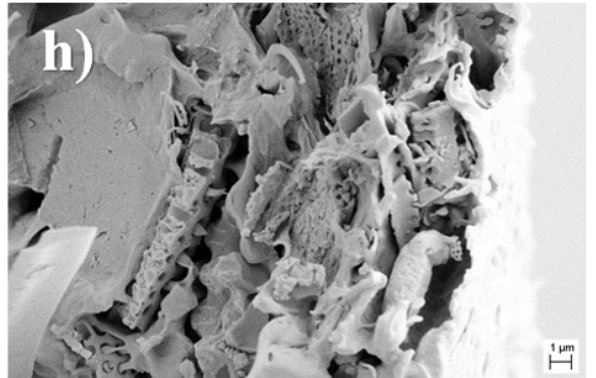
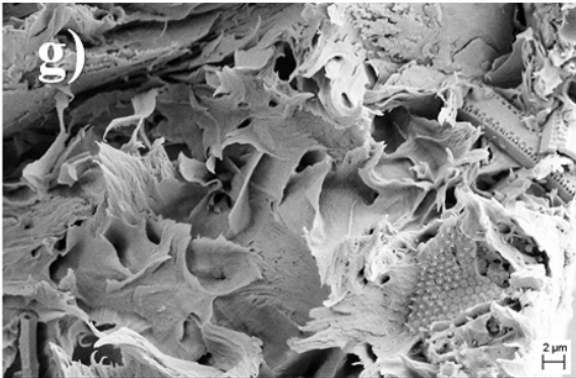
PLA-D



PLA-E



PLA-DE



PLA pellet



Coffee grounds



Diatomite powder

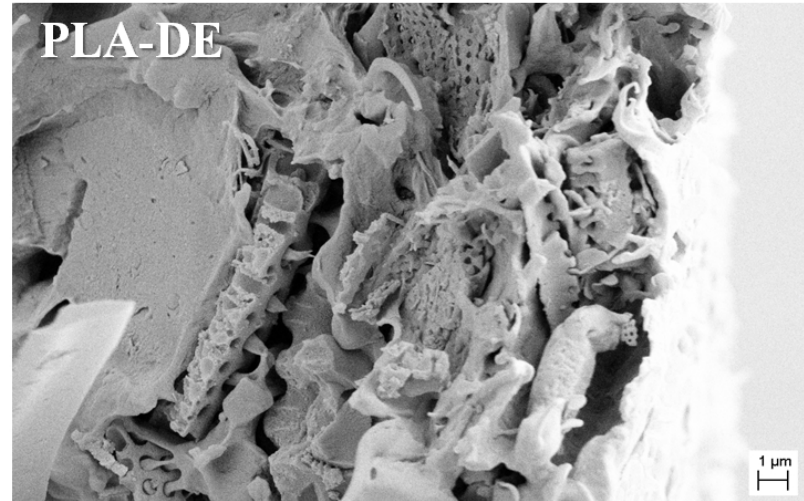
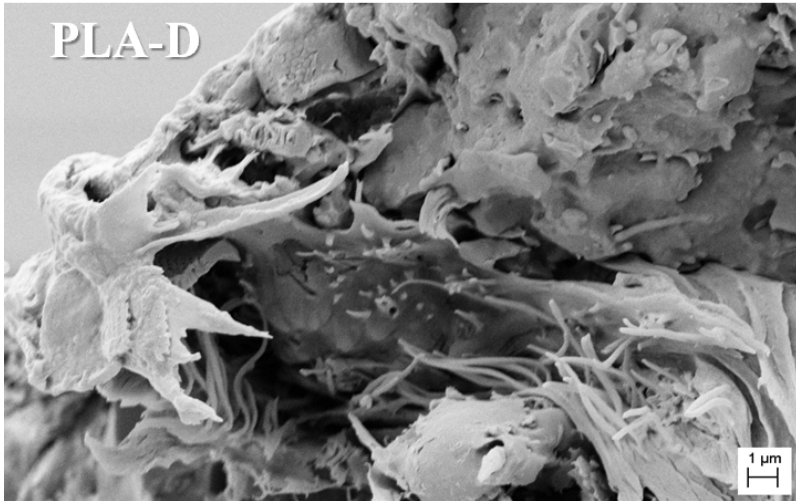
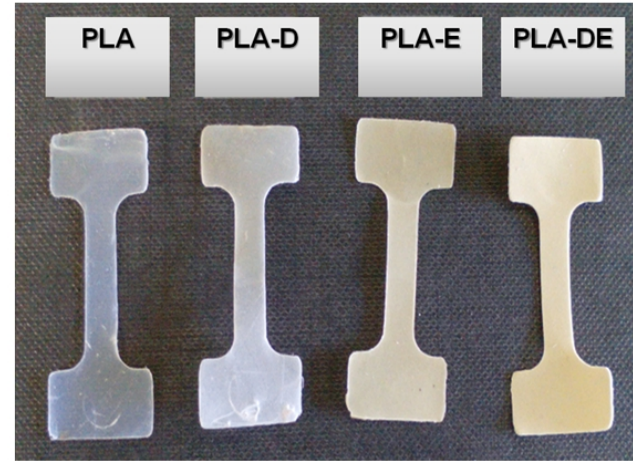


Table 1. Differential scanning calorimetry (DSC) data for PLA based films.

	I heating						
	T_{gI} (°C)	T_{ccI} (°C)	ΔH_{ccI} (J/g)	T_{m1I} (°C)	T_{m2I} (°C)	ΔH_{mI} (J/g)	χ_I (%)
PLA	43	105	12.98	148	154	37.64	26.52
PLA-D	44	110	11.38	150	154	30.69	21.86
PLA-E	50	116	1.11	148	151	31.57	32.75
PLA-DE	46	118	0.39	151	147	30.17	33.71
	II heating						
	T_{gII} (°C)	T_{ccII} (°C)	ΔH_{ccII} (J/g)	T_{m1II} (°C)	T_{m2II} (°C)	ΔH_{mII} (J/g)	χ_{II} (%)
PLA	60	115	33.09	148	154	35.09	2.15
PLA-D	61	117	29.17	150	155	30.56	1.57
PLA-E	47	113	31.19	142	151	32.66	1.58
PLA-DE	40	116	31.74	135	144	33.10	1.54

Table 2. Tensile modulus (E), ultimate tensile stress (σ_{\max}) and yield stress (σ_y) of PLA based films

(all values are expressed as mean values \pm standard deviation (SD)).

Sample	σ_y (MPa)	σ_{\max} (MPa)	E (MPa)	ϵ_{\max} (%)
PLA	11 \pm 2	12 \pm 2	532 \pm 3	249 \pm 30
PLA-D	14 \pm 1	11 \pm 1	806 \pm 9	172 \pm 7
PLA-E	10 \pm 1	13 \pm 1	485 \pm 6	20 \pm 2
PLA-DE	14 \pm 1	15 \pm 1	813 \pm 12	10 \pm 1

Eco-sustainable systems based on poly(lactic acid), diatomite and coffee grounds extract for food packaging

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