



Article

Optical and Thermal Studies, Isothermal Crystallization Kinetics and Mechanical Properties of Poly(lactic acid) Nanocomposites Based on Hybrid Lignin/MWCNT Nanomaterial

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Abstract

A depth study of optical, isothermal crystallization and mechanical properties was conducted on a series of poly(lactic acid) (PLA) nanocomposites based on lignin/multi-walled carbon nanotubes (MWCNTs) hybrid nanomaterial. The preparation was performed via solution casting followed by melt mixing. For comparison reasons, a group of PLA/lignin polymeric materials were prepared. Infrared spectroscopy (FTIR) did not reveal any significant impact on the main peaks of the nanocomposites by the incorporation of the additives. The optical properties were strongly affected by the content of the additive, as long as the thermal transitions parameters as evaluated from the differential scanning calorimetry (DSC) show important differences between cold and melt crystallization. X-ray diffraction (XRD) showed the semicrystalline behavior of the materials, while during isothermal crystallization experiments, the hybrid conductive nanomaterial acted as nucleation agent by promoting crystallization. Under evaluation of the mechanical properties, Young's modulus tensile parameter increased significantly while the content of the hybrid nanomaterial increased, and the bending experiments of the materials with low content of the additives did not break. Thus, these substrates could be promising candidates for engineering applications, such as printed electronics.

Keywords: poly(lactic acid); hybrid nanomaterial; lignin; MWCNTs; optical and mechanical properties; isothermal melt crystallization



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1. Introduction

Since the 20th century, conventional fossil-based plastics derived, such as polyethylene (PE, polypropylene (PP) and poly(ethylene terephthalate) (PET), have known significant growth in global markets because of their exceptional properties (i.e., thermal and mechanical), low cost, and easy processability. Their increased consumption and lack of degradation led to their accumulation to the ecosystems, causing serious environmental issues [1–5]. Additionally, the depletion of petrochemical sources, in combination with the release of huge amounts of greenhouse gases into the atmosphere, should not be overlooked. As expected, plastic pollution has been recognized as one of the 10 most serious environmental

issues in 2020 and the predictions that quantities of plastic waste will overcome 25 billion tons by 2050 cause intense concerns [6,7].

Through the aforementioned issues, the production of bioplastics and biopolymers from renewable sources was necessary in order to overcome some of the issues that the production of fossil-based polymer have caused. Several examples of alternative polymers are poly(lactic acid) (PLA), poly(ethylene adipate) (PEAd), poly(butylene succinate) (PBS), and cellulose acetate to substitute the fossil-based conventional polymers [8–13]. Among them, PLA constitutes one of the most promising bioplastics, due to its similar thermal properties and superior economic processing compared to conventional polymers. PLA is an aliphatic polyester, which can be synthesized through ring opening polymerization (ROP) of L-lactide, which can be produced by fermentation from corn starch, cassava, beet or sugar cane and other renewable resources [14–18].

PLA has been investigated for its utilization in several application fields such as packaging, medicine, tissue engineering, electronic devices, textiles, automotive industry, and agriculture [19–22]. In terms of thermal behavior, PLA exhibits a relatively high glass transition (T_g) (50–60 °C), melting temperature (T_m) (160–175 °C), and a broad cold crystallization temperature at 100–120 °C, depending on its molecular weight. PLA has a low crystallization rate, because the methyl group of the repeatable structure hinders the crystallization process, and directly affects the overall performance of the material [23–25]. Aiming to become a suitable polymer for electronic, 3D printing, and other advanced applications, several types of particles such as metal particles, metal oxides, graphene, and multi-walled carbon nanotubes (MWCNTs) have been incorporated into the PLA matrix in order to enhance its crystallization behavior, thus its thermal resistance and mechanical strength [26–30].

Lignin constitutes a natural biopolymer, which is derived from wood and is ranked as the second most abundant biomass component and the first aromatic/phenolic polymer in nature. Lignin structure includes three phenylpropanoid monomers, generally named as monolignols or lignols, coniferyl (G-Units), p-coumaryl (H-Units), and sinapyl (S-Units) alcohols. These contain carboxyl, hydroxyl, methoxy, and carbonyl functional groups, which could form hydrogen bonds with the carboxyl groups of PLA, when incorporated as an additive via melt mixing or through the in situ formation of PLA copolyesters. Simultaneously, the interfacial adhesion of PLA and lignin could be enhanced by the π - π interactions between aromatic rings of lignols and carbonyl groups of PLA. All these features constitute lignin as a suitable bio-additive, offering high mechanical stiffness, antioxidant, antimicrobial, and barrier properties [31–35].

Carbon nanotubes (CNTs) are an allotropic form of carbon, and they attracted tremendous interest due to their excellent electrical, thermal, and optical properties. They are made by graphene layers forming a cylindrical tube in hexagonal lattice with a sp^2 hybrid configuration. This tube bends, which forms a degree of sp^3 hybridization and, finally, CNTs present a combination of sp^2 and sp^3 configurations. Owing to overlapping p-orbitals beyond the graphene layers, delocalized π -bonds are formed in the surface of nanotubes. The creation of π -bonds results in CNTs interacting with macromolecular chains by forming non-covalent bonds, acting as nucleation agents improving the crystallization rate and, generally, the mechanical performance of polymer nanocomposites [36–40].

Since the 1980s, hybrid materials constitute a category of materials with increasing research interest. The scientific community defined hybrid materials as the materials consisting of at least two components which are molecularly dispersed in these. They can be used when manufacturing electronic and optoelectronic devices due to their desirable mechanical and thermal properties, high transparency, and easy processability [41,42]. Lignin and CNTs can be blended to form hybrids, in order to improve the dispersion of CNTs in

several solvents such as water or DMSO. Among them, Van der Waals and π -stacking interactions can be developed between the aromatic rings of lignin and hydrophobic surfaces of CNTs, while the presence of -OH groups at lignin's structure increases the water solubility of hybrids. Simultaneously, CNTs can be blended with lignin to form hybrid materials [43]. For instance, sulfonated lignin/CNT hybrids were prepared by Lee et al. and incorporated into a poly(vinyl alcohol) (PVA) matrix, leading to a significant enhancement of the mechanical properties of PVA [44]. Furthermore, recent studies from our group showed that lignin can improve the electrical conductivity of PLA in the presence of CNTs by preparing nanocomposites containing hybrid conductive lignin/CNTs nanomaterial [45]. In general, hybrid nanocomposite systems combine properties of the prepared nanoparticles, where CNTs, for instance, can act as nucleation agents, promoting crystallization, both from the melt and the glassy state, and the nanocomposite samples in the presence of lignin usually exhibit improved mechanical properties, such as tensile strength and Young's modulus. Thus, by combining both CNTs and lignin, it is possible to tune the overall properties of the PLA-based nanocomposites via selected composition [32,33,38,43,45].

In this work, the combined impact of both lignin and CNTs on the optical, thermal, crystallization, and mechanical properties of PLA were studied. Thus, PLA nanocomposites were prepared via solution casting and melt mixing using a conductive hybrid nanomaterial as an additive, which contains lignin and 10% of MWCNTs. For comparison reasons, PLA composites samples including lignin were prepared as well. For the characterization of materials, thin films were fabricated by compression molding. The chemical structure, thermal and crystalline response of the materials were studied by FTIR, DSC, and XRD, respectively. Color measurements have been conducted to study the impact of the different additives and content on the optical properties of the samples. Isothermal crystallization was studied by DSC and PLM, proposing the hybrid material acted as nucleation agent, enhancing the crystallizability of the PLA nanocomposites. Lignin exhibits lower crystallization rates for the PLA composites, compared with the ones with the hybrid nanomaterial. Moreover, the overall mechanical performance of PLA nanocomposites improved in comparison with the neat PLA sample. The aforementioned results are relevant in the present work, as the prepared materials are intended for use as substrates in printed electronic applications [46–50]. Last but not least, the water contact angle significantly depended on the type of additive and its corresponding concentration.

2. Materials and Methods

2.1. Materials

The hybrid materials consist of soda lignin/CNTs with a 90/10 ratio wt%, synthesized by Creative Nano PC (Athens, Greece). The hybrids were synthesized via a controlled ultrasound-assisted method [51]. Soda lignin (Protobind 1000) was purchased from Tanovis AG (Rüschlikon, Switzerland) and MWCNTs with >96% purity and outside diameter 8–18 nm were purchased from Nanografi (Ankara, Turkey), whereas the Luminy® PLA L175 of melt flow index (MFI) at 8 g/10min (Flow, 210 °C/2.16 kg) and 3 g/10 min (Flow, 190 °C/2.16 kg) was purchased from Corbion N.V. (Gorinchem, The Netherlands). All other materials and solvents used were of analytical grade.

2.2. Preparation of PLA Lignin-Based (Nano)Composites with Solution Casting Followed by Melt Mixing

PLA hybrid nanomaterial masterbatches were initially prepared by solution casting. In brief, the quantity of the hybrid nanomaterial required for a final concentration of 0.5 wt%, 1.0 wt%, 2.5 wt%, 5 wt%, 10 wt%, 20 wt%, and 30 wt% (Table 1) in 10 g of PLA nanocomposites was diluted in chloroform (3% *w/v*) and was dispersed in a ultrasonication

bath for 1 h, while PLA was diluted in chloroform (3% *w/v*) under magnetic stirring. The two different solutions were mixed under magnetic stirring, placed in Petri dishes, and left overnight under vacuum at 80 °C for the solvents to evaporate. The same procedure was followed for the preparation of the PLA composites containing raw lignin at three different loadings, 0.5 wt%, 1.0 wt%, and 2.5 wt%, for comparison reasons (Table 1).

Table 1. Sample abbreviations and compositions.

Abbreviation	Content wt%		
	PLA	Lignin	Hybrid (Lignin/10%MWCNTs)
PLA	100	-	-
PLA/lignin	99.5	0.5	-
PLA/lignin	99.0	1.0	-
PLA/lignin	97.5	2.5	-
PLA/hybrid	99.5	-	0.5 (0.05 wt% of CNTs)
PLA/hybrid	99.0	-	1.0 (0.1 wt% of CNTs)
PLA/hybrid	97.5	-	2.5 (0.25 wt% of CNTs)
PLA/hybrid	95	-	5.0 (0.5 wt% of CNTs)
PLA/hybrid	90	-	10 (1.0 wt% of CNTs)
PLA/hybrid	80	-	20 (2.0 wt% of CNTs)
PLA/hybrid	70	-	30 (3.0 wt% of CNTs)

The PLA, PLA lignin, and hybrid nanomaterial masterbatches were dried overnight under vacuum at 80 °C. To prepare the materials by melt mixing, the amount of each dried masterbatch and dried PLA were included in a melt-mixer, Haake–Buchler twin screw co-rotating extruder, and a mixing head with a volumetric capacity of 11 cm³, at 190 °C, 30 rpm, and 5 min for each sample. In total, eleven materials were prepared, three containing the raw lignin, seven containing the hybrid nanomaterial and the neat PLA.

Film Preparation

Compression molding was used to prepare PLA composites films (Figure 1), and specifically Otto Weber, Type PW 30 hydraulic press was used with an Omron E5AX Temperature Controller (Kyoto, Japan), at a temperature of 172.5 ± 2.5 °C and a hydraulic pressure of 100 mbar. Quenching was applied after melting the samples by rapid cooling at room temperature. The films had similar thicknesses around 0.40 ± 0.03 mm.

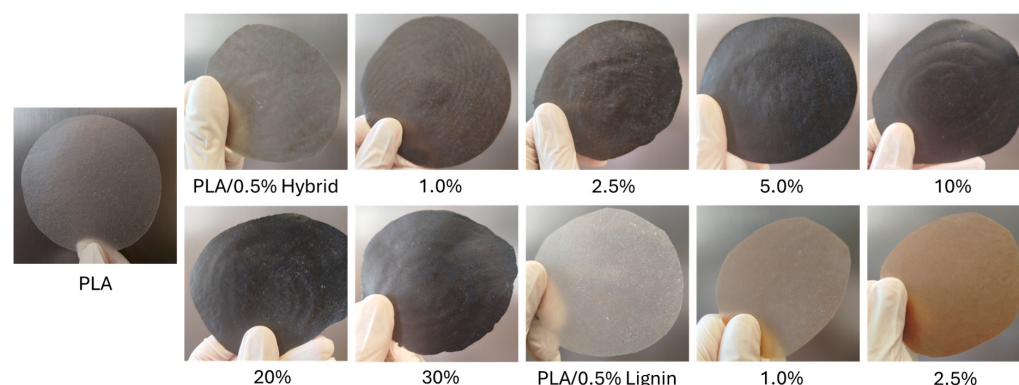


Figure 1. Compression molded samples of PLA and PLA (nano)composites.

2.3. Characterization Techniques

2.3.1. Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR)

The samples' ATR-FTIR spectra were recorded utilizing an IRTracer-100 (Shimadzu, Kyoto, Japan), which was equipped with a QATR™ 10 Single-Reflection ATR Accessory with a Diamond Crystal. The FTIR spectra have been collected in the range from 450 to 4000 cm^{-1} using a resolution of 2 cm^{-1} (16 co-added scans, in total), where at the same time, the baseline was corrected as absorbance. Measurements were performed in triplicate.

2.3.2. Color Measurements

Color measurements were performed using a Gretag Macbeth Color-Eye 7000A (New York, NY, USA) reflectance spectrophotometer, coupled with Color iMatch 10.0 software. A lamp D65 was used as a light source and the observing angle for the samples was 10°. The instrument was calibrated by a white and a black tile. Initially, film samples with specified thickness were placed on the white tile. In each case, the measurements were performed five times by utilizing a special holder (Datacolor, Lawrenceville, NJ, USA) where the mean values were collected. The color values were calculated using the CIE L*a*b* color space system.

2.3.3. Differential Scanning Calorimetry (DSC)

PerkinElmer Pyris Diamond DSC was used as differential scanning calorimeter and pure metals, such as indium, zinc, and tin were used as standards, so the DSC was calibrated. It was used to conduct differential scanning calorimetry measurements in a nitrogen atmosphere. The sample mass was 5 mg $\pm$ 0.1 and was sealed in aluminum pans.

First a heating step was conducted at 20 °C/min up to a temperature $T = T_m + 40$ °C to evaluate their melting temperature. Amorphous materials were obtained by heating the samples to 40 °C up to the melting temperature and holding them there for 3 min to erase their thermal history. The cooling step was performed at the highest rate possible. Thus, the glass transition temperature (T_g), cold (T_{cc}) and melting temperature (T_m) were measured for the quenched samples during the heating step at 20 °C/min. Finally, the materials were cooled from the melt ($T_m + 40$ °C) at 10 °C/min to a temperature below T_g ($T_g - 40$ °C) for the determination of the crystallization temperature (T_c).

For the isothermal melt crystallization experiments on the samples, a heating step was employed at 40 °C above their T_m and held there for 3 min to erase any thermal history, then a cooling step in the DSC at the highest rate possible was performed at 120 °C. The final step was subsequent heating at 40 °C above their T_m , with a heating step at 20 °C/min. All the measurements were performed two times.

2.3.4. X-Ray Diffraction (XRD)

Samples were subjected to X-ray diffraction measurements using a MiniFlex II XRD system from Rigaku Co. (Tokyo, Japan), coupled with CuK α radiation ($\lambda = 0.154$ nm) in the 2 θ angle range from 5 to 45° at a scan speed of 1 °/min. The measurements were performed in triplicate.

2.3.5. Polarized Light Microscopy (PLM)

For the PLM observations, a polarized light microscope (Nikon, Optiphot-1, Tokyo, Japan), which was equipped with a Linkam THMS 600 heating stage, a Linkam TP 91 control unit, and a Jenoptic Gryphax Arktur camera with Gryphax software, version 2.1, was used. Isothermal melt crystallization experiments were conducted following the procedure used for the corresponding DSC isothermal crystallization from the melt experiments. All the measurements were conducted two times.

2.3.6. Mechanical Properties

Shimadzu EZ Test Tensile Tester was used for the tensile measurements, and a Model EZ-LX with a 2 kN load cell, in accordance with ASTM D882, using a crosshead speed of 5 mm/min. Dumb-bell-shaped tensile test specimens (central portions 5×0.5 mm thick, 22 mm gauge length) were cut in a Wallace cutting press after preparing compression-molded samples using a thermopress. Each sample was measured five times.

Three-point bending tests were performed using a Shimadzu EZ Flexural Tester Model EZ-LX, with a 2 kN load cell, according to ASTM D790-17. Compression-molded samples were prepared using a thermopress with appropriate dimensions; 12.7 mm wide and <1.6 mm thickness. The samples were tested flatwise on the support span, resulting in a support span-to-depth ratio of 16:1 (tolerance ± 1). Each sample was measured five times.

2.3.7. Contact Angle

Water contact angle measurements were conducted using an optical tensiometer, which was the One Attention (Biolin Scientific, Espoo, Finland). The sessile water droplet method was used to examine the hydrophilicity and hydrophobicity of the samples. The measurements were performed in triplicate.

3. Results and Discussion

3.1. Structural and Optical Properties

The characteristic FTIR peaks of PLA (Figure 2a) were observed at 2900, 1758, 1450, and 1100 cm^{-1} , which were associated with C-H and C=O stretching vibrations, C-H bending vibrations, and C-O stretching vibrations, respectively. These peaks did not alter by the incorporation of the additives due to their weak chemical interactions with the PLA matrix (Figure 2b). In addition, a weak broad absorbance peak at 1510–1560 cm^{-1} and a small peak at 1420 cm^{-1} corresponding to C=C double bond stretching of aromatic rings of lignin were observed. The broad peak became distinct only at 20 and 30 wt% hybrid content and it was absent at PLA/lignin composites, while the small one appeared in almost all (nano)composite samples [32,33].

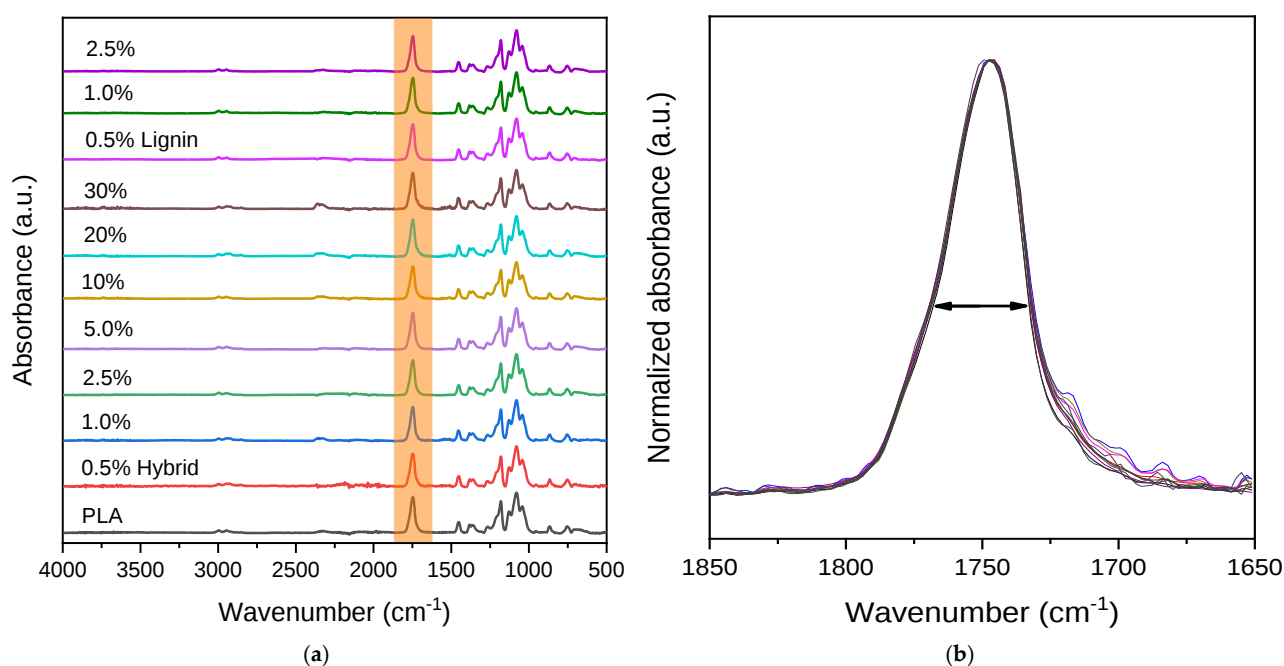


Figure 2. (a) ATR-FTIR spectra of PLA and PLA (nano)composites, and (b) zoom area at the carbonylic region.

The optical differences between the materials are expressed by $L^*a^*b^*$ parameters and they are presented in Figure 3a,b, while Figures 4 and 5 show their transmittance and color, as recorded from the spectrophotometer.

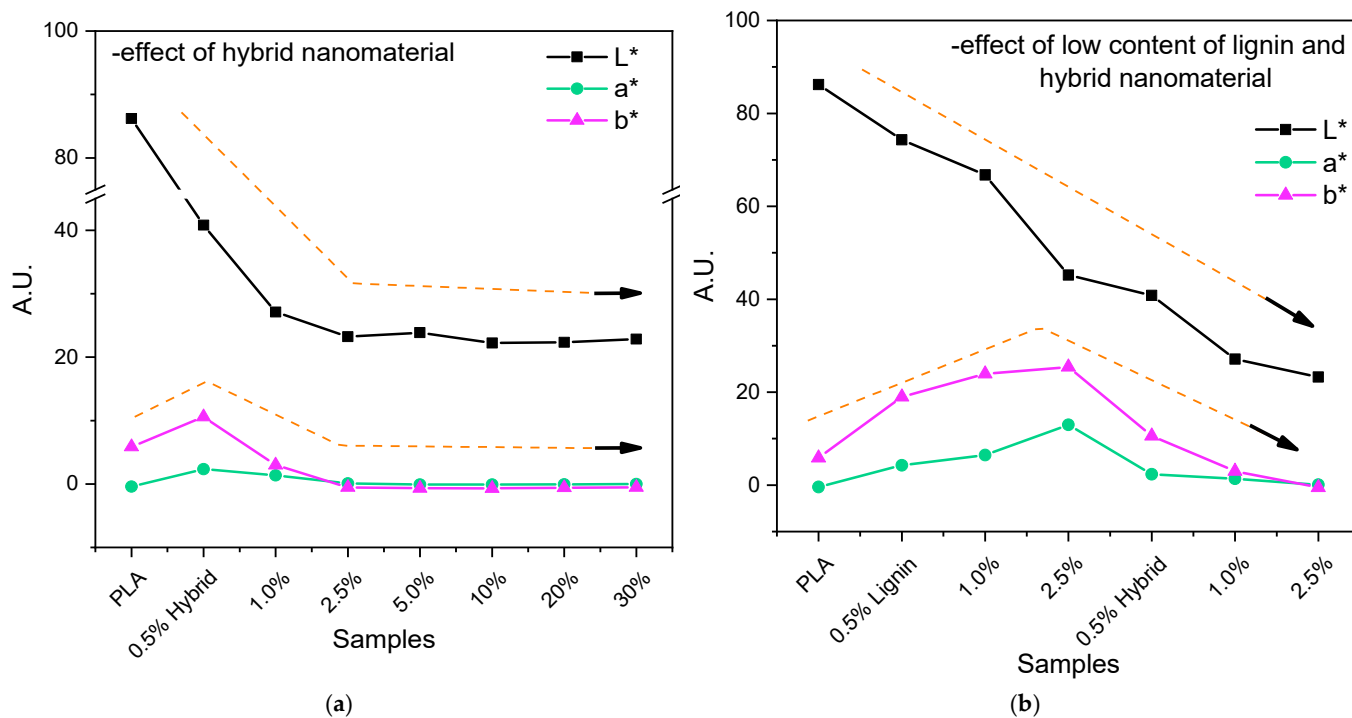


Figure 3. CIE $L^*a^*b^*$ coordinates of PLA, PEAz, and PLA (nano)composites., L^* : perceptual lightness, a^* and b^* : red–green and blue–yellow.

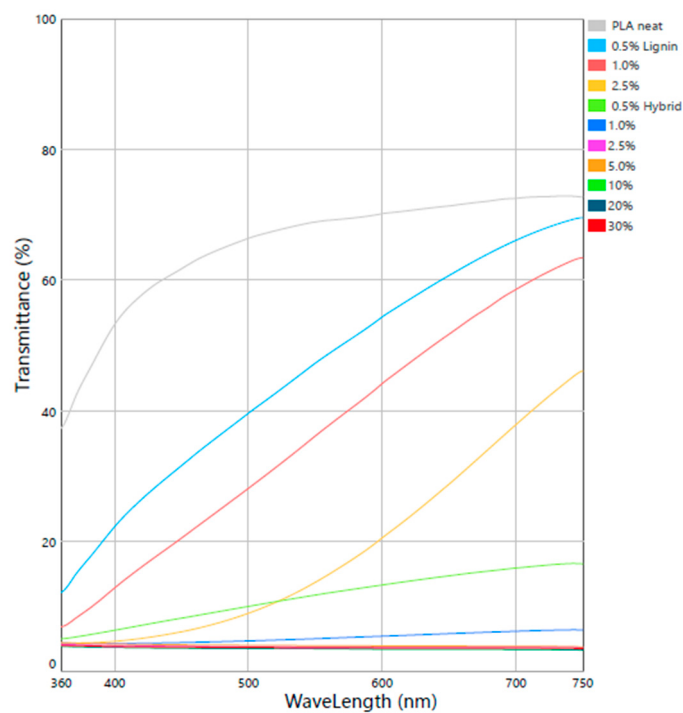


Figure 4. Optical properties of PLA and PLA (nano)composites.

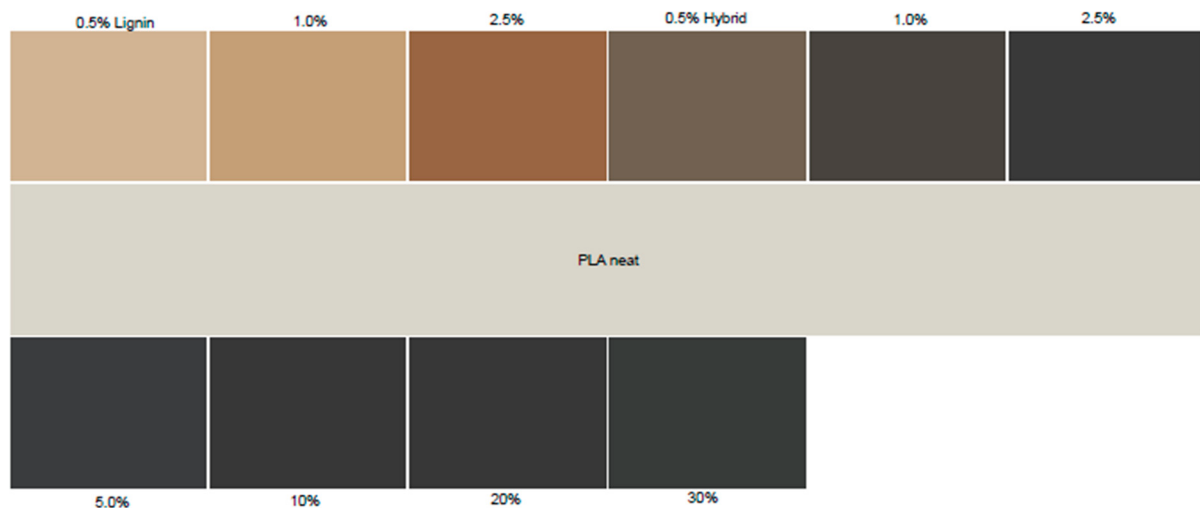


Figure 5. PLA and PLA (nano)composites samples.

Figure 3a shows that the high lightness of PLA neat decreased by the addition of hybrid nanomaterial and reached a plateau at 2.5% content. The a^* values remained stable at all samples close to zero, except for the sample with 0.5 and 1.0% hybrid, which presented a small increase above zero, exhibiting a hue closest to red. The PLA neat sample presents a negative a^* value at -0.40 and therefore a hue close to green. The b^* value of PLA neat was measured at 5.86 , exhibiting a hue closer to yellow. By the addition of hybrid, the b^* value only increased at 0.5% concentration, following a rapid decrease at a higher hybrid content, and stabilized below zero from 2.5% hybrid content, presenting a hue close to blue [32]. Concerning the lignin-based samples, they exhibited the highest lightness (Figure 3b) compared to the ones with hybrid additives, as was expected due to the lack of carbon nanotubes. Both a^* and b^* values were significantly higher compared with the respective ones of PLA/hybrid nanocomposites.

In Figure 4, the optical properties of the materials were expressed by transmittance. The transmittance expresses the monochromatic light beam that can penetrate the sample surface and is considered a critical parameter for materials related to printed electronics [52,53]. For the neat PLA sample, a high transmittance (T%) was observed, which decreased significantly with increasing additive content. The PLA/lignin composites presented enhanced transmittance compared to the PLA/hybrid ones [54]. This happened due to the presence of carbon nanotubes, in the case of PLA nanocomposites, which resulted in very low T%, in the case of 1.0 to 30 wt% loadings.

3.2. Thermal Properties, Crystalline Behavior, and Isothermal Melt Crystallization

The next figure shows the DSC scans of the compression-molded samples during the 1st, 2nd heating, and slow cooling. In all cases there was no significant improvement regarding the melting temperature (T_m) of the samples caused by the presence of lignin or the hybrid nanomaterial (Figure 6a), except for the PLA/hybrid samples with 0.5 and 1.0 wt% additive, where an additional distinct T_m was recorded at 182°C (Table 2). This can be attributed to the presence of small concentrations of CNTs, which acted as highly efficient nucleating agents, promoting the formation of multiple crystal populations with enhanced thermodynamic thermal stability within the PLA matrix. Multiple distinct peaks were also observed during the second heating (Figure 6b) in the case of the PLA/hybrid (i.e., from 1.0 up to 10 wt%) and for all PLA/lignin-based samples. The presence of multiple crystal populations was consistent by the DSC observations, where, in addition to the exothermic cold crystallization temperatures (T_{cc}), which recorded during the second heating of the

quenched samples (Figures 6b and 7a), secondary exothermic re-crystallization peaks appeared just before melting. This suggested that less stable or imperfect crystals formed during the initial crystallization and transformed into more stable crystalline structures upon reheating, reflecting the heterogeneous nature and stability of the crystals. This phenomenon was also observed during the subsequent heating scans after the isothermal crystallization experiments from the melt (Figure S2b).

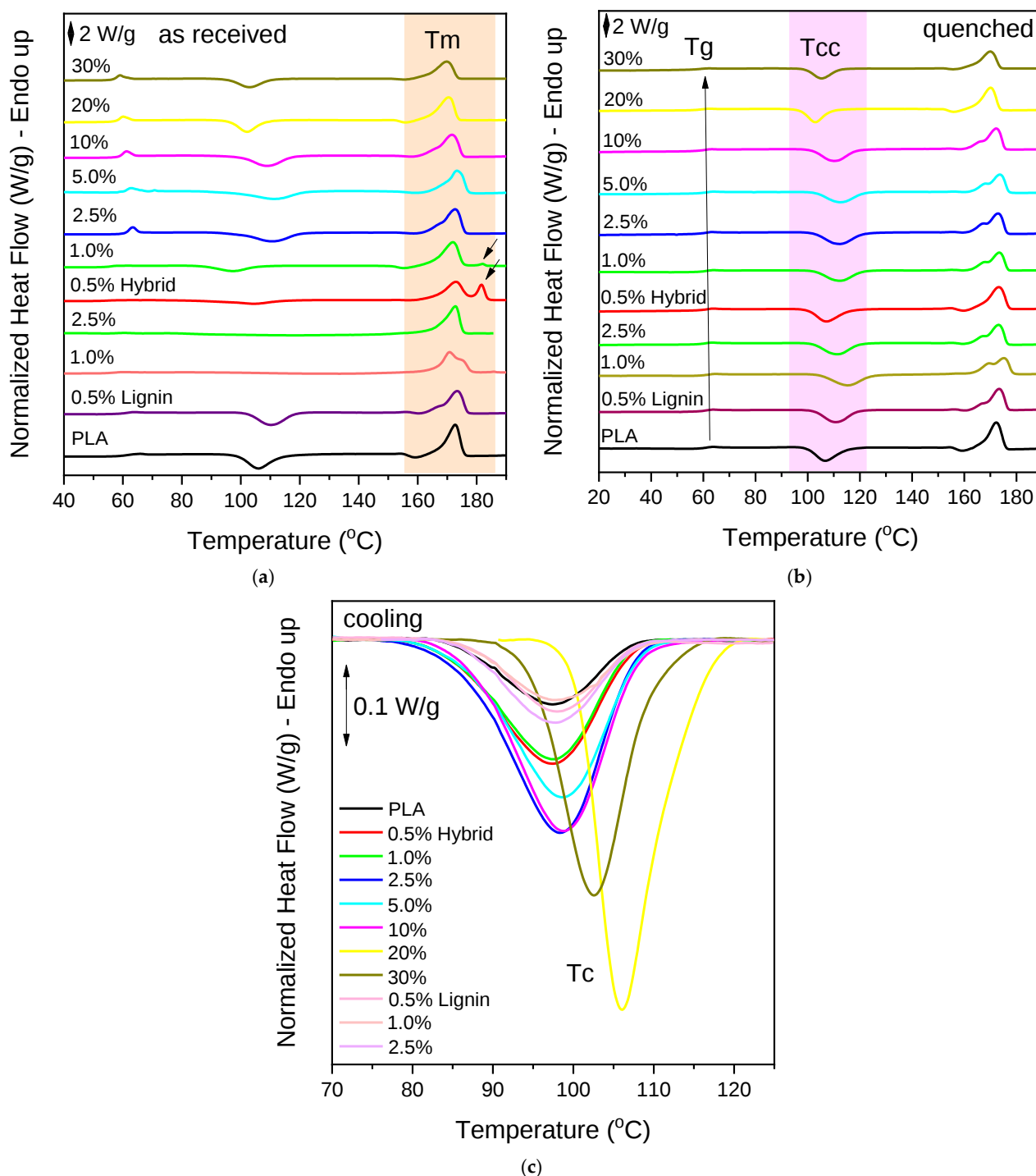


Figure 6. DSC curves of PLA and PLA (nano)composites during (a) the first and the (b) second heating at 20 °C/min, and (c) cooling at 10 °C/min.

Table 2. Thermal properties of PLA and PLA (nano)composites.

Sample	As Received				Quenched			Cooling			
	T_m (°C)	ΔH_m (J/g)	T_g (°C)	ΔC_p [J/(g·°C)]	T_{cc} (°C)	ΔH_{cc} (J/g)	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)	CF_c (%)
PLA	172.7	41.1	60.9	0.409	106.8	32.3	172.2	38.3	97.2	8.3	8.9
0.5% Hybrid	173.0 + 181.7	45.6 + 8.4	60.7	0.403	107.2	36.3	173.3	37.1	97.5	13.7	14.8
1.0%	172.1 + 182.1	42.4 + 3.7	60.5	0.393	112.4	35.8	173.5	33.1	97.4	15.2	16.5
2.5%	172.8	41.5	60.4	0.391	112.1	37.2	172.8	39.8	98.5	20.1	22.2
5.0%	173.1	39.7	60.3	0.390	112.5	33.3	173.8	34.8	98.6	17.3	19.6
10%	171.5	38.1	59.9	0.380	110.1	34.3	172.1	37.2	98.6	21.9	26.2
20%	170.4	32.6	59.1	0.325	103.2	27	170.1	31.9	106.1	30.0	40.3
30%	169.8	27.7	58.4	0.285	105.3	23	170.1	26.5	102.6	22.1	34.0
0.5% Lignin	173.4	37.2	60.4	0.392	110.7	36.4	174.3	36.8	98.2	7.2	7.8
1.0%	170.7	38.9	61.1	0.390	115.1	35.8	175.1	36.0	98.4	4.5	4.9
2.5%	172.8	41.0	59.8	0.316	111.1	33.7	173.2	33.7	98.0	6.4	7.1

CF_c was calculated based on theoretical heat of fusion of 100% crystalline PLA, which corresponds to 93 J/g [45].

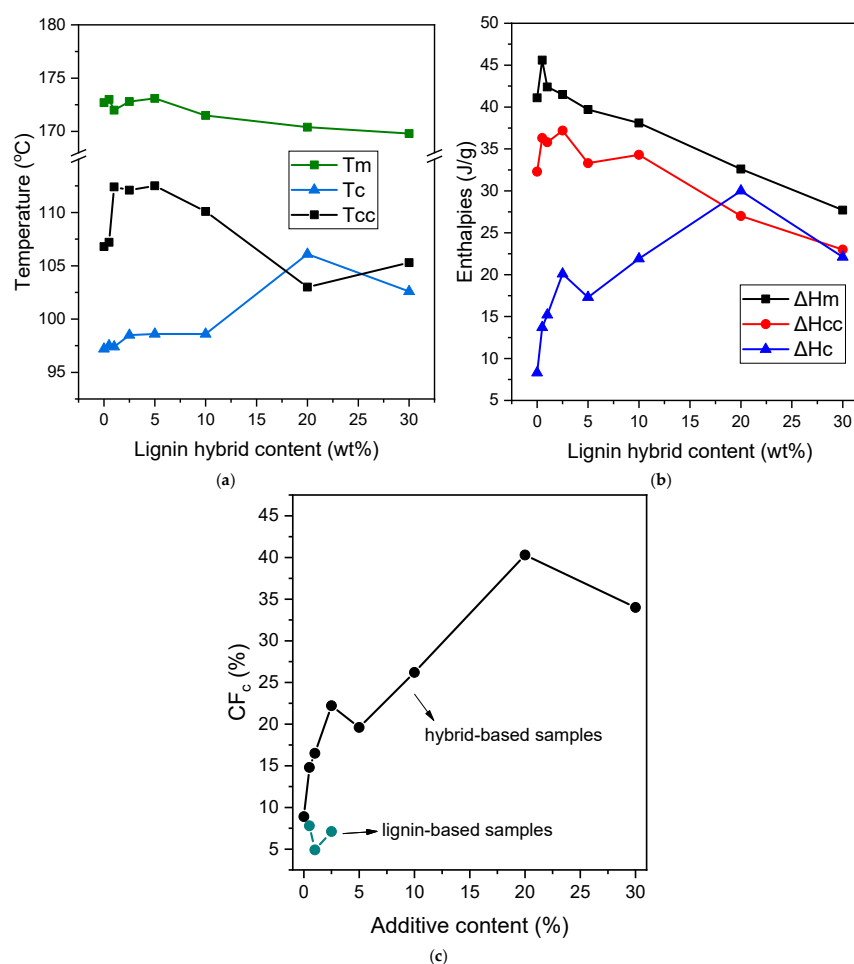


Figure 7. (a) Thermal transitions of PLA and PLA nanocomposites, (b) the heat of fusion (ΔH_m) from the first DSC scan, enthalpy of cold (ΔH_{cc}) and melt (ΔH_c) crystallization, and (c) the crystalline fraction during melt crystallization (cooling step) as a function of the additive content.

Glass transition temperature (T_g) did not significantly change, as was expected, by the presence of the hybrid nanomaterial or lignin particles (Table 2). On the other hand, T_{cc} altered towards higher temperatures, as the hybrid content increased (up to 10 wt%), due to the restriction that the nanoparticles caused to the molecular mobility of the macromolecular

chains of PLA. However, at higher loadings, the T_{cc} was lower compared to PLA, meaning that it was influenced directly by the presence of CNTs nanoparticles and affected the molecular mobility of the samples.

Concerning the crystallization from the melt, PLA exhibited low crystallization ability, particularly ΔH_c close to 8, which corresponds to 9% crystallinity (Figure S1, Table 2). But, as the hybrid content increased, the crystalline fraction increased significantly up to 40%. This was clearly associated with the aforementioned nucleation effect, where the crystallization temperatures (T_c s) also became sharper, compared with neat PLA and the nanocomposites with low hybrid content. Moreover, T_c s shifted towards higher temperatures, which was accompanied by the nucleation effect, once again, of CNTs nanoparticles. It is noteworthy that at high hybrid content T_c shifted almost 10 °C at higher temperatures compared to the neat PLA sample. The CF_c of lignin-based samples was even lower than that of PLA, resulting in restriction effects towards crystallization (Figure 7c, Table 2) [23,39,45]. In all cases, the thermal transitions, in general, of the PLA-based nanocomposites are in agreement with previous studies [32,33,35,38]. PLA, the PLA composites based on neat lignin, presented low crystalline fractions (below 10%) (Table 2), while in the case of hybrid nanocomposites, and specifically at high CNTs content (Table 1), the samples reached crystalline fraction from the melt close to 35 and 40%. In every case, the suggested data on CF_c are in agreement with previous work on PLA nanocomposites based on lignin and CNTs [32,45].

X-ray diffraction (XRD) patterns (Figure 8) confirmed the semicrystalline nature of all samples, exhibiting the characteristic diffraction peaks of PLA at 15.2°, 16.8°, and 19.1°. No additional distinct crystalline peaks attributable to the incorporated additives were detected. Besides that, small differences were observed regarding the intensity of the peaks, where in the case of PLA/hybrids materials, the intensity of the peaks were intensified compared to the neat PLA sample, but also to the PLA/lignin materials. Moreover, due to the majority of lignin nanoparticles in PLA nanocomposite samples, an overlapping was caused concerning the peaks that would have been correlated due to the presence of CNT nanoparticles.

In the case of PLA nanocomposites, polymer crystallization represents a key aspect among the various characterization techniques employed to establish correlations between microstructure and overall material performance. Investigation of isothermal crystallization kinetics may reveal how several properties such as nanoparticle type and interfacial interactions influence crystalline behavior and, consequently, the mechanical, thermal, and functional properties of the nanocomposites. Thus, these measurements are essential for optimizing material formulations, thereby enabling a more reliable connection between structural features and targeted application requirements [55–58].

Isothermal melt crystallization kinetics of PLA and PLA (nano)composites were examined via DSC at 120 °C. The temperature, 120 °C, was selected because it is the lowest temperature where the proper baseline graphs were received for all the samples and that avoids crystallization during the rapid cooling step. These suggestions on isothermal crystallization kinetics were made by Müller's group [58]. Crystallization exothermic peaks are shown in Figure 9a. The relative degree of crystallinity $X(t)$ was calculated based on the equation below to estimate the crystallization rate of the materials. $X(t)$ as a function of crystallization time at different temperatures was obtained (Figure S2a) based on the fact that the evolution of crystallinity was linearly proportional to the evolution of heat which was released during the crystallization.

$$X(t) = \frac{\int_0^t (dH_c / dt) dt}{\int_0^\infty (dH_c / dt) dt} \quad (1)$$

where dH_c denotes the enthalpy of crystallization of the slightest fraction of time interval dt . The limits t and ∞ on the integrals indicate the elapsed time during the process of crystallization and at the end of the crystallization, accordingly. $X(t)$ indicates the necessary time required to reach 50% of the overall crystallinity during the isothermal melt crystallization process. Then, the $\tau_{1/2}$ data were calculated (Figure 9b) in order to estimate the crystallization rate of the materials. The subsequent heating traces were also recorded (Figure S2b).

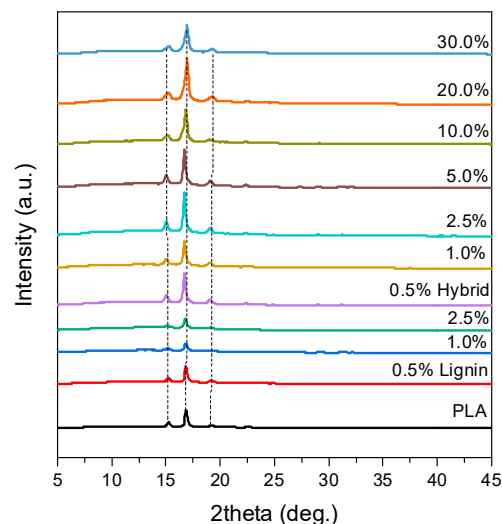


Figure 8. XRD patterns of PLA and PLA (nano)composites.

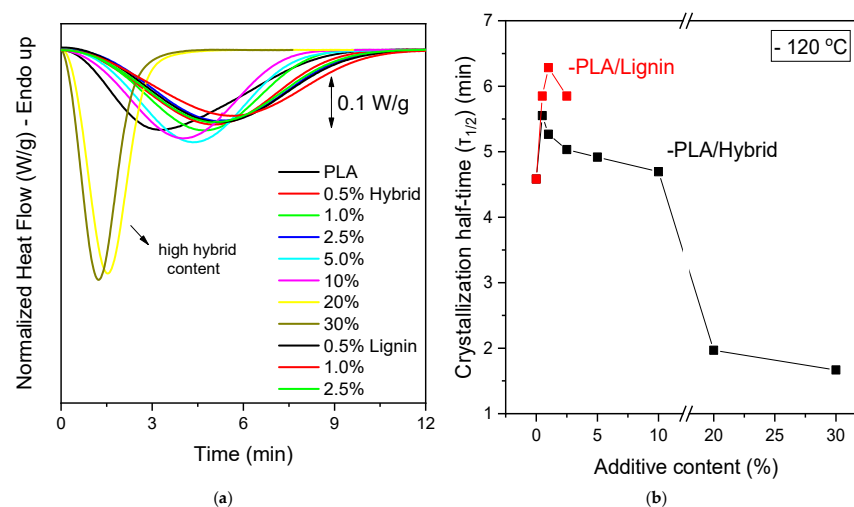


Figure 9. Isothermal melt crystallization kinetics at 120 °C. (a) Exothermic crystallization curves and (b) crystallization half-time as a function of lignin hybrid content.

The peak intensity of the crystallization curves (Figure 9a) was directly connected with the crystallization kinetics of the materials, meaning that the samples with sharper curves (samples with high hybrid content) corresponded to low values of crystallization half-times (Figure 9b). In detail, Figure 9b shows that as the hybrid content increased up to 10 wt%, the $\tau_{1/2}$ gradually decreased. This behavior can be attributed to the role of the CNTs, which can act as effective nucleating agents, providing additional heterogeneous nucleation sites facilitating the crystallization process of the macromolecular chains of PLA [59]. At higher loadings (i.e., at 20 and 30 wt%), the density of these nucleation sites increased significantly, thus accelerating the crystallization. The observed crystallization trend suggested that controlled additive incorporation can be an effective strategy to tailor the crystallization

behavior of PLA nanocomposites [60]. Furthermore, comparing the crystallization rates of the samples that contain lignin particles with the PLA nanocomposites rich with CNTs nanoparticles, the crystallization half-time was higher (Figure S2c). Lignin can form agglomeration and generally lacks nucleation ability, thus leading to slower crystallization kinetics. The results underline the critical role of additive morphology in controlling the crystallization performance of PLA-based (nano)composites [24].

PLM observations (Figure 10) were conducted under isothermal crystallization conditions, which revealed some differences in spherulitic morphology and more concerning the density between the PLA nanocomposites containing CNTs and those incorporating only lignin. In the CNT-based systems, higher spherulite density was observed, indicating the presence of a larger number of nucleation sites, supporting, in this case, the crystallization kinetics results, where shorter half-times were recorded. In contrast, the lignin-containing composites exhibited a lower spherulite density, suggesting fewer effective nucleation sites, especially in the case of the samples which contained 2.5 wt% of lignin.

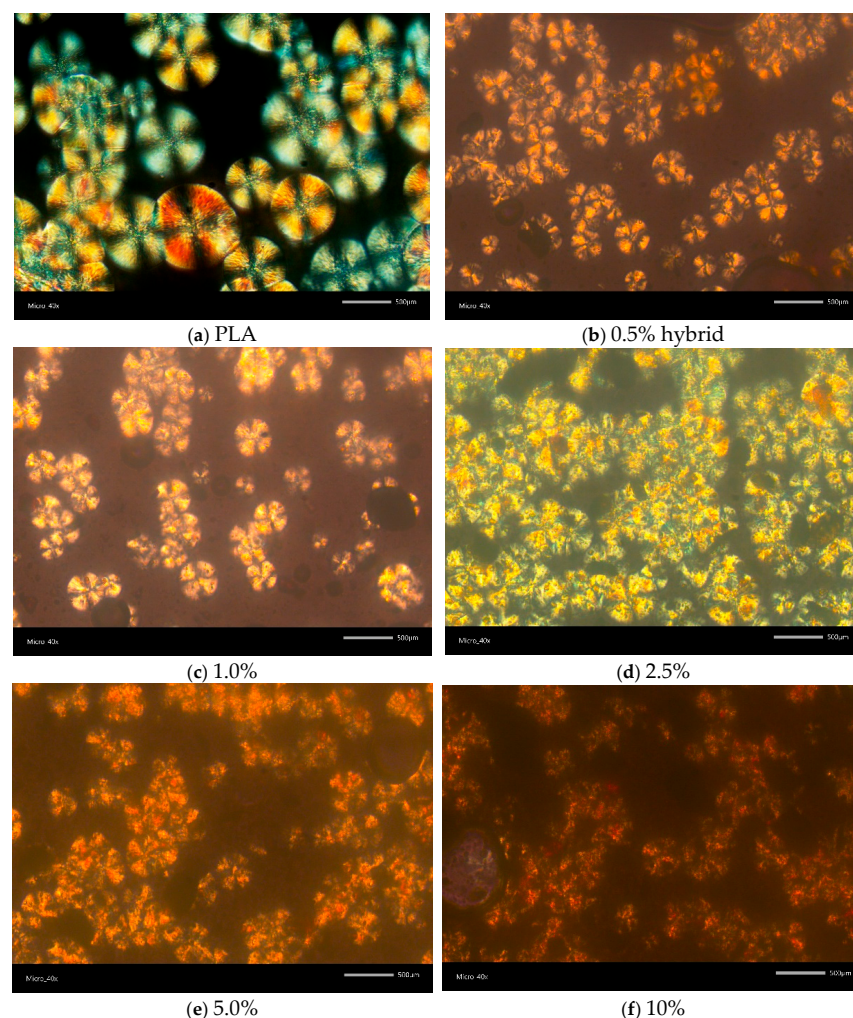


Figure 10. Cont.

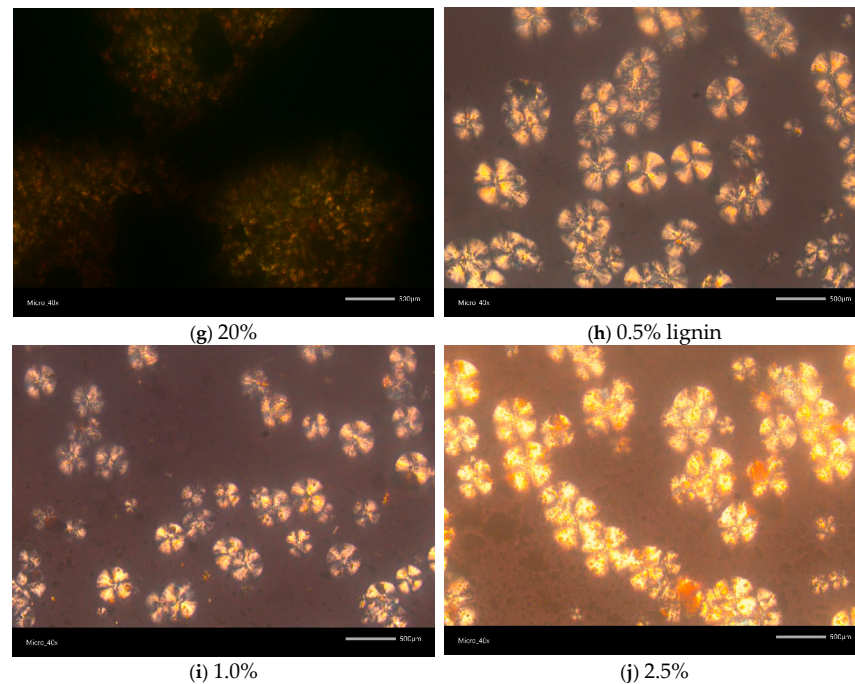


Figure 10. PLM observations under isothermal melt crystallization at 120 °C of PLA and PLA (nano)composites. The scale bar was set at 500 μm .

3.3. Mechanical Evaluation via Tensile and 3-Point Bending Tests

The impact of lignin and MWCNTs on the tensile behavior of PLA nanocomposites are presented in Figures 11 and 12. Figure 11 shows the tensile stress–strain curves.

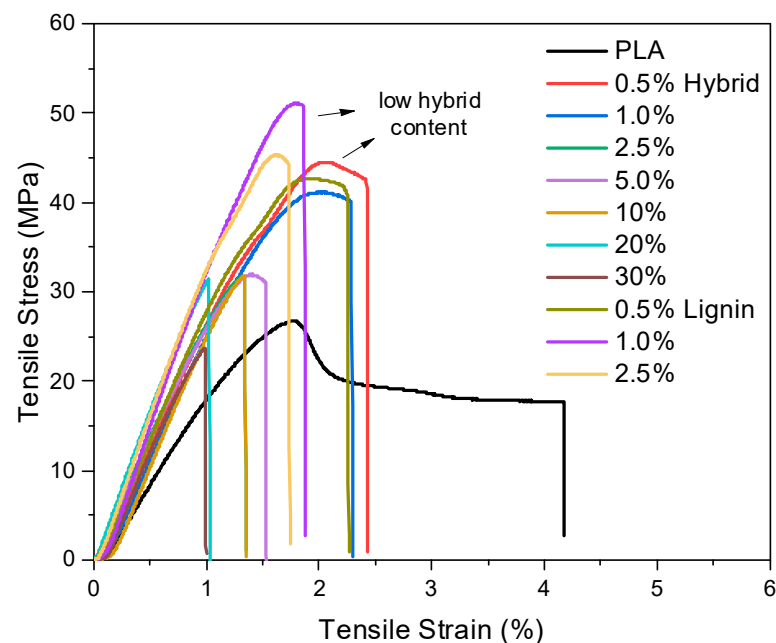


Figure 11. Representative tensile stress–strain curves.

At Figure 12a, an initial rise in Young's modulus was observed by the addition of 0.5 wt% hybrid, followed by a reduction in 1.0 and 2.5 wt%, while for the cases of 5.0 up to 30 wt% hybrid content there was a continuous improvement on the modulus. The modulus corresponds to the resistance of the material in changing from elastic to plastic deformation, meaning that the nanocomposites in all cases presented higher stiffness compared to the PLA sample. Also, the stiffness was higher for high loadings, probably due to the higher

crystalline fraction of the samples in comparison with the samples with low concentrations of hybrid nanomaterial. This phenomenon correlated with the formation of a network between the amorphous regions of PLA matrix and the crystalline regions, resulting in enhanced mechanical performance [39,61,62].

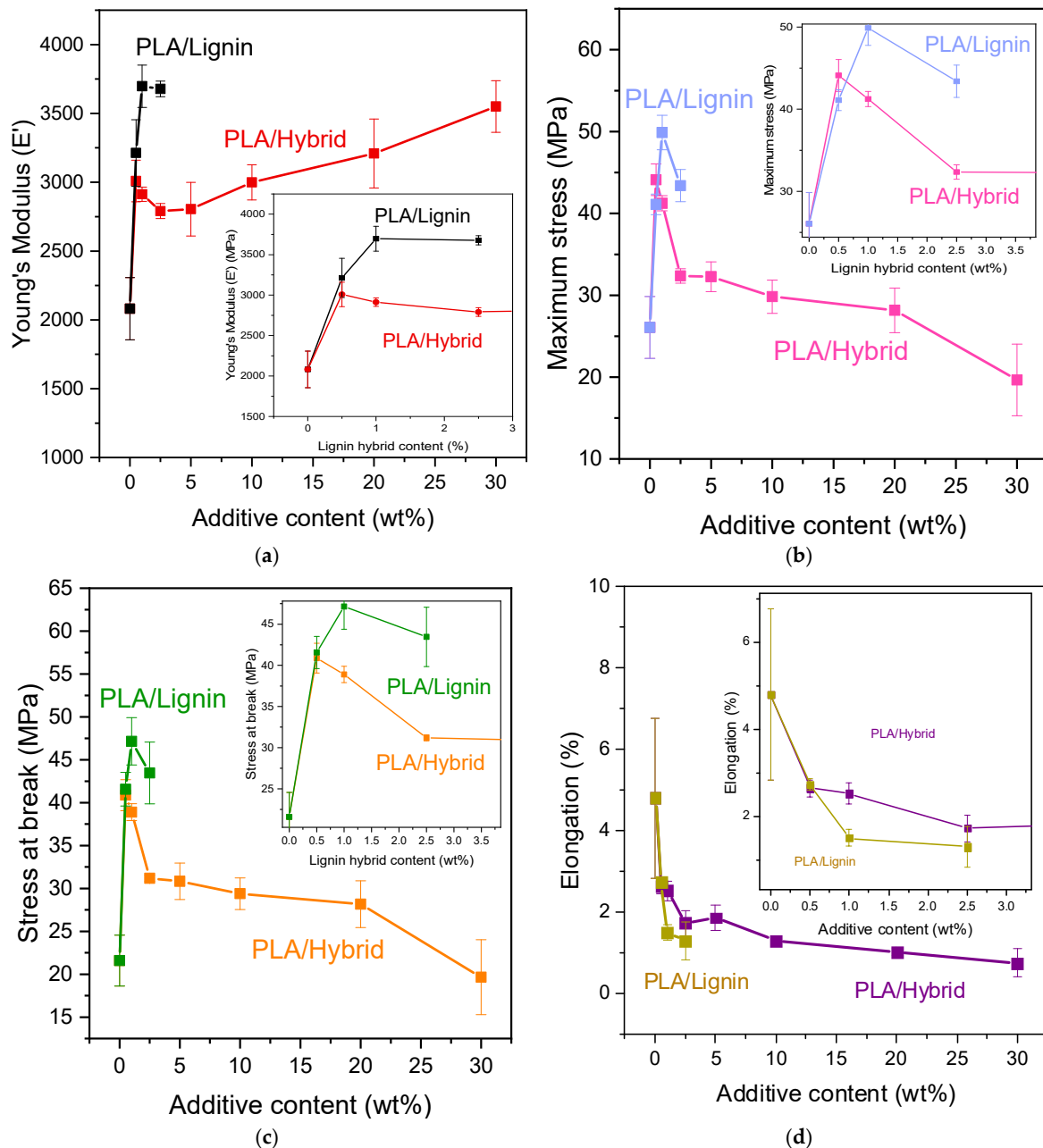


Figure 12. Tensile properties of the PLA nanocomposite materials. (a) Young's Modulus, (b) Maximum stress, (c) Stress at break, and (d) Elongation as a function of additive content.

Figure 12b,c shows the maximum stress and stress at break following the same trend. In contrast to the increase in modulus observed at high loadings, the tensile properties associated with the plastic and failure regions, such as ultimate tensile strength and stress at break, exhibited an opposite trend, decreasing significantly as the additive content increased. This opposite trend was attributed to the presence of the hybrid nanomaterial, which introduced discontinuity sites within the PLA matrix. These sites hindered the ability of the macromolecular chains to slide past one another under load, thereby reducing the material's capacity for plastic deformation, thus lowering the tensile strength of the

materials due to defects formation that hybrid nanoparticles have created. As a result, samples with higher hybrid content broke at lower tensile stress values compared to those with lower hybrid content. Figure 12d presents the elongation of the samples, and as was expected, all the PLA-based (nano)composites had lower tensile strain values than PLA. However, the PLA/hybrid materials exhibited higher elongation compared to PLA/lignin ones at the same concentrations (the case of 1.0 and 2.5 wt%), meaning that the presence of the hybrid nanomaterial improved the overall mechanical performance of the samples.

Furthermore, flexural testing is essential tool for advanced applications such as printed electronics because it evaluates how a potential device could perform under bending and deformation conditions. These experiments provide mechanical data for more reliable, well-designed printed devices and also reveal deformation limits before functional failure [63]. The effect of lignin and MWCNTs on the flexural behavior of PLA-based materials are shown in Figures 13 and 14. Figure 13 presents the flexural stress–strain curves.

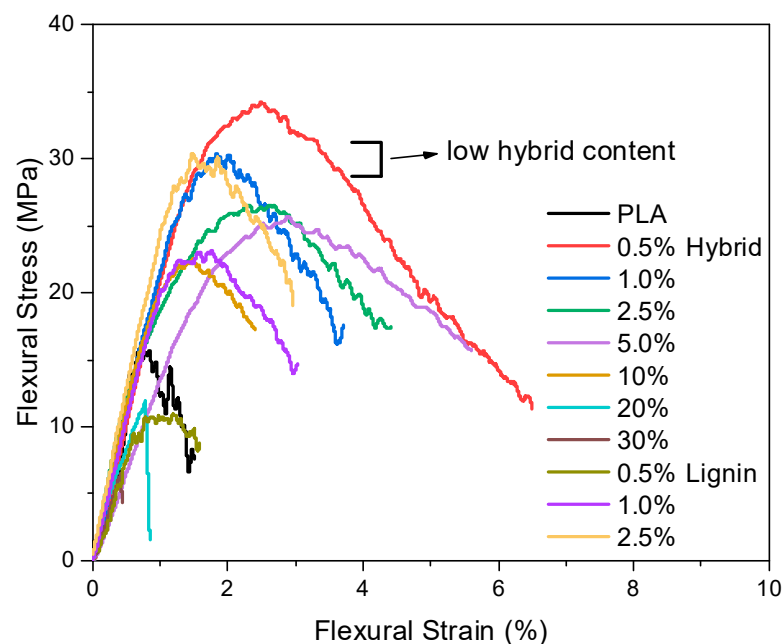


Figure 13. Representative flexural stress–strain curves.

According to Figure 14a, a significant improvement in flexural strength of PLA was observed by the addition of just 0.50 wt% of hybrid nanomaterial, while at a higher concentration, a small reduction was observed. In the case of the samples with high hybrid content (over 10 wt%), the flexural strength decreased rapidly, following the trend of the tensile stress, and exhibited lower values in comparison with PLA. For the PLA/lignin composites, the incorporation of lignin gradually improved the flexural strength of PLA. Regarding the flexural modulus of the materials (Figure 14b), a similar trend compared to flexural strength was observed, where the incorporation of hybrid up to 1.0 wt% caused a gradual reduction on the modulus. However, at higher concentrations, the materials presented a lower flexural modulus than PLA neat. Comparing the effect of hybrid and lignin at the same concentrations to the flexural behavior of PLA, we conclude that the presence of MWCNTs at 0.5 wt% of hybrid contributed significantly to the overall mechanical performance because it exhibited higher tensile and flexural parameters than all the other samples. Regarding the flexibility of the materials, only the ones with high hybrid content broke during the experiments (i.e., ≥ 10 wt%).

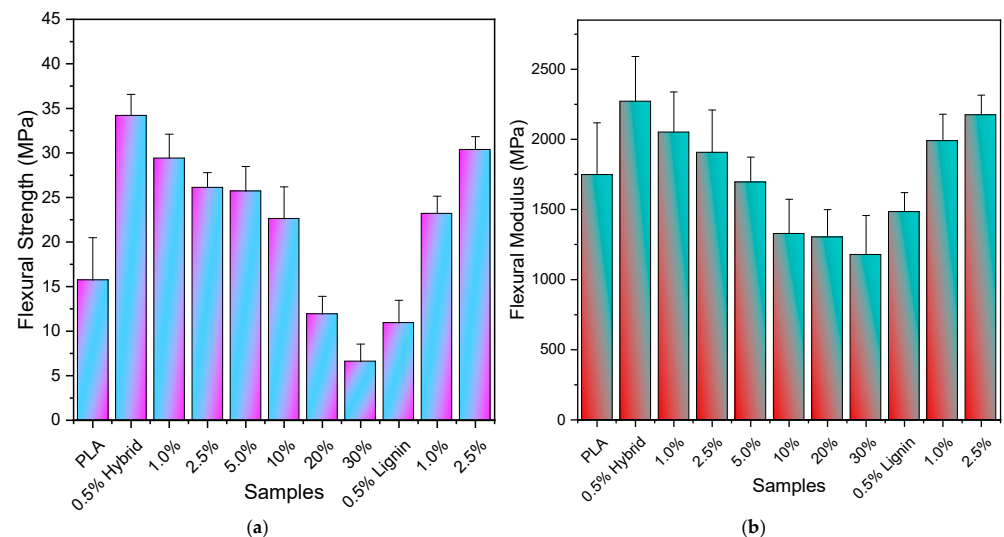


Figure 14. Flexural properties of the PLA nanocomposite materials. (a) Flexural strength, and (b) Flexural Modulus of the samples. The Flexural strength indicates the maximum flexural stress the material can withstand during the experiments.

3.4. Surface Properties

Water contact angle experiments were conducted (Figure 15). The contact angle of PLA neat was measured around 70° . The addition of the hybrid or lignin content resulted in a decrease in the water contact angle of more than 10 degrees, due to its hydrophilic character. For higher concentrations of hybrid (from 5.0%), the contact angle increased by about 10%, overcoming the one of PLA neat, owing to the hydrophobic character of MWCNTs. Additionally, comparing the materials for the same concentrations of lignin and hybrid particles, it was observed that the contact angle of PLA/hybrid nanocomposites was higher, confirming again the effect of the presence of MWCNTs.

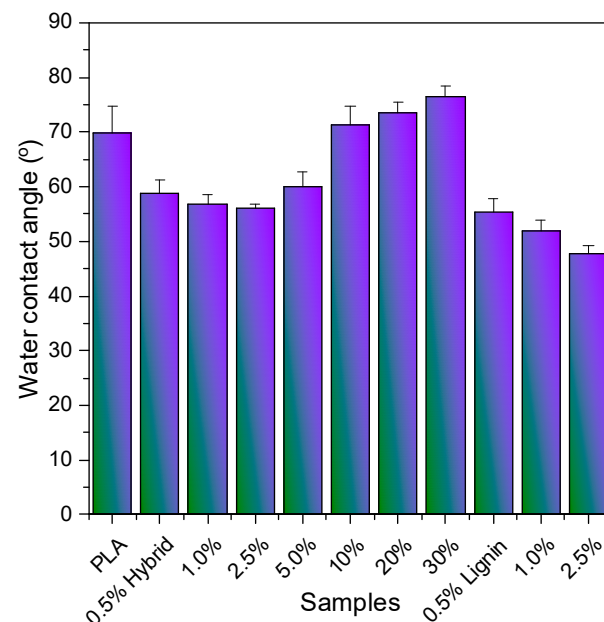


Figure 15. Water contact angle of PLA and PLA (nano)composites.

4. Conclusions

In the present work, a series of PLA-based nanocomposites were prepared, incorporating lignin/MWCNTs hybrid nanomaterial at concentrations from 0.5 to 30 wt%. In parallel,

a group of PLA/lignin composite samples from 0.5 to 2.5 wt% content was prepared as well, for comparison reasons. A two-stage procedure was developed; the preparation of masterbatches via the solution casting, followed by melt mixing. Aiming to investigate the materials, the compression molding technique was utilized, receiving thin film samples. PLA composites based on lignin exhibited a brown color, while in the case of MWCNTs-based composites, a black hue was observed. The investigation of the optical properties of materials with 1.0–30 wt% hybrid content indicated high transmittance. The DSC measurements showed nucleation effect due to the presence of MWCNTs, resulting in change in the crystallization temperature and crystalline fraction during cooling from the melt. The XRD patterns revealed the semicrystalline nature of PLA, accompanied by small differences at peaks of PLA-based composites, compared with PLA neat. Furthermore, under isothermal melt crystallization conditions, PLA nanocomposites with a high content of hybrid nanomaterial exhibited a significantly enhanced crystallization rate than PLA, and in all cases, lower crystallization half-time compared to the PLA/lignin composites. Regarding the mechanical properties of PLA, the tensile and flexural tests revealed that the addition of hybrid at 0.5 wt% content led to tougher material compared to neat PLA sample. Contact angle experiments confirmed the hydrophobic character of MWCNTs and the hydrophilic one of lignin.

In summary, the incorporation of lignin/MWCNTs hybrid nanomaterial onto the PLA matrix improved the thermal, crystallization, and mechanical properties of PLA. Where additional melting peaks appeared, at a low content of hybrid nanoparticles, also promoting crystallization by shifting the crystallization temperature from the melt towards higher temperatures, in this case, the hybrid-based nanocomposite samples exhibited significantly higher crystallization rates than the ones containing only neat lignin particles. Last but not least, the elongation at break, under the tensile tests, was slightly better for the samples that contained low hybrid content compared with the composites with low lignin content, and thus these complex series of nanocomposites can be used as substrates for engineering applications such as printed electronics.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/jcs9100560/s1>, Figure S1: Thermal transitions of PLA and PLA nanocomposites, differences between the low content of PLA nanocomposites and composites, the case of ΔH_m , ΔH_{cc} and ΔH_c ; Figure S2: Isothermal crystallization of the samples at 120 °C. (a) Relative degree of crystallinity as a function of time, (b) subsequent heating traces, and (c) crystallization half-time as a function of hybrid and lignin content.

Author Contributions: Conceptualization, methodology, investigation, formal analysis, writing—original draft, A.P. and R.O.I.; investigation, formal analysis, writing—review and editing, S.M. and S.K.; investigation, validation, writing—review and editing, A.G.; resources, validation, writing—review and editing, I.D.; resources, supervision, validation, writing—review and editing, A.Z.-K.; review and editing, E.X.; supervision, conceptualization, resources, validation, writing—review and editing, D.N.B. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The, FTIR, CIE, DSC, XRD, tensile and flexural raw data are available on Zenodo (<https://zenodo.org/records/17304798>). The rest of the data supporting this article have been included as part of the Supplementary Materials file. The rest of the data supporting this article will be available upon request to the corresponding authors, uniquely in the frame of private communication.

Conflicts of Interest: Authors (Dr. Sofia Makri, Mrs. Stefania Koutsourea, Dr. Alexios Grigoropoulos, Dr. Alexandros Zoikis-Karathanasis) were employed by the company Creative Nano PC, Author (Dr. Ioanna Deligkiozi) was employed by the company AXIA Innovation GmbH. The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest. All authors declare no conflicts of interest.

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