

Supplementary information

Solvolysis Depolymerization of Additive-Containing Poly(lactic Acid) Composites for Sustainable Ethyl Lactate Production

References in the Supplementary Information continue the numbering from the main manuscript.

SI 1 Characterization of the thermal behaviour of materials using DSC

Melting points (T_m) varied from the temperature measured for the original PLA (prior to the process) and PLA dry matter dissolved in chloroform (Table S1). Equation 3 was applied to evaluate crystallinity values for the materials before (χ_c^a) and after decomposition (χ_c^c), and for the original matrix dissolved in chloroform (χ_c^b). Differences in the crystallinity of the original samples and samples dissolved in chloroform point to structural differences [16], similar to those observed in the present samples. The specimens dissolved in chloroform showed significant structural differences (see Table S1).

Table S1 Values for T_m and the crystallinity of the samples (PLA-A-F), as determined by DSC; RSD: $2.9 \pm 0.5\%$ (three or more measurements), no statistically significant differences were observed between replicate measurements ($P > 0.05$)

Sample	T_m (°C) ^a	T_m (°C) ^b	T_m (°C) ^c	χ_c (%) ^a	χ_c (%) ^b	χ_c (%) ^c
PLA-A	150.56	150.56	n.a.	42.60	12.20	n.a.*
PLA-B	154.35	135.79	104.28; 150.11	37.28	26.36	13.02
PLA-C	149.62	151.26	149.62	40.24	25.58	0
PLA-D	161.46	162.56	n.a.	49.41	39.80	n.a.*
PLA-E	147.23	148.46	145.1	30.23	22.43	0
PLA-F	169.93	122.48	113.92	0.48	1.87	n.a.*

T_m^a - melt temperatures (°C) of the original PLA material

T_m^b - melt temperatures (°C) of the PLA samples as dry matter dissolved in chloroform

T_m^c - melt temperatures (°C) of the PLA residue

χ_c (%)^a - degree of crystallinity (%) of the original PLA material

χ_c (%)^b - degree of crystallinity (%) of the original PLA material as dry matter dissolved in chloroform

χ_c (%)^c - degree of crystallinity (%) of the PLA residue

* n.a. – not available (the PLA content and degree of crystallinity could not be determined)

T_m values were also calculated for the samples that had not fully decomposed (PLA-B, C, E, F), for which crystallization could also be evaluated of the non-dissolved parts. The PLA-A sample had completely decomposed, and the crystallinity values (original matrices) indicated it was more amorphous when dissolved in chloroform (Table S1). Sample PLA-B, after decomposition, still contained 5 wt% of the material (Table 2), according to the T_m value for the remnant tested. Hence, it might have contained a small amount of PLA and other additives (Table 1) that prevented its complete breakdown, consequently, two T_m values are given. Dissolving it in chloroform led to a rise in its amorphousness, similar to PLA-A. The PLA-C sample became more amorphous after being dissolved in chloroform. Its crystallinity at the stage after solvolysis was virtually at 0, the melting value of the remaining part reflecting the presence of the polymer and additives at a higher amount (Table 1, main text), which was equivalent to only ca 69 wt% of decomposition (Table 2). Similarly, melting temperatures (T_m) of polymer matrices remain primarily unchanged as by Mahapatro, Gorna et al., [55,56]. The PLA-D sample had decomposed entirely, despite not comprising PLA solely (Table 1). It appeared to be more amorphous than the original sample after the reaction with chloroform, since it only contained a small amount of the additive (Table 1, Table S1). The PLA-E sample also showed a greater degree of amorphousness after dissolution in chloroform compared to the original sample. According to the T_m value, the non-decomposed part (7%, w/w) could still contain a residual polymer fraction. This could also be attributed to additives and other polymers that the sample contained. The crystallinity value of the undissolved part was thus close to zero (Table S1). The PLA-F sample behaved in a more crystalline manner when dissolved in chloroform. The remnant that had not degraded (49 wt%) corresponded to the non-PLA matrix components (Table 1), which corresponded with its value for decomposition (61%; see Table 2). Unlike the other materials, it was not possible to accurately evaluate the crystallization of the non-decomposed portion, as it proved impossible to estimate the PLA and other polymeric components in percent (Table S1). However, the non-PLA constituents accounted for over 50% of the material, as evidenced by DSC in the resultant curves (Figures S1-S3). Such analysis was performed to evaluate differences in PLA crystallinity.

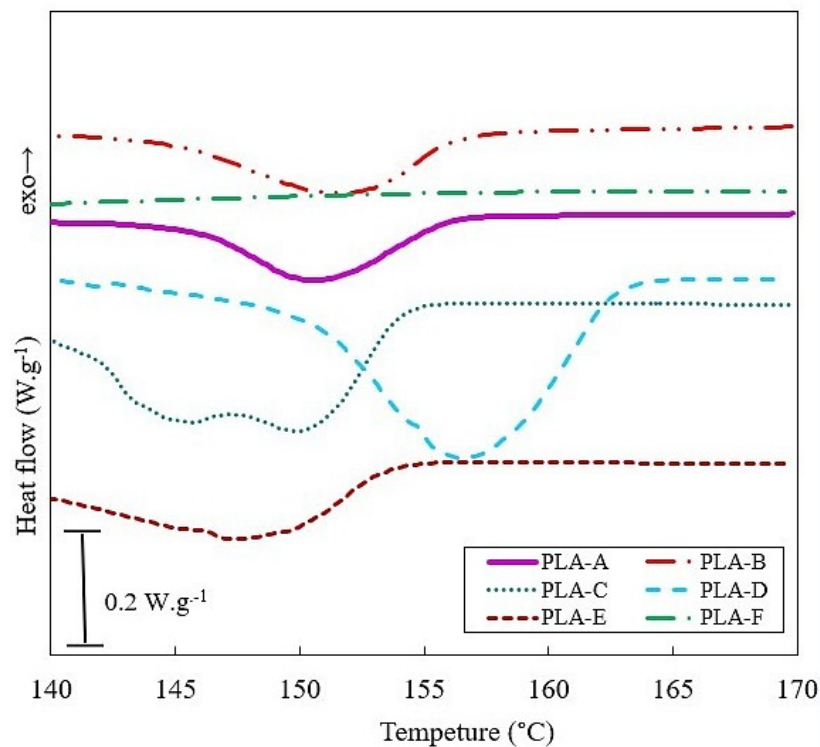


Figure S1 DSC curves (2nd heating scan) of the tested samples (PLA-A-F) in the temperature range of 140-170°C

The DSC curves in Figure S1 consider the crystalline or more amorphous nature of the individual materials and correspond to the values from Table S1. Only the PLA-F sample did not undergo the typical course of DSC analysis (straight line, see Figure S2). This is because the material contained a larger part of the non-PLA matrix – cellulose (see Table 1). Cellulose could be identified in the first heating area (Figure S1). The course of the DSC analysis of the sample after the decomposition reaction is also shown here, which indicates that the material, particularly part of the cellulose fraction, may have been partially decomposed, whereas the PLA was completely degraded.

In summary, the glass transition on the DSC curve is difficult to detect in cases of increased crystallinity in the PLA sample. The transition region (T_g) exhibits lower intensity for crystalline PLA samples and PLA composites due to the reduced chain mobility in the presence of crystalline regions (metastable phase), whose properties depend on the crystallization conditions, as described in the literature [6]. PLA with an amorphous structure exhibits cold crystallization (T_{cc}). At elevated temperatures, PLA polymer molecules, as well as those in PLA-based composite materials, tend to rearrange from the amorphous phase into a more stable crystalline state, an exothermic process. This is a recrystallization process of PLA. In the composite material PLA-C, the cold crystallization transition upon heating above the glass transition temperature was observed at a lower

temperature (110.6 °C) compared to the neat pure PLA (118.3 °C) [7]. This behaviour is attributed to the presence of CaCO₃ filler particles, which act as nucleating agents. In the melting temperature (T_m) region of the amorphous composite material (PLA-C), a double peak is observed (approximately 145 °C and 150 °C), corresponding to the α' and α crystalline forms [8]. The α' crystalline form has been described as a disordered variant of the α-form [9,57]. For the amorphous PLA-A material, the melting temperature (T_m) is 150.5 °C (Figure S1, Table S1), corresponding to the α-crystalline form. The melting temperature (T_m) of the crystalline PLA-C composite is approximately 1 °C lower (149.62 °C) than that of the crystalline pure PLA-A (150.56 °C). The PLA composite also exhibits a slightly lower degree of crystallinity χ_c at 40.24%, compared to the crystalline neat PLA-A sample (42.60%), which is consistent with previously published findings [8]. The PLA-C composite blend contains 4% wt% of the PLA/PEG plasticizer. Plasticizers are widely used to improve the ductility, flexibility, and processability of polymers. According to the literature, an effective plasticizer should reduce the glass transition temperature (T_g), melting temperature (T_m), and degree of crystallinity (χ_c) in the semicrystalline PLA matrix [58]. The DSC analysis confirmed the effect of the plasticizer on the T_g behaviour.

Figure S3 details the thermal analysis by DSC of the original PLA materials in the form of dry mass after dissolving in chloroform. Most of the samples showed enhanced amorphousness, varying in accordance with the given material and its additives. Related factors could comprise their structural arrangements, the extent to which the polymer had degraded, and the other substances within them (Tables 1, 2, main text). DSC thus confirmed that differences existed in the structures of the PLA samples, brought about by the admixture present and the consequent degree of decomposition during the solvolysis reaction. In line with the DSC observations, the effect of cellulose on thermal stability has been reported by literature [53], cellulose fibers improve the thermal stability of polymer matrices. This corresponds with the present findings, suggesting reduced susceptibility of the matrix to hydrolysis.

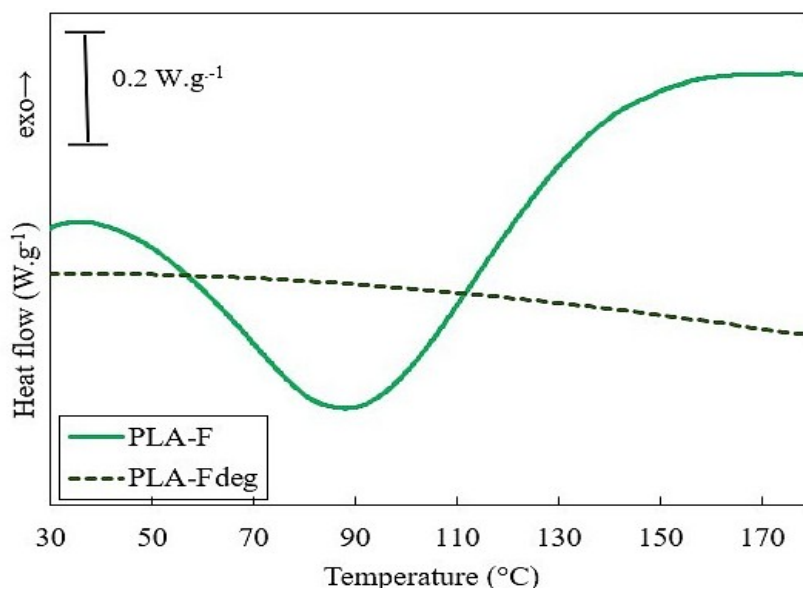


Figure S2 DSC curves (1st heating scan) of tested PLA-F before and after the solvolysis experiment

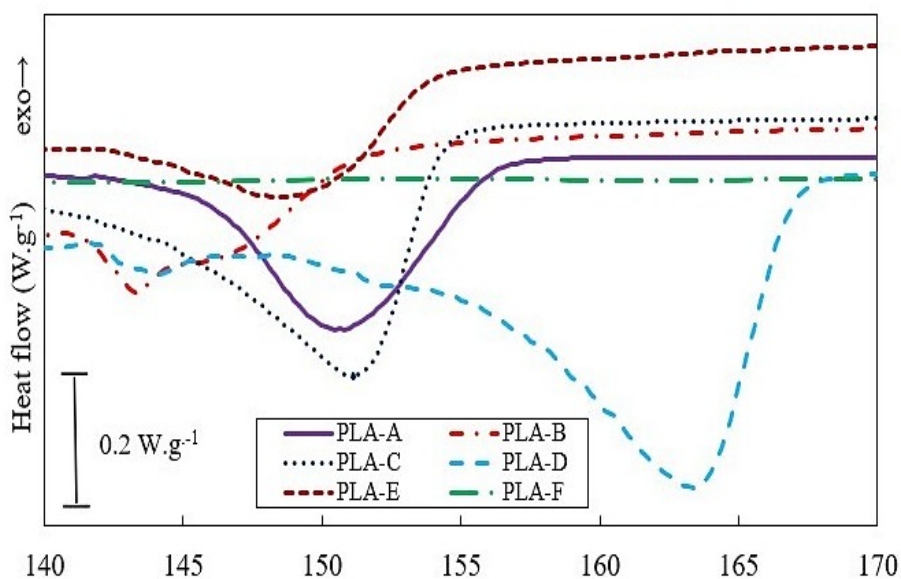


Figure S3 5 DSC curves (2nd heating scan) of the original samples (PLA-A-F) in the form of dry mass dissolved in chloroform

SI 2 TGA Analysis of PLA Materials

Thermogravimetric analysis (TGA) of the PLA materials revealed distinct degradation behaviours depending on the sample composition and the presence of additives. The pure PLA-A material exhibited a single-step decomposition, occurring predominantly between 300 and 350 °C, with an onset temperature of approximately

305 °C [3,4,42,47–52,55,56,59–61]. After solvolysis, this sample was fully decomposed, leaving no detectable residues.

In contrast, the PLA-B sample displayed a multi-step degradation profile. An initial weight loss occurred between 100 and 200 °C, likely due to low-molecular-weight substances or residual moisture [3,4,55,56,59–61]. The main degradation of PLA took place between 250 and 350 °C, corresponding to approximately 95% mass loss. A third step between 550 and 700 °C reflected the decomposition of the CaCO₃ filler into CaO and CO₂ [16,24–26]. Following solvolysis, the residual CaCO₃ content increased from 1% to roughly 35% of the remaining material.

The PLA-C material exhibited initial mass loss in the range of 130–150 °C, which was attributed to the presence of the PEG-based plasticizer and residual moisture. The main degradation step occurred between 250 and 350 °C, with a partial PLA decomposition of approximately 69%. The CaCO₃ content decreased from 10% in the original sample to 0.6% post-solvolysis, reflecting the selective removal of the polymer matrix. The plasticizer in PLA-C also contributed to a slightly lower decomposition onset compared to pure PLA [24,37,38].

PLA-D showed a two-phase degradation pattern, with the first mass loss observed between 150 and 250 °C, likely arising from low-molecular-weight substances or DETPE-based plasticizer, and a second phase between 330 and 380 °C, reflecting the degradation of the PLA matrix and minor crystalline regions. CaCO₃ and carbon black residues were detected between 550 and 800 °C [4,24,25].

Similarly, PLA-E displayed an early weight loss between 100 and 200 °C, followed by primary PLA degradation from 250 to 400 °C, corresponding to approximately 93% of the polymer matrix. The residual fraction of CaCO₃ increased from 1% to 5.5%, and carbon black was also present in the remnants.

PLA-F exhibited early mass loss between 100 and 250 °C, reflecting a substantial content of cellulose (>50%) and low-molecular-weight components. The PLA portion decomposed between 230 and 320 °C, with an onset at ~240 °C. Decomposition of CaCO₃ occurred between 550 and 700 °C, increasing the residual fraction from 3.5% to 13.8%. The higher thermal stability observed for PLA-F is consistent with its higher cellulose content, as also confirmed by DSC measurements [53].

Overall, TGA results indicate that PLA degradation predominantly occurred in the temperature range of 150–400 °C, attributed to moisture-induced and intramolecular degradation reactions [35,36]. The thermal stability of

the materials was strongly influenced by the presence of fillers and plasticizers, which generally reduced decomposition temperatures, whereas cellulose content improved stability. Residual mass analyses confirm the presence of all additives and allow quantitative comparison of samples before and after solvolysis.

Figures 4 and 5 illustrate the TGA curves of the original PLA materials and post-solvolysis samples, respectively, highlighting the differences in decomposition behaviour and residual fractions. Quantitative data are summarized in Tables S2 and S3. This detailed sample-specific analysis complements the main text (Section 3.2.2.2) and provides additional information for reproducibility.

Sample	Initial Mass	Main PLA degradation	PLA degradation	Onset	Notes
	Loss (°C)	(°C)	(%)	(°C)	
PLA-A	/	300 - 350	100	305	Fully decomposed, trace residue
PLA-B	100 -200	250 - 350	95	263	Multi-step, residual CaCO ₃ : 35 %
PLA-C	130 - 150	250 - 350	69	257	PEG plasticizer, CaCO ₃ 0.6 %
PLA-D	105 - 250/ 330 - 380	330 - 380	100	258	Two-phase, minor crystalline
PLA-E	100 - 200	250 - 400	93	161	Residual CaCO ₃ : 5.5 %, carbon black
PLA-F	100 - 250	230 - 320	61	240	High cellulose, residual CaCO ₃ : 13.8 %

Table S2 Quantitative TGA data of PLA A-F

Sample	CaCO ₃	Carbon Black	Other Inorganic	Notes
	(%)	(%)		
PLA-B	35	trace	/	Residual after ~ 95% degradation
PLA-C	0.6	/	/	Residual after ~ 69% degradation
PLA-E	5.5	trace	/	Residual after ~ 93% degradation
PLA-F	13.8	/	/	High cellulose prevents full PLA decomposition

Table S3 Residual composition post-solvolysis

SI 3 FTIR analysis of PLA composites

In order to verify that PLA was indeed the core component of the matrix (excluding the PLA-F sample), FTIR analysis was performed. This involved the original raw PLA materials (Figures S4, S5), samples dissolved in chloroform (Figures S6, S7) and non-disintegrated/undissolved parts of samples (PLA-B, C, E, and F; see Figures S8, S9). Comparing the FTIR spectra for all of the original PLA-A-F materials revealed that they were virtually identical, with peaks evident at 1752, 1454, 1211, 1184, 1085 and 1047 cm^{-1} [2,3]; and only slight differences were revealed in the fingerprint area (around 700 and less cm^{-1} ; Figures S4, S5); [62–64]. The most prominent peak was in region 1752 cm^{-1} , associated with COO- stretching of carboxyl groups, which correlated with other characteristic peak vibration at 1211-1184 cm^{-1} and 1085 cm^{-1} corresponding to C-CO-C vibration (ester group) [4–8]. Peaks observed at ca 2950 and 3000 cm^{-1} pertained to the asymmetric and symmetric stretching vibrations of the CH_2 group typical for PLA (data not shown). Thus, all tested PLA samples contained the polylactide matrix, as also evidenced by the previously cited literature.

It is important to emphasize that the characteristic peaks of the PLA matrix remain consistent across Figures S4 - S9, as all samples are based on the same PLA material. However, in solvolysis-treated samples (Figures S8, S9), the intensity of these bands is reduced due to degradation processes (1752, 1454, 1211 cm^{-1} etc).

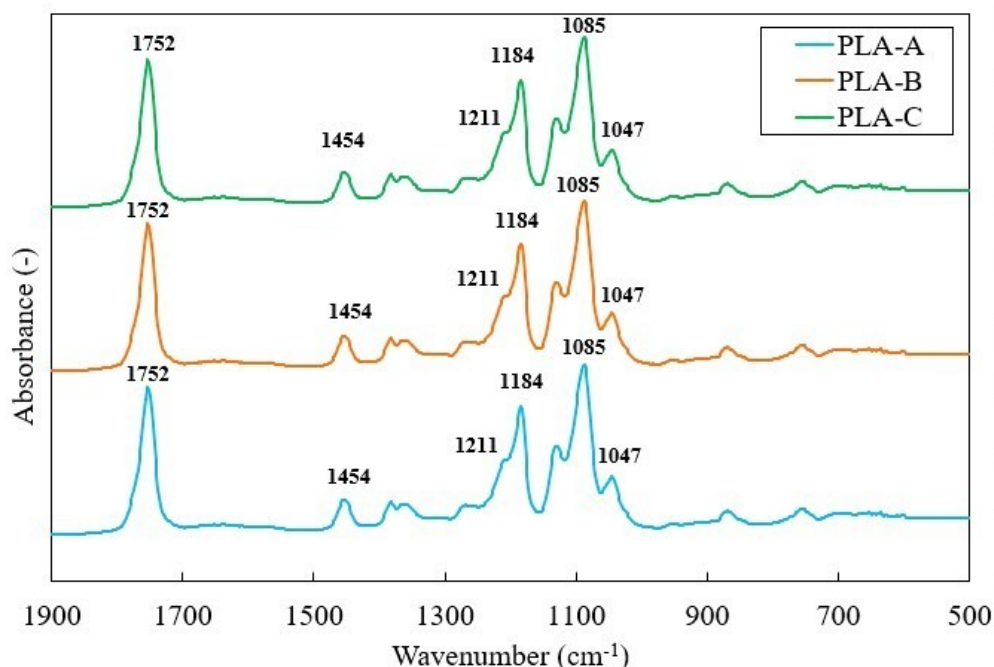


Figure S4 FTIR spectra for the input raw PLA materials (PLA-A-C) with the most significant polylactide peaks

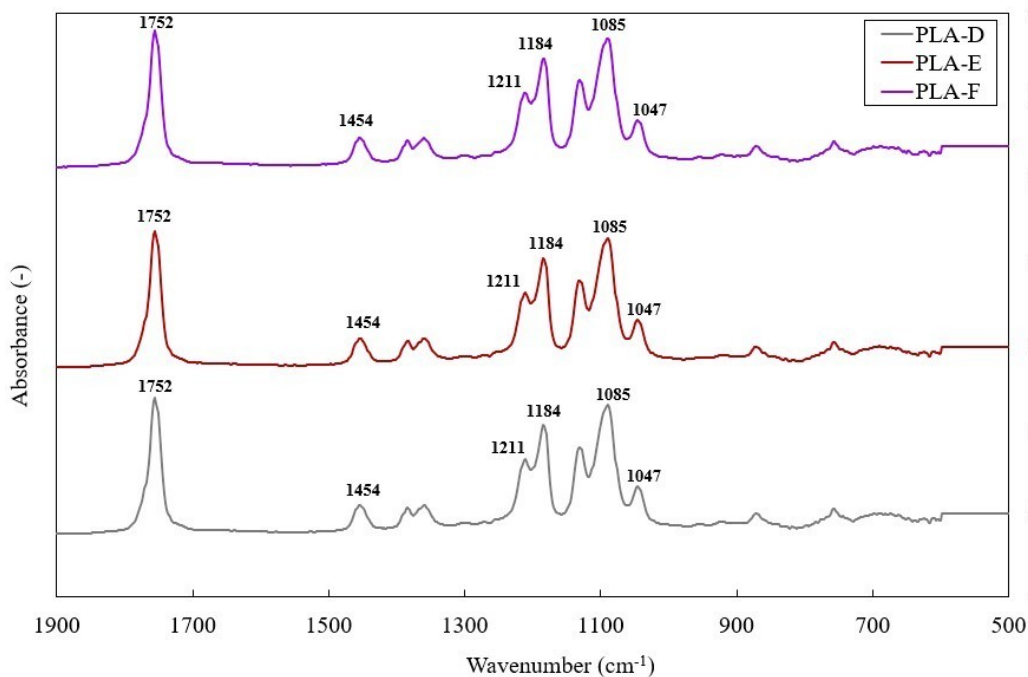


Figure S5 FTIR spectra for the input raw PLA materials (PLA-D, PLA-E) with the most significant polylactide peaks

The FTIR spectra for the PLA samples dissolved in chloroform (Figures S6, S7) showed notable differences from those for the original matrices (Figures S4, S5). Changes in the intensities and shapes of peaks were observed in regions at ca 1650–1750 cm^{-1} and 1000–1210 cm^{-1} . A distinct peak was also present at ca 721 cm^{-1} in spectra for the PLA-E and PLA-F samples (Figure S5), possibly related to the presence of another organic substance within the samples. Younes, Cohn, and others report two characteristic peaks associated with the crystalline and amorphous phases of PLA, observed at 755 cm^{-1} and 875 cm^{-1} . The peak at 755 cm^{-1} can be assigned to the crystalline phase, whereas peak at 875 cm^{-1} corresponds to the amorphous phase [65–67], which supports the results presented herein.

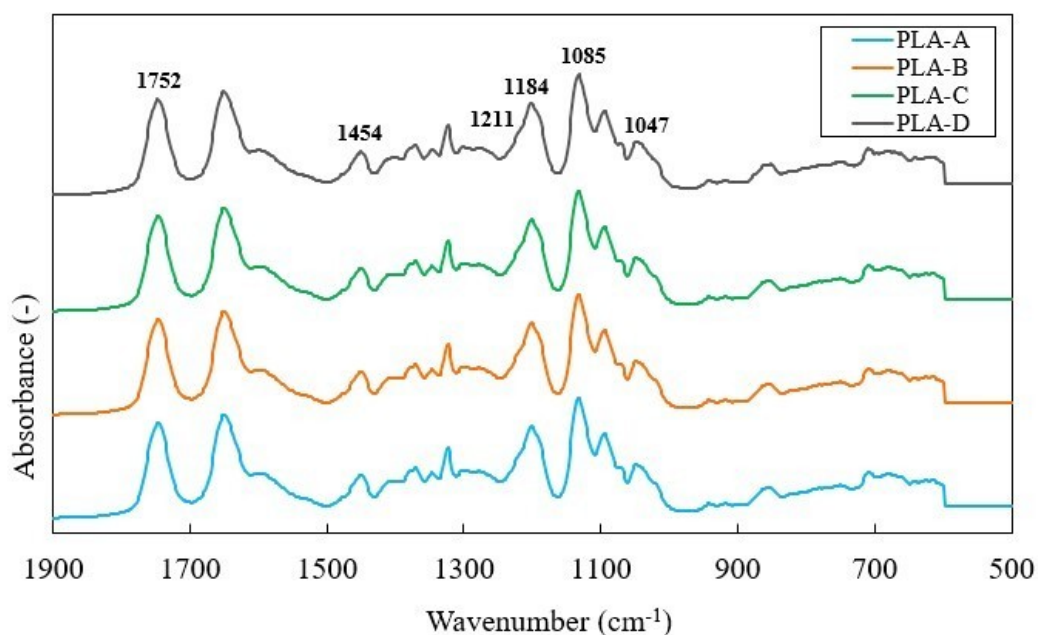


Figure S6 FTIR spectra for the PLA samples as dry mass dissolved in chloroform (PLA-A-D), with the most significant peaks recorded

The heights of peaks varied between the PLA-A, PLA-B, PLAC, PLA-D and PLA-E, PLA-F samples (Figures S6, S7) at 1700–1750 cm^{-1} , a region corresponding to carboxyl groups in the polymer chain. Additional deviations from major peaks for PLA (Figures S4, S5) were attributed to variations in the structures of the materials. These differences arose through the distinct compositions of the materials and their forms (e.g. granules, foil, and textile), as well as the presence of additives or secondary polymers in the samples (see DSC and TGA analyses, Figures 6-9, Table S1). The differences in the analysed materials could also result from the degree of mixing with additives and other polymer matrices. These structural variations are directly related to differences in chain arrangement, length, and other molecular characteristics, as reflected in the GPC (Table 3). FTIR analysis of the PLA remnants (i.e. the undissolved portions, see Figures S8, S9) revealed distinct and pronounced peaks, particularly for the PLA samples B, C, E and F, resulting from their crystalline structures instigated by the CaCO_3 inorganic filler and carbon black, which contrasted with those seen for the original PLA material (Figures S4, S5). This finding was further supported by DSC (Table S1), confirming that the structural differences between the tested materials were caused by their composition (Table 1).

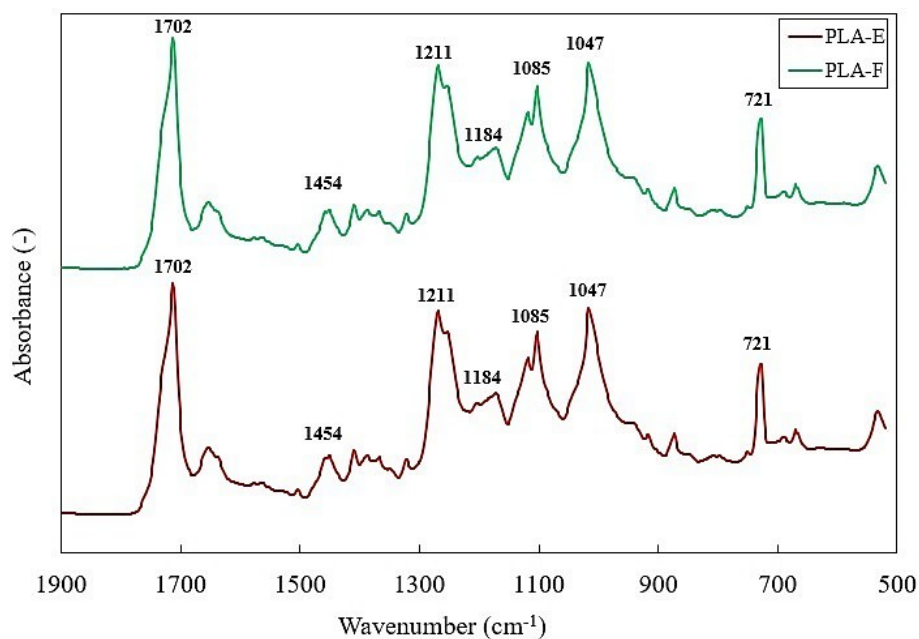


Figure S7 FTIR spectra for the PLA samples as dry mass dissolved in chloroform (PLA-E, PLA-F), with the most significant peaks recorded

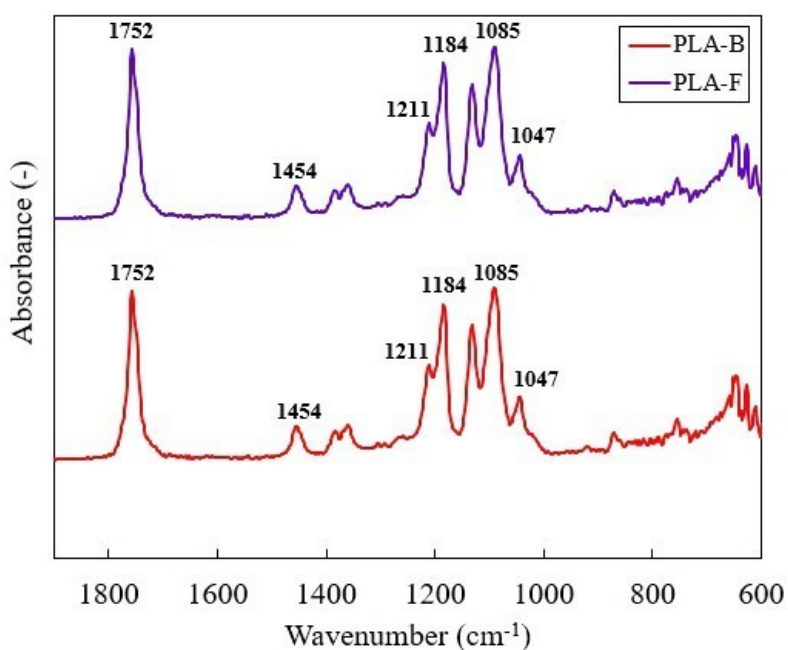


Figure S8 FTIR spectra for the remnants of the PLA materials (PLA-B, PLA-F) after the decomposition process, with the most significant polylactide peaks recorded

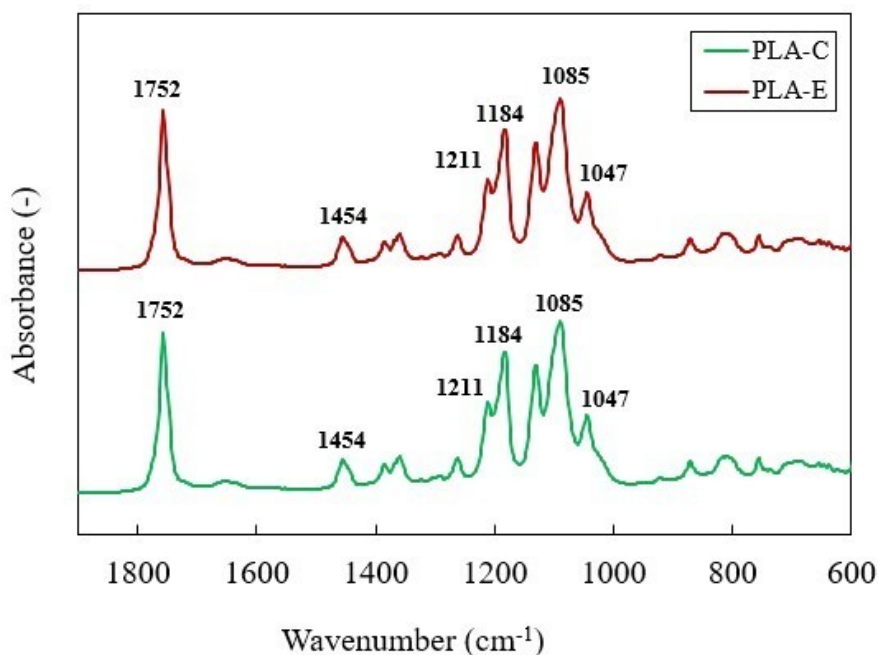


Figure S9 FTIR spectra for the remnants of the PLA materials (PLA-C, PLA-E) after the decomposition process, with the most significant polylactide peaks recorded

XRD and FTIR analyses confirmed that all tested materials were based on PLA, though structural variations were observed due to the presence of additives and secondary polymers. These components influenced crystallinity and peak intensities, particularly in residual fractions after solvolysis. However, the overall degradability of the materials was largely retained, indicating that the additives did not significantly inhibit depolymerization under the applied conditions.

SI 4 Elemental analysis of PLA composites

Elemental analysis using the EDX-XRF method confirmed the presence of CHON-based polymer matrix in all the PLA (A-F). Calcium was detected in a small amount in PLA-B, D, E and F, with a notably higher content in PLA-C. Other elements appeared only in trace amounts, likely below the detection limit of 0.1% (Table S4), and thus are considered insignificant for this study. PLA is classified as a CHON polymer matrix, while secondary polymers were identified in the PLA-D and PLA-E samples, with cellulose in PLA-F and the carbon black additive (high in carbon content) in the PLA-B and PLA-F specimens. The applied analytical technique enabled both identification and semi-quantitative evaluation of the polymer matrices and additives, including calcium carbonate (CaCO_3) and carbon black, in accordance with the target additive concentration (Table S4). These results are consistent with the support findings obtained from FTIR, DSC, TGA, and XRD analyses.

Table S4 Elemental analysis of PLA (A-F) samples via the EDX-XRF method, RSD: $1.1 \pm 0.2\%$; no statistically significant differences were observed ($P > 0.05$)

Sample	CHON* (%)	Ca (%)	Fe (%)	As (%)	In (%)	Sb (%)	Sn (%)	< 0.005 (%)
PLA-A	99.99	/	/	/	0.010	/	/	/
PLA-B	98.87	1.081	/	0.0105	0.0095	0.0079	0.0078	Ti, Nb, Mo
PLA-C	89.54	9.881	0.034	0.023	0.011	/	0.023	Nb, Mo
PLA-D	98.36	1.532	/	/	0.016	0.075	/	W, Zr, Mo
PLA-E	98.84	0.89	0.051	0.012	0.054	0.028	0.071	Ti, Zn, Zr
PLA-F	96.41	3.48	/	0.054	0.023	0.014	0.009	Al, Pb, Bi

CHON* - polymer matrices

% - weight percentage (w/w)

Studies by Chang et al [68], Garskaite et al and Lin et al on PLA-based composites, including those incorporating hydroxyapatite and chitosan coatings, have confirmed the presence of calcium using EDX analysis [69,70]. These findings align with our results, demonstrating that EDX is an effective method for detecting calcium-containing additives in PLA materials.