Polylactic Acid/Cellulose Fibres Based Composites for Food Packaging Applications

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PLA-based composites containing CF in the range 0 to 10 wt. % were prepared by melt mixing technique. The prepared composites were investigated in terms of processability, chemical structure (by Attenuated total reflectance - Fourier Transform Infrared - ATR-FT-IR analysis), thermal (Differential Scanning Calorimetry - DSC), optical properties (using UV-Vis spectrometry), barrier and migration in distilled water. Also, the behaviour of PLA based composites at sterilization was performed by examination the changes in their chemical structure. This study shows the feasibility of improving of PLA properties by using cellulose fibres, designed for flexible food packaging.

Keywords: PLA; cellulose fibres; properties; food packaging

Food packaging is becoming increasingly important in the food industry, where advances in functionality such as convenience and portioning are gaining more attention. Furthermore, there is an increased awareness on sustainability, which can in general be achieved on different levels. On the level of raw materials, the use of recycled materials or use of renewable resources are two strategies to reduce CO_2 emissions and the dependency on fossil resources [1, 2]. Polymers derived from renewable resources are now considered as promising alternatives to traditional polymers as they fulfil current environmental concerns in terms of environmental pollution, greenhouse gas emissions and the depletion of fossil resources [3]. The necesarry characteristics of a polymeric material to be used as flexible food packaging envisage: good processability on the existent processing equipments, flexibility, protecting the product from UV light, act as a barrier for water and gases and the overall migration does not exceed the accepted value according to EU Regulation No 10/2011 for plastic materials and articles intended to come into contact with food [4]. In particular, composites of biodegradable polymers, such as polycaprolactone, poly(hydroxybutyrate) or polylactides with natural fillers appear very promising for the development of environmentally friendly materials. Polylactic acid (PLA), a degradable polymer which can be produced from annually renewable resources such as corn, rice, sugar beets, and potato starch [5 - 8], has recently gained growing attention [9] because it is a good material candidate to replace commodity petro-based plastics with the increasing global demand for the agricultural and environmentally sustainable bioproducts [5]. PLA compared to other biopolymers shows good stiffness, high strength, superior transparency, availability in the market [3], excellent printability and a high rate of disintegration in compost [3, 10]. The limitations of use of PLA for commercial applications are related to low elongation at break, excessive rigidity, slow crystallization rate, low thermal resistance, high cost and relatively low barrier properties [10, 11]. One way to improve the PLA properties is to incorporate other polymers (such as PHB) [12], plasticizers [13, 14] or filler like starch [15], carbon [16] and cellulose fibres [17] into thermoplastic matrix. Darie-Niã et al. [18] investigated the PLA properties by incorporation of PLA oligomer, L-lactide, poly(ethylene glycol), and epoxidized soybean oil (USE) into PLA matrix and found an improved melt flow and processability of the resulted plasticized PLA systems. USE significantly increased the elongation at break, reduced the glass transition temperature, and increased the PLA chain mobility.

The great potential of natural fibres to reinforce the thermoplastic matrix is consisting of their fully biodegradability, non-toxic and low density. Cellulose is the most widely spread natural polymer and is derived by a delignification from wood pulp or cotton linters [1, 19]. The strengthening of the polymer matrix by fibre reinforcements is dependent upon the aspect ratio, geometry and orientation of the fibres, and the interface adhesion between the fibre and the matrix, as well as the microstructural features within the matrix. Dispersed microstructures offer higher elastic properties than equivalent aggregated microstructures due to the more efficient reinforcement of a dispersed system [20]. The purpose of the present study was to develop and characterize new composite materials based on PLA and cellulose fibres (CF) in order to study their behaviour for further utilization in food packaging and processing.

Experimental part

Materials and methods

In order to obtain biodegradable blends based on PLA and cellulose fibres, PLA 2003D (NatureWorks) modified with bis[2-(2-butoxyethoxy)ethyl] adipate (DBEEA), Proviplast 01422 (PROVIRON, Belgium) and cellulose fibres type EFC 1000 (Rettenmeier & Söhne AG, Germania) were used. The PLA has a density of 1.24 g· cm^{-3} and the melt flow index of 5 - 7 g/10 min (210 °C/2.16 kg). The plasticizer presents the following characteristics: density of 1.015 g· cm^{-3}, water content max. 0.2 %, dynamic viscosity of 17 MPa·s and molecular weight of 434.56 g · mol^{-1}.

PLA based composites processing procedure

Five formulations coded: PLA, PLA/CF0, PLA/CF2, PLA/CF5 and PLA/CF10, containing cellulose fibres from 0 to

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Table 1
COMPOSITION OF PLA/CF COMPOSITES

Sample	Composition, wt.%		
	PLA	DBEEA	CF
PLA	100		
PLA/CF0	90	10	
PLA/CF2	88.2	9.8	2
PLA/CF5	85.5	9.5	5
PLA/CF10	81	9	10

10 wt. % and the ratio 9:1 between PLA and plasticizer (DBEEA) were carried out as it is shown in table 1. Neat PLA was used as reference. The PLA pellets and CF were dried for 4 hours at 80 °C before processing. The melting of blends was performed using a BRABENDER Plastograph at a temperature of 170 ± 5 °C, mixing time of 10 min and 40 rpm. Films with thickness of 0.1 mm were obtained by compression molding in the following conditions: pressing at a temperature of 175 °C, preheated time of 5 min, pressing time of 2 min under a pressure of 150 Pa followed by a cooling time of 40 min.

Processing characteristics

Processing behavior was evaluated by analyzing of the processing characteristics following the torque-time curves registered during blending in the Brabender mixer. Melt viscosity index (η) and power consumption (P) of the developed composites were evaluated based on Equations (1) and (2):

$$\eta = k \cdot (Q/S)\ (N{\cdot}m/rpm) \quad (1)$$

where: Q is the torque (N· m); S (rpm) is the speed of rotors; k is a constant depending on temperature.

$$P = Q \cdot \omega\ (W) \quad (2)$$

where: ω is the input shaft rotation ($2\pi S/60$).

Attenuated Total Reflection - Fourier Transform Infrared Spectra (FTIR analysis)

The FTIR analyses were carried out with a FTLA 2000-104 Spectrophotometer (ABB, Canada) equipped with ZnSe crystal, via the attenuated total reflectance (ATR) method in the range of 4000 cm^{-1} - 750 cm^{-1}. All spectra were recorded at 4 cm^{-1} resolution, in transmission mode.

Differential Scanning Calorimetry measurements (DSC)

Thermal analysis of PLA loaded with cellulose fibres was performing using a DSC 823^e (Mettler Toledo, Swizerland) calibrated with indium. The samples weighing between 4 and 9 mg were cut in square forms, packed in aluminium pans and placed in the DSC cell. The tested samples were first heated from ambient temperature up to 250 °C at a heating rate of 10 °C/min in order to erase any previous thermal history. Then, the samples were cooled until the ambient temperature and heated again to 250 °C at a heating rate of 10 °C/min. From DSC curves, second run, the glass transition temperature (T_g) melting temperature (T_m), enthalpy of melting (ΔH_m), cold crystallization temperature and (T_{cc}) and its enthalpy and degree of crystallinity (X_c) were estimated from all samples. The degree of crystallinity of the PLA samples was obtained by using the equation (3):

$$X_c = (\Delta H_m/\Delta H_0 \cdot w_{PLA}) \cdot 100\ (\%) \quad (3)$$

where: ΔH_m is the melting enthalpy for the blend; ΔH_0 is the melting enthalpy for 100% crystalline PLA; and w_{PLA} is the weight fraction of PLA in each sample. The heat, required for melting of 100% crystalline PLA, is 93.1 J· g^{-1} [21].

Optical properties

From each film specimen it was cut a rectangular shape sample and placed directly in a UV/Vis HELIOS ALPHA Spectrophotometer (Thermo Spectronic), the readings being made at wavelengths from 200 to 800 nm. Measurements were performed using air as reference. The results have been expressed as percentage of transmittance. The measurements were performed in triplicates, and the average of the three spectra was calculated.

The transparency was measured at 600 nm (T_{600}) and it was obtained using Equation (4) [22].

$$T_{600} = -log\%T/b \quad (4)$$

where: $\%T$ is percentage of transmittance and b is the film thickness (mm).

Water vapour transmission rate (WVTR)

The water vapour transmission rate (WVTR) of the samples was determined with PBI-Dansensor L 80-5000 equipment, at 23 °C, on specimens with dimensions of 108 x 108 x 0.1 mm, the apparatus being calibrated before the testing of the samples.

Overall migration properties

The overall migration of components was tested by immersing of samples into distilled water as food simulant, for 10 days at 40°C. After the contact time expired, the liquid of extraction was transferred into another recipient from which 200 mL (simulant) were taken to work with, for the determination of ceded soluble substances. The simulant was then evaporated in a platinum capsule previously brought to constant weight. After the evaporation was complete, the drying continued at 105°C in the oven for 1 h. The capsule was then cooled in a dessicator for 1 h and weighed. Conventionally, the specific weight for all simulants is considered to be 1, so that the milligrams of substance ceded per litre of simulant ($mg{\cdot}L^{-1}$) will correspond numerically to the milligrams of substances ceded per kilogram of simulant.

The formula used for the determination of overall migration (M) is:

$$M = (m - m_1/V) \cdot 1000 \quad (mg{\cdot}L^{-1}) \quad (5)$$

where: m represents the quantity of substance ceded by the sample (mg); m_1 represents the quantity of substance ceded by the control (mg) and V represents the volume of the extraction liquid that was evaporated (mL). The evaluation of the results was made according to HG no. 1197/2002 and EC Regulation no. 10/2011.

PLA based composites's sterilization behavior

The developed composite materials were immersed in distilled water and sterilized at 120 °C for 15 min. The samples were then investigated by Attenuated total reflectance - Fourier Transform Infrared Spectra analysis in order to observe the spectral modifications compared with initial samples.

Results and discussions

Processing characteristics

The PLA was initially charged into the mixing chamber for 4 min followed by the addition of plasticizer and CF until constant torque was obtained. From the data

Table 2
TORQUE (Q) * EXPRESSED AS N·m FOR PLA AND STUDIED COMPOSITES AT 170 °C ± 5 °C AND 40 rpm

Sample	Q_{1min}	Q_{2min}	Q_{4min}	Q_{6min}	Q_{8min}	Q_{10min}
PLA	54	34-40	28-34	24-30	24-28	23-26
PLA/CF0	50	40	24-28	19-23	16-20	15-18
PLA/CF2	30	26-30	22-24	17-20	15-17	13-16
PLA/CF5	28	22	23-26	22-25	17-20	14-17
PLA/CF10	22	22	26-32	22-27	18-22	16-18

*Q, torque after different periods of melt processing (1 to 10 min)

presented in table 2 it can be observed an improvement in the melt processability of PLA composites by adding of DBEEA with respect to neat PLA. This is explained by improvement of the flow. The adding of CF leads to an increasing torque and consequently an increasing melt viscosity.

The melt viscosity index of the PLA composites and the arithmetic average of the torque recorded at 10 min is presented in table 3 together with the power at mixing.

Data presented in table 3 show that the introduction of plasticizer (10 wt% in content) into polymeric matrix led to a decrease of the melt viscosity index (0.41 N·m/rpm) compared to neat PLA (0.61 Nm/rpm), due to the plasticizer effect that enhances the mobility of the PLA chains. Also, by incorporation of cellulose fibres in plasticized PLA, the melt viscosity recorded low values than neat PLA. 2 % CF in content led to the lowest melt viscosity. The power at mixing of PLA based composites had the same behaviour as melt viscosity. Even at a loading of 10 % CF content into plasticized PLA, the power at mixing is lower than that of neat PLA; this means that PLA composites are easier to process on conventional equipments for plastic materials without high energy consumption.

Table 3
PROCESSING PARAMETERS EVALUATED FROM TORQUE-TIME PROFILES FOR PLA-BASED COMPOSITES

Sample	Melt viscosity index, (η), N·m/rpm	Power at mixing (P), W
PLA	0.61	10.25
PLA/CF0	0.41	6.90
PLA/CF2	0.36	6.07
PLA/CF5	0.38	6.48
PLA/CF10	0.42	7.11

Fourier - transform infrared (FTIR) spectroscopy

Figure 1 shows the FTIR spectra of plasticized PLA/CF composites in comparison with neat PLA. It can be observed three FT-IR spectra regions to identify the interactions in composites. The first region appeared at 1749 cm^{-1}, ascribed to carbonyl (-C=O) characteristic stretching peak of PLA. The second one was ascribed to –C-O- bond stretching in -CH-O- group of PLA at 1182 cm^{-1}. The last region was composed of three characteristic peaks, ascribed to -C-O- stretching vibration in -O-C=O group at 1128, 1082 and 1041 cm^{-1}, respectively. The bands at 868 cm^{-1} and 754 cm^{-1} are associated with the amorphous and crystalline phases of PLA, respectively. These

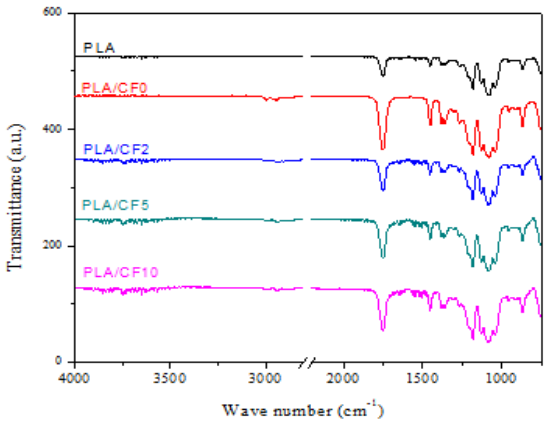

Fig. 1. FTIR-ATR spectra of PLA composites loaded with different cellulose fibres contents

characteristics peaks are also found in literature [16]. With increasing of CF content in each composite, the width bands shifted towards higher values with respect to neat PLA. For example, at 1182 cm^{-1}, the width band of composites increased from 93 cm^{-1} for neat PLA, to 104 cm^{-1} for PLA/CF2 and to 102 cm^{-1} for PLA/CF5. Also, at 1041 cm^{-1}, the width band increased from 83 cm^{-1} in the case of neat PLA to 89 cm^{-1} for all PLA composites. These increases of width band for PLA composites were ascribed to the interactions between PLA and CF.

Differential Scanning Calorimetry measurements (DSC)

The DSC curves of the neat PLA and PLA/CF biocomposites are presented in figure 2, and the determined thermal characteristics are given in table 4. From DSC thermograms of samples (fig. 2) it can be observed the glass transition temperature (T_g), an exothermic peak assigned to cold crystallization temperature (T_{cc}) and an endothermal peak due to the melting temperature (T_m). The neat PLA shows a T_g at 58 °C and a small endothermic peak with a maxim at 152.1 °C. Incorporation of plasticizer and cellulose fibres into PLA matrix led to the decrease of glass transition temperature (T_g) and appearance of double melting peak around 142°C due to the melting of different crystallites types and to the melting of crystals formed through a melt recrystallization process during a heating scan, respectively [23]. The decrease of T_g for plasticized composites is related to the segmental mobility of amorphous pure PLA that increases due to the addition of plasticizer [18] and filler. Also from figure 2 and table 4 it is observed that the loading of cellulose fibres led to an increased cold crystallization temperature (T_{cc}) from 85.8 °C in the case of plasticized PLA to 107.1 °C for PLA/CF10 composite. By loading of CF in content of 5 wt.% it was observed that the ability to re-crystallize increased for PLA/CF5, with a reduction in the cold crystallization temperature

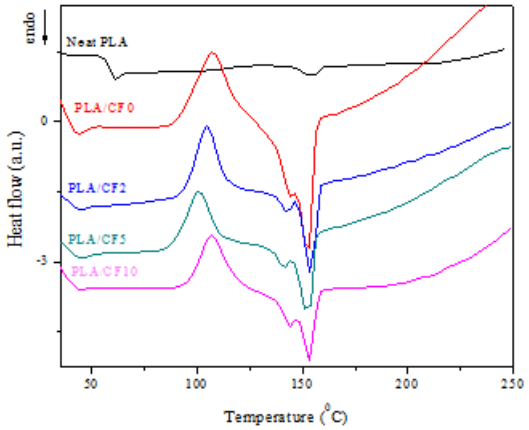

Fig. 2. DSC spectra, second heating run, for PLA composites

Sample	Tg, °C	ΔH_m, J/g	T_m, °C	ΔH_{cc}, J/g	T_{cc}, °C	X_c, %
PLA	58.6	2.42	152.1	-	-	2.6
PLA/CF0	47.1	23.7	1526 143.6	27.4	85.8	28.2
PLA/CF2	46.2	21.1	1548 142.7	28.6	104.7	25.6
PLA/CF5	46.0	28.7	1526 141.1	26.6	100.7	36.0
PLA/CF10	50.7	23.5	153.3 143.7	22.6	107.1	31.1

Table 4
THE OBTAINED PARAMETERS FROM DSC DIAGRAMS FOR NEAT PLA AND PLA-BASED COMPOSITES

(T_{cc}) from 104.6 °C in the case of plasticized PLA/CF2 to 100.7 °C for PLA/CF5 composite, which is favourable to the crystallization process.

The ΔH_m is used as an indicator of blend crystallinity [24]. The ΔH_m of neat PLA was 2.4 Jg^{-1}, while ΔH_m of plasticized PLA was 23.7 Jg^{-1} (table 4). The lower ΔH_m for PLA/CF2 and PLA/CF10 composites was attributable to the disruption of regularity in chain structure and increased spacing between chains indicating a lower degree of crystallinity. Addition of 5% CF to plasticized PLA favoured the mobilization of the PLA macromolecular chain and led to the obtaining of an ordered alignment with the crystal lattice. As a consequence, X_c is higher than the other composites. However, by incorporation of plasticizer and cellulose fibres into PLA matrix, the degree of crystallinity increased as compared with neat PLA, meaning that both plasticizer and FC act as nucleating agents.

Optical properties

From figure 3 it can be observed that the transmittance of composites between 200-800 nm decreased as the content of cellulose fibres increased, from 88% for plasticized PLA to 20% for PLA/CF10. Cellulose fibres show a blocking effect on the transmittance of PLA matrix at the UV spectra region (250-400 nm). The addition of plasticizer (10% DBEEA) leads to a slowly increase of the transmittance of the PLA matrix.

Based on equation (6) transparency was calculated (T_{600} - table 5). Neat PLA has a T_{600} of 14.9. Plasticized PLA film (PLA/CF0) proved to have higher transparency than all PLA/CF tested composites. These data are correlated with the transmittance of the tested samples presented in figure 3. Together with the increasing of cellulose fibre content, T_{600} decreased up to 4.12% for PLA/CF2, 16.2% for PLA/CF5 and to 49% for PLA/CF10 compared to plasticized PLA (PLA/CF0).

Water vapour transmission rate

The WVTR values (table 6) of tested samples have increased with the addition of CF. PLA/CF5 composite recorded a small decrease of the permeability compared to PLA/CF2, but it is still higher than neat PLA and plasticized PLA. This is due to the hydrophilic nature of cellulose fibres that is not easily uniformly dispersed in non-polar polymer matrix. However, the results obtained from water vapour transmission rate tests are correlated with the crystallinity samples (table 4). When the permeability is high, the crystallinity of samples is low.

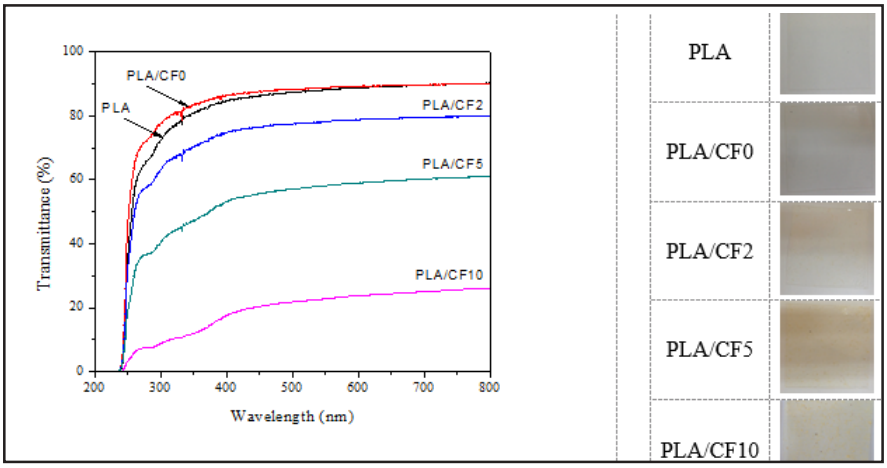

Fig. 3. Transmittance of the PLA composites compared to neat PLA (on film tests). In right side the appearance of films is showed

Sample	T_{600}
PLA	14.9±0.4
PLA/CF0	16.2±0.6
PLA/CF2	15.5±0.3
PLA/CF5	13.6±0.3
PLA/CF10	8.2±0.2

Table 5
TRANSPARENCY OF PLA AND PLA BASED COMPOSITES FILMS

Sample	WVTR, $g/m^2/24$ h
PLA	15.33 ± 0.02
PLA/CF0	18.58 ± 0.04
PLA/CF2	24.32 ± 0.02
PLA/CF5	22.00 ± 0.04
PLA/CF10	24.77 ± 0.02

Table 6
THE EFFECT OF CF OVER THE PERMEABILITY OF THE TESTED SAMPLES COMPARED WITH NEAT PLA

Table 7
THE MIGRATION TEST RESULTS FOR THE PLA/CF COMPOSITES IMMERSED IN DISTILLED WATER FOR 10 DAYS AT 40 °C

Sample	Overall migration, ppm	Overall migration, mg·dm^{-2}
PLA	27.6	4.60
PLA/CF0	47.8	7.97
PLA/CF2	51.0	8.50
PLA/CF5	33.6	5.60
PLA/CF10	53.2	8.87

Overall migration properties

The results obtained on overall migration simulant are presented in table 7. From these results it can be observed that the analyzed samples did not exceed the limit imposed by the Regulation no 10/2011, which is of 60 ppm (10 mg·dm^{-2}), that make these materials as being suitable for food packaging applications.

Composite testing - behaviour at sterilization process

From the functional groups analysis of the tested samples subjected to the sterilization test (fig. 4) it was observed that the polymeric composites films show the same allure with the unexposed samples, except the intensity of the characteristic peaks that decreased and the disspearing of absorption bands in the region 2995-2945 cm^{-1} (stretching vibration of the C-H in -CH_3 group). The decrease of the amorphous band intensity at 869 cm^{-1} (C-O-C) and of the absorption band related to C=O stretching vibration at 1749 cm^{-1} are evidenced with the increase of cellulose fibres content. This is a result of subjecting the samples to the process of sterilization that led to increase the crystallinity of PLA based composites, this effect should be favorable for barrier properties. This results take us to the conclusion that the sterilizing process is adequate for food product packaging.

Conclusions

One way to improve the properties of PLA biopolymer is the addition of cellulose fibres. It was observed that the addition of cellulose fibres facilitates the processing of PLA/CF composites, without high energy consumption. The melt viscosity index has decreased for PLA/CF2. The transparency of the tested samples decreased proportionally with the addition of CF. The permeability of tested samples has increased proportionally with the addition of CF. The results obtained from permeability tests are in good agreement with the crystallinity of samples. The overall migration did not exceed the regulated limit value. Furthermore, it was established that the changes in the absorption characteristic bands of the tested composites occurred due to sterilization process are proper for the composites to be used for packaging of e.g. s*ous vide* pasteurized or sterilized vegetable *ready to use* products. The next step for this work is the application of these new biobased materials in food packaging, testing their compatibility with different food products, using or not the sterilization process along the packaging chain.

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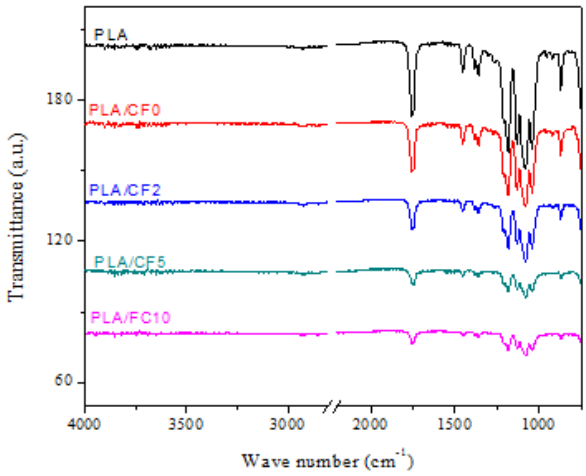

Fig. 4. FTIR-ATR spectra for PLA and PLA composites after the sterilization process

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