



Influence of biochar on the physico-mechanical properties and biodegradation of PLA films



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This study investigated how pyrolysis temperature and walnut-shell biochar content affect the structural, thermal and biodegradation behaviour of polylactic acid (PLA) films. Biochars produced at 400 and 700 °C were incorporated at 2 and 10 wt.%. Increasing pyrolysis temperature transformed biochar from hydrophobic to hydrophilic, increased its specific surface area from 2.1 to 356 m² g⁻¹ and pore volume by 395%, and decreased its water contact angle by 16%. These pyrolysis-dependent changes altered particle–matrix contact and PLA structural ordering. At 10 wt.% loading, low-temperature biochar increased initial crystallinity to 8.0%, whereas high-temperature biochar reduced it to 2.0% and caused the largest reduction in thermal stability. Under thermophilic composting, low-temperature biochar at 2 wt.% yielded the highest biodegradation degree (77.2% after 16 weeks), whereas at 10 wt.% it produced the slowest response. At this higher loading, films containing high-temperature biochar biodegraded faster than those containing low-temperature biochar. The results demonstrate that the effect of biochar on PLA biodegradation depends on the interaction between pyrolysis temperature and filler content, mediated by wettability, pore structure, particle–matrix contact and PLA structural ordering.

Poly(lactic acid) (PLA) is one of the most widely used biodegradable bioplastics and is commercially available in multiple grades that differ in molecular weight, optical clarity and blending strategy. The degradation behaviour of PLA has already been investigated in a broad range of environments^{1–8}.

Many studies have assessed biodegradation by monitoring mass loss. However, such data primarily describe the initial phase of disintegration and do not capture the subsequent microbial conversion of the organic fraction of the biopolymer. In commercial applications, PLA, like other polymeric materials, is rarely used in its neat form. Various additives are incorporated to tailor its properties and processing characteristics. In view of current performance demands and regulatory frameworks for plastic materials, modern functional additives are expected to comply with circular sustainability principles and stringent environmental safety criteria. For biodegradable materials, it is particularly advantageous if additives can enrich the degradation environment over short or long timescales. Calcium carbonate (CaCO₃) represents one such additive. It is a mineral filler with a potential heterogeneous nucleation effect in semi-crystalline polymers, which could, in principle, slow down biodegradation. However, our previous studies led

to a different conclusion: the presence of CaCO₃ accelerated the microbial degradation kinetics of PLA even in environments with low degradation potential^{9,10}. In addition, Miftah et al.¹¹, Melo et al.¹² reported a long-term positive effect of CaCO₃ on soil stability and crop growth. Biochar is another intensively discussed additive in agricultural applications. Biochar is a carbon-rich material with high chemical and thermal stability. Its incorporation into soil can enhance water and nutrient retention^{13–16}. It can also increase cation-exchange capacity and improve nitrogen use efficiency, thereby reducing the need for mineral fertiliser inputs^{17,18}. In addition, it buffers soil acidification and, owing to its porous structure, can stimulate microbial activity and functional diversity in the rhizosphere^{19,20}. Zheng et al.²¹ and O’Laughlin et al.²² further reported that biochar amendment may mitigate greenhouse gas emissions from soils, particularly nitrous oxide and methane, making it a highly promising biogenic component for improving soil quality. Similar to CaCO₃, biochar can, under suitable processing conditions, increase the degree of crystallinity of PLA, which in turn enhances the mechanical properties as well as the thermal and dimensional stability of PLA-based materials. Bajwa et al.²³ and Pudielko et al.²⁴ observed that biochar increases water uptake in PLA biocomposites, a phenomenon

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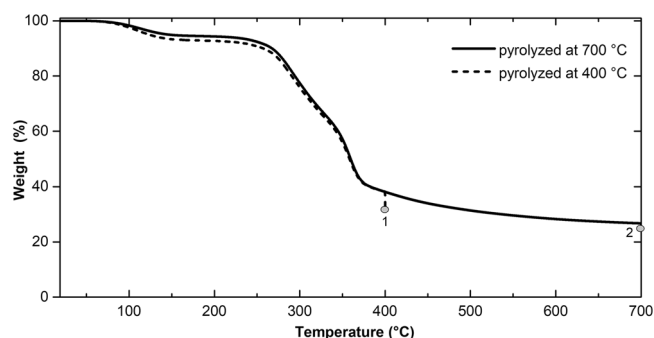


Fig. 1 | Thermal degradation during the production of biochar from walnut shells.

that may accelerate hydrolytic degradation, which is the dominant mechanism governing PLA biodegradation kinetics²⁵. Biochar can therefore simultaneously affect both the physico-mechanical properties of PLA films and their biodegradation kinetics.

The properties of biochar and its performance in polymer composites depend strongly on the biomass feedstock and pyrolysis conditions, which determine carbon content, surface chemistry, specific surface area, porosity and ash composition. Aup-Ngoen et al.²⁶ and Pudelko et al.²⁴ demonstrated that the mechanical, structural and thermal properties of PLA-based composites are strongly affected by the origin and characteristics of biochar. Das et al.²⁷ showed that a higher carbon content and larger specific surface area of biochar can increase the strength and elastic modulus of polymer composites. The chemical composition and functional performance of biochar also depend on its production method, particularly pyrolysis temperature, which affects polarity, pore architecture and mineral composition. Paleri et al.²⁸ reported improved mechanical performance of polypropylene biocomposites containing biochar produced at 700 °C compared with low-temperature biochar. Lignocellulosic residues, including walnut shells, are suitable feedstocks for biochar production because their intrinsic structure can generate porous carbon materials with high specific surface area and water-sorption capacity, as reported by Liu et al.²⁹. Pyrolysis therefore provides a route for the valorisation of agricultural residues while enabling the adjustment of biochar properties relevant to polymer processing, composite performance and environmental applications.

This study examines the influence of biochar production temperature and filler content on the physical, mechanical, thermal and biodegradation behaviour of PLA films under thermophilic composting conditions. Walnut-shell biochars prepared under low- and high-temperature pyrolysis conditions were used to investigate how pyrolysis-dependent differences in biochar surface characteristics, porosity and wettability influence the structure, processing response and degradation kinetics of PLA-based films. The study further evaluates how the effect of these biochar properties changes with filler content and aims to identify the coupled mechanisms governing the biodegradation behaviour of PLA/biochar films.

Results

Thermal analysis of biochar (TGA)

Several distinct regions can be identified during the thermal degradation of walnut shells (Fig. 1). The initial mass loss between 50 and 150 °C corresponds to the decomposition of volatile organic carbon components. According to Zornozi et al.³⁰, the decrease observed between 200 and 380 °C is attributed to the decomposition of labile organic carbon components, including aliphatic carbon (primarily cellulose). This region, together with the decomposition of aromatic and recalcitrant carbon (primarily lignin) occurring between 380 and 475 °C, represents the zone of maximum weight loss. In the temperature range of 475–600 °C, corresponding to the continued degradation of aromatic carbon, including polycondensed lipids, no further significant changes were observed. Because the samples remained stable during the 90 min hold at the selected pyrolysis temperatures (points

Table 1 | Composition of biochar produced from walnut shells

Chemical element	Biochar pyrolyzed at 400 °C	Biochar pyrolyzed at 700 °C
Ash Content	1.8%	2.6%
C	76.2%	74.4%
O	21.1%	22.3%
N	0.21%	0.19%
P	0.02%	0.04%
K	0.22%	0.15%
Mg	0.02%	0.02%
Ca	0.46%	0.28%
S	0.01%	0.01%
Hg	0.06 mg kg ⁻¹	0.05 mg kg ⁻¹
As	<1 mg kg ⁻¹	<1 mg kg ⁻¹
Be	<0.1 mg kg ⁻¹	<0.1 mg kg ⁻¹
Cd	0.05 mg kg ⁻¹	0.05 mg kg ⁻¹
Co	1.93 mg kg ⁻¹	<1.00 mg kg ⁻¹
Cr	<5 mg kg ⁻¹	5.8 mg kg ⁻¹
Cu	8.1 mg kg ⁻¹	6.8 mg kg ⁻¹
Mn	30 mg kg ⁻¹	<10 mg kg ⁻¹
Mo	3.98 mg kg ⁻¹	5.35 mg kg ⁻¹
Ni	2.3 mg kg ⁻¹	2.7 mg kg ⁻¹
Pb	<5.0 mg kg ⁻¹	<5.0 mg kg ⁻¹
V	<5.0 mg kg ⁻¹	<5.0 mg kg ⁻¹
Zn	12.6 mg kg ⁻¹	12.6 mg kg ⁻¹

1 and 2), the overall differences in mass loss between the two variants were minimal. Consequently, the yield of both biochar types produced was comparable. Photographs of structure of walnut-shell biochars produced at 400 and 700 °C are provided in Supplementary Figs. S1 and S2.

Chemical composition of biochar

The results of the chemical composition analysis are presented in Table 1. Biochar produced at 700 °C exhibited a slightly lower total carbon content than biochar produced at 400 °C (74.4 vs. 76.2 wt.%), together with a higher ash content (2.6 vs. 1.8 wt.%). An increase in the carbon fraction with increasing pyrolysis temperature is frequently reported. However, this relationship is not necessarily monotonic. It also depends on feedstock composition, process atmosphere, heating programme, residence time and the relative contribution of the mineral fraction. Zornoza et al.³⁰ demonstrated that both pyrolysis temperature and feedstock substantially affect the stability and nutrient composition of biochars, whereas Elnour et al.³¹ reported that thermal treatment affects the evolution of ash content and microstructural characteristics. In the present study, the small decrease in the mass-normalised carbon content of B700 may be associated with the relative enrichment of ash-forming mineral constituents in the solid residue at the higher treatment temperature. Differences in the removal of volatile carbon- and oxygen-containing fractions during pyrolysis may also have contributed. The observed difference in bulk carbon content should therefore not be interpreted as a lower degree of carbonisation of B700. Rather, it reflects the final mass-normalised composition of the solid residue after the more severe thermal treatment. The markedly different porous structures of B400 and B700, discussed in the following section, provide independent evidence of the substantially greater structural reorganisation induced at 700 °C. Biochars derived from walnut shells are generally characterised by a high carbon content, but their ultimate composition depends strongly on the biomass composition and pyrolysis conditions. Yin et al.³² who investigated biochar obtained from co-pyrolysis of sewage sludge

Fig. 2 | SEM micrograph of milled walnut-shell biochar produced at 400 °C. B400 denotes biochar produced at 400 °C.

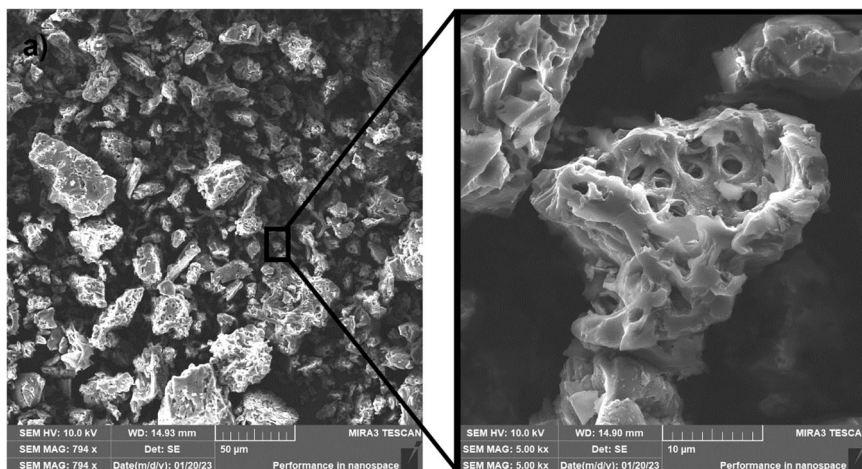
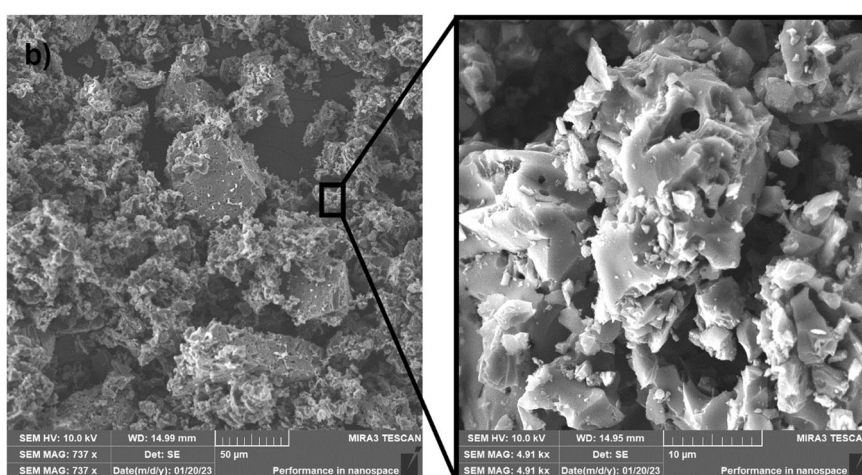


Fig. 3 | SEM micrograph of milled walnut-shell biochar produced at 700 °C. B700 denotes biochar produced at 700 °C.



and walnut shell, likewise demonstrated that the chemical composition of walnut-shell-containing biochars is process-dependent. The substantially greater porosity and specific surface area of B700 therefore provide a more relevant indication of the higher treatment severity than the small 1.8 percentage-point difference in its bulk carbon content.

Apart from the modest differences in total carbon and ash contents, no major systematic changes were observed in the contents of O, N, P, K, Mg, or in the analysed trace-element concentrations between the two biochars. Minor variations in individual elements are expected because the reported values represent mass-normalised concentrations in solid residues obtained under different thermal-treatment conditions. Importantly, the measured concentrations of the analysed potentially toxic elements were below the limit values stated in the EBC-Agro and EBC-FeedPlus standards consulted for this study.

Size and distribution of biochar

SEM micrographs of the milled biochars (Figs. 2 and 3) confirmed that the porous architecture of the walnut shells was retained after grinding. The mean particle size was 41 µm for B400 and 52 µm for B700. The corresponding particle-size distribution curves are provided in Supplementary Figs. S3 and S4. Both biochars exhibited broadly similar distribution profiles; therefore, particle size was not considered the primary variable responsible for the subsequent differences in the properties of the PLA/biochar films. The detailed distribution curves are presented in the Supporting Materials because they provide supporting characterisation of the filler rather than the central evidence for the biodegradation mechanism.

Specific surface area and porosity of biochar

Specific surface area and porosity are shown in Figs. 4–7. Biochar produced at 400 °C exhibited markedly lower porosity and specific surface area compared to biochar pyrolyzed at 700 °C. Low-temperature biochar had a specific surface area of 2.1 m² g⁻¹ and a total pore volume of 0.102 cm³ g⁻¹, whereas high-temperature biochar exhibited a specific surface area of 356 m² g⁻¹ and a pore volume of 0.505 cm³ g⁻¹. These substantial differences are attributed to limited lignin decomposition at lower pyrolysis temperatures. Zhao et al.³³ and Elnour et al.³¹ reported similar trends during pyrolysis of apple tree branches and date palm residues, where specific surface area remained minimal at 400 °C but increased significantly at 700 °C alongside enhanced porosity. For biochar produced at 400 °C, the surface area and pore volume showed gradual increases within the mesopore range of 2–32 nm, with no distinct predominance of any particular pore size class. In contrast, high-temperature biochar exhibited the highest pore concentration in the micropore range of 1–8 nm, with surface area and pore volume several-fold higher than those of biochar produced at 400 °C.

Contact angle of biochar

The water contact-angle results are shown in Fig. 8. A contact angle of 90° is commonly used as a practical threshold between hydrophilic and hydrophobic surface behaviour. Values below 90° indicate preferential wetting by water, whereas values above 90° indicate limited water affinity. Under the present measurement conditions, B700 exhibited a contact angle of 79.1 ± 1.3° and was therefore classified as hydrophilic, whereas B400 exhibited a contact angle of 94.5 ± 0.9° and showed hydrophobic behaviour.

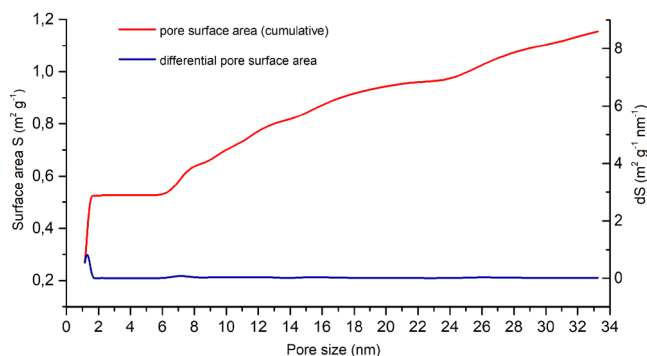


Fig. 4 | Pore surface area versus pore size for walnut-shell biochar produced at 400 °C.

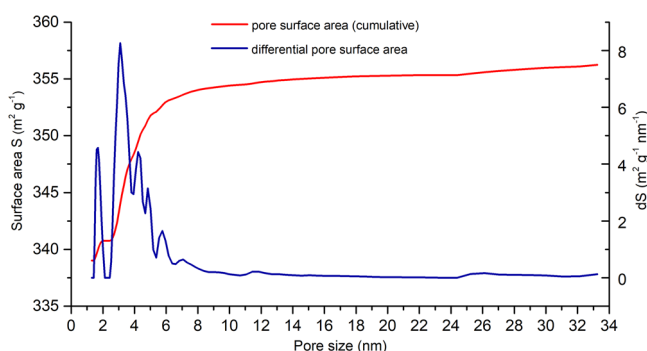


Fig. 5 | Pore surface area versus pore size for walnut-shell biochar produced at 700 °C.

The difference in wetting behaviour is consistent with the markedly different pore architectures of the two biochars. B700 exhibited a much larger specific surface area ($356 \text{ m}^2 \text{ g}^{-1}$) and total pore volume ($0.505 \text{ cm}^3 \text{ g}^{-1}$) than B400 ($2.1 \text{ m}^2 \text{ g}^{-1}$ and $0.102 \text{ cm}^3 \text{ g}^{-1}$, respectively). The high-temperature treatment therefore generated a substantially more accessible porous carbon structure, which can facilitate wetting and capillary water accommodation. In contrast, the lower surface area and lower pore volume of B400 limited the accessible solid–water contact area and were associated with its hydrophobic response.

This interpretation agrees with the literature. Liu et al.³⁴ and Mao et al.³⁵ identified biochar structure, surface area, porosity and the abundance of polar oxygen-containing groups as important parameters controlling wetting behaviour. Gray et al.³⁶ similarly related the higher water sorption of bark-derived biochar to its more developed porous structure. Zornoza et al.³⁰ reported that the hydrophobicity of biochar produced from several feedstocks decreases with increasing pyrolysis temperature, while Das et al.³⁷ associated the lower water affinity of low-temperature biochars with limited specific surface area, smaller pore volume and the presence of aliphatic surface structures. In agreement with these trends, Usevičiūtė et al.³⁸ observed that pyrolysis at 700 °C substantially reduced the water contact angle of wood-derived biochars compared with low-temperature pyrolysis.

In the present study, the bulk oxygen contents of B400 and B700 were comparable, 21.1 and 22.3 wt.%, respectively. Ash contents were also similar, 1.8 and 2.6 wt.%, respectively. The substantially different contact angles are therefore more consistently associated with the pronounced differences in accessible surface area and pore volume than with a major difference in bulk elemental composition. The contact-angle results consequently provide direct experimental evidence that pyrolysis temperature altered the water affinity of the biochar surface available to the external environment.

For the PLA composites, this result should be interpreted as a difference in the potential availability and local distribution of water at the biochar-containing regions of the film. The contact-angle data thus

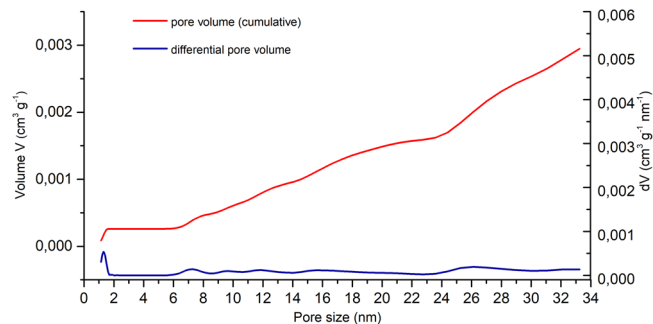


Fig. 6 | Pore volume versus pore size for walnut-shell biochar produced at 400 °C.

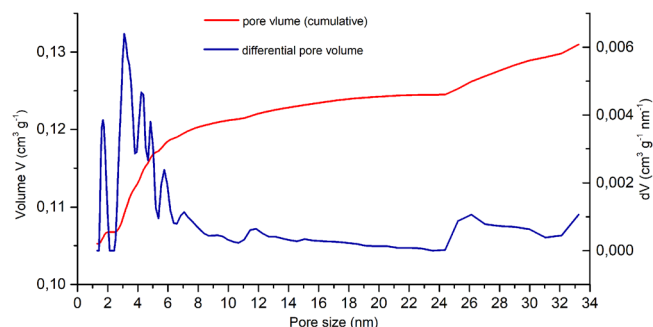


Fig. 7 | Pore volume versus pore size for walnut-shell biochar produced at 700 °C.

complement the BET and pore-volume measurements and provide a physically meaningful basis for discussing the effect of biochar production temperature on the structure and environmental response of the PLA composite films.

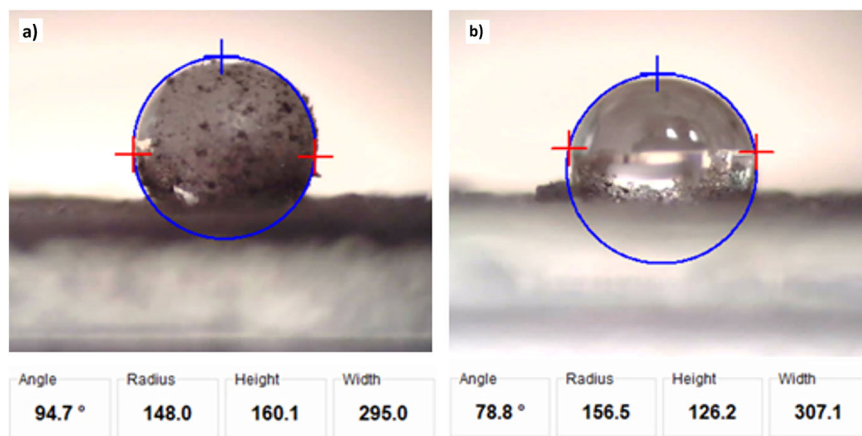
Mechanical properties of PLA films

The measured mechanical properties of the PLA biocomposite films are shown in Figs. 9–11. The effect of biochar on these properties is closely related to its particle size, specific surface area, porosity, chemical composition and loading level. Mozrall et al.³⁹ reported a significant increase in elastic modulus, tensile strength and elongation at break when low concentrations ($\leq 5 \text{ wt.}\%$) of biochar derived from coffee grounds with a particle size below $10 \mu\text{m}$ were incorporated into PLA. In contrast, larger biochar particles did not alter the elastic modulus of PLA, but led to a reduction in tensile strength and elongation at break. Zaouari et al.⁴⁰ observed that PLA biocomposites containing 5 wt.% biochar produced from beech wood, with a characteristic particle size of approximately $75 \mu\text{m}$, a specific surface area of $37.24 \text{ m}^2 \text{ g}^{-1}$ and a porosity of $0.012 \text{ cm}^3 \text{ g}^{-1}$, exhibited an increased tensile modulus, only minor changes in tensile strength and a decrease in elongation.

A similar trend was observed for the PLA biocomposite films analysed in this study and containing 2 wt.% biochar produced from walnut shells by high-temperature pyrolysis. Biochar obtained at the lower pyrolysis temperature caused a slight decrease in tensile strength and elongation at break, while leaving the elastic modulus of PLA essentially unchanged. As both biochars exhibited comparable particle size and size distribution, the predominant factor underlying these differences can be attributed to variations in specific surface area and porosity. It can therefore be hypothesised that higher porosity and specific surface area increase the potential particle–matrix contact area and may promote mechanical interlocking and more effective stress transfer between biochar and the PLA matrix.

When 10 wt.% of either biochar type was incorporated, a pronounced decrease in tensile strength and elongation at break of the PLA films was observed, whereas the tensile modulus reached values comparable to those of PLA biocomposites containing 2 wt.% biochar. In line with these findings,

Fig. 8 | Water contact angles of walnut-shell biochars produced at 400 °C and 700 °C. a Biochar produced at 400 °C. **b** Biochar produced at 700 °C.



Zouari et al.⁴⁰, Mozrall et al.³⁹, Ho et al.⁴¹, and Arrigo et al.⁴² also reported a deterioration of mechanical properties with increasing biochar content in PLA matrices. This decline at higher loadings is commonly attributed to biochar agglomeration, cluster formation and the initiation of microcracks. Reduced dispersion and less homogeneous distribution of the filler are thought to impair interfacial adhesion between the biochar and the polymer matrix, thereby limiting efficient stress transfer across the two phases.

The influence of biochar incorporation on the mechanical performance of PLA films was also assessed statistically. One-way ANOVA performed on the mechanical dataset (tensile strength, elongation at break and tensile modulus for all formulations) revealed a highly significant effect of formulation on mechanical properties ($F = 1447.4$, $F_{crit} = 1.72$, $p < 0.001$). In agreement with the evaluated trends (Figs. 9–11), neat PLA and the formulation containing 2 wt.% biochar produced at 700 °C exhibited the highest tensile strength, whereas both 10 wt.% biochar formulations showed markedly reduced strength and ductility. The tensile modulus increased most notably for PLA10B700, indicating a stiffening effect of the high-surface-area biochar at higher loading. These statistical results confirm that both the biochar loading and its production temperature have a strong and systematic impact on the mechanical behaviour of PLA-based films.

Rheological properties of PLA composites

The melt flow index results are listed in Table 2. The neat PLA films exhibited a melt volume-flow rate (MVR) of 11.8 cm³ per 10 min, whereas Polidar et al.⁴³ reported a substantially lower value of 6.6 cm³ per 10 min for the same grade. The higher MVR observed in the present study indicates a lower apparent resistance to flow under the selected test conditions. One possible explanation is a reduction in melt viscosity associated with processing-induced thermo-mechanical degradation and molecular chain scission during compounding and film extrusion. To assess the effect of processing, the MVR of the as-received pellets was also determined, yielding 5.8 ± 0.3 cm³ per 10 min. The substantial increase in MVR after compounding and film extrusion suggests that processing altered the melt-flow behaviour of Luminy L175 PLA. This change is consistent with processing-induced degradation, potentially including chain scission.

For PLA films containing 2 wt.% biochar, a slight decrease in MVR was observed, suggesting a modest reduction in the apparent flowability of the melt. This behaviour may be related to reduced chain mobility caused by particle–matrix interactions, steric hindrance, or other filler-induced changes in melt flow. At this loading, the differences between the two biochars were too small to support firm conclusions.

At the higher biochar loading of 10 wt.%, clear differences in MVR were observed. Both biochar-containing formulations exhibited higher MVR values than neat PLA, with the increase being particularly pronounced for PLA10B700. This behaviour indicates a substantial change in the apparent melt-flow behaviour of the filled systems. One possible explanation is that the higher amount of particulate filler modified the local flow

conditions during compounding and film extrusion. This may have increased the susceptibility of PLA to thermo-mechanical degradation. Liu et al.⁴⁴ proposed that particulate fillers can increase melt shear stresses and internal frictional heating during processing, thereby accelerating degradation phenomena in PLA-based composites. When comparing the formulations containing 10 wt.% biochar, PLA10B700 showed a markedly higher MVR than PLA10B400. The higher specific surface area of the biochar produced at 700 °C may have increased the particle–matrix contact area and modified local flow conditions during processing. This could have contributed to the markedly higher apparent melt flow of PLA10B700.

The markedly higher MVR of PLA10B700 than of PLA10B400 could, at first sight, be expected to result in a greater deterioration of tensile properties. However, this apparent inconsistency should be interpreted with caution. MVR is an indirect and apparent flow parameter measured on the filled melt under one specific shear stress and temperature, rather than a direct measurement of the molecular weight of the PLA matrix. In particulate-filled systems, the flow response is governed not only by matrix molecular weight. It is also affected by filler loading, particle–particle and particle–matrix interactions, filler dispersion and possible flow effects at the capillary wall. Therefore, the approximately 3.4-fold difference in MVR between PLA10B400 and PLA10B700 cannot be interpreted as a proportional difference in PLA molecular weight.

For entangled linear PLA, melt viscosity depends non-linearly on molecular weight, commonly following the relationship $\eta_0 \propto M_w^{3.4-4.5}$. Consequently, even a considerable increase in melt flow does not necessarily lead to a corresponding decrease in tensile strength or modulus, provided that the polymer chains remain sufficiently entangled. Direct confirmation of the molecular-weight distributions by SEC/GPC was not available in the present study; therefore, the MVR results are interpreted as evidence of a substantially altered melt-flow behaviour, consistent with more pronounced processing-induced chain scission in PLA10B700, rather than as a quantitative measure of its molecular weight.

The mechanical response at 10 wt.% biochar is additionally controlled by competing microstructural factors. Both 10 wt.% formulations contained the same filler loading and biochars with comparable particle-size distributions; hence, both systems were similarly affected by filler-induced stress concentrations, agglomeration and interfacial debonding, which can dominate tensile failure in particulate composites. At the same time, the high surface area and pore volume of B700 may increase the effective particle–matrix contact area and promote mechanical interlocking. This may improve stress transfer and partially compensate for the negative influence of lower melt viscosity. This interpretation is consistent with the comparatively high tensile modulus of PLA10B700. In contrast, PLA10B400 exhibited a higher degree of crystallinity, which may partially compensate for its lower potential particle–matrix contact area and mechanical interlocking. The similar tensile properties of the two 10 wt.%

Fig. 9 | Elongation at break of neat PLA and PLA/biochar films. In the sample designations, 2 and 10 denote biochar contents of 2 wt.% and 10 wt.%, respectively, whereas B400 and B700 denote walnut-shell biochar produced at 400 °C and 700 °C, respectively. Error bars represent standard deviations.

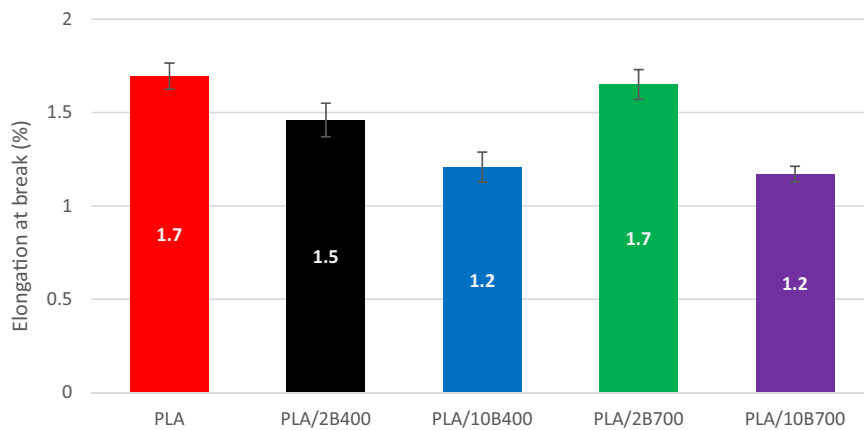
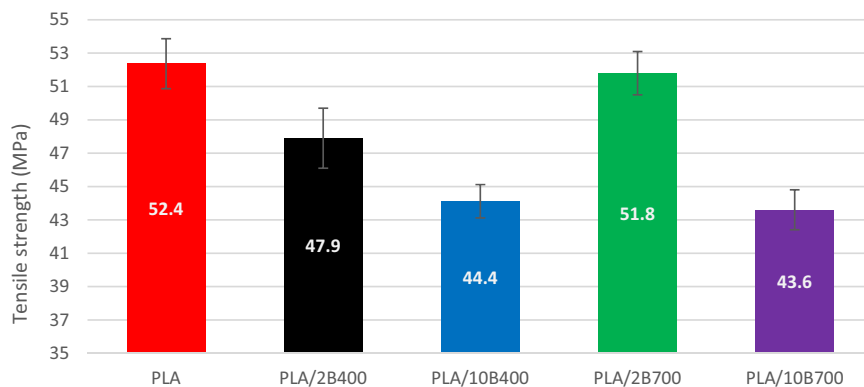


Fig. 10 | Tensile strength of neat PLA and PLA/biochar films. PLA denotes polylactic acid. Error bars represent standard deviations.



formulations therefore reflect the balance of these competing effects, rather than an absence of processing-induced degradation in PLA10B700.

One-way ANOVA applied to the MVR data for all formulations confirmed that these differences in melt flow behaviour between neat PLA, low-loading (2 wt.%) and high-loading (10 wt.%) biocomposites, as well as between the two biochar types at 10 wt.%, are statistically highly significant ($p < 0.001$).

Differential scanning calorimetry (DSC) of PLA films

Prior to thermophilic composting, the structural and thermal properties of the as-produced PLA-based films were assessed by differential scanning calorimetry. The results of the first non-isothermal heating of the as-prepared PLA-based samples are presented in Fig. 12 and summarized in Table 3. The interpretation presented below is based primarily on the directly measured calorimetric quantities, namely the cold-crystallisation enthalpy (ΔH_{sc}), pre-melt crystallisation enthalpy (ΔH_{pc}), melting enthalpy (ΔH_m), and the associated transition temperatures. These quantities do not depend on normalisation to the PLA mass fraction in the composite. The degree of crystallinity (X_c) is therefore used as a derived comparative parameter. The low disintegration degrees measured during the 45-day exposure period (0.4–2.2 wt.% for the biocomposites; Table 5) indicate that a possible change in the PLA mass fraction due to additive release would have only a negligible effect on the calculated X_c values and would not affect the observed relative trends. Accordingly, the mechanistic discussion below focuses on the evolution of the measured DSC enthalpies and transition temperatures, while the X_c values are used to facilitate comparison between formulations and exposure times.

The neat PLA film exhibited a glass-transition temperature of 60.4 ± 0.5 °C, a cold-crystallisation enthalpy of 28.1 ± 0.6 J g⁻¹, a pre-melt crystallisation enthalpy of 4.8 ± 0.6 J g⁻¹, and a melting enthalpy of 35.9 ± 0.5 J g⁻¹. The simultaneous occurrence of cold crystallisation and pre-

melt crystallisation during the first heating scan indicates that the rapidly extruded neat PLA film retained a predominantly disordered structure. Additional structural reorganisation occurred upon heating. However, the rapid cooling inherent to film extrusion promoted secondary crystallization and recrystallization prior to melting. Upon reheating, a relatively low degree of crystallinity (3.2% for neat PLA) was observed. Similar to heterogeneous nucleating agents, biochar incorporation was expected to promote structural ordering. Given the relatively high crystallization kinetics of the PLA grade used, this effect might have been amplified. Nevertheless, the addition of 2 wt.% biochar produced by low-temperature (400 °C) pyrolysis had only a marginal effect on PLA crystallinity, while increasing the loading to 10 wt.% led to a more pronounced enhancement ($X_c = 8.0\%$). This increase likely stems from a higher density of heterogeneous nucleation sites as well as possible chain scission, which enhances molecular mobility. At this concentration, biochar evidently exerts a substantial influence on the crystallization kinetics of PLA, even under rapid cooling conditions. Kane et al.⁴⁶ similarly reported an increase in crystallinity at biochar contents ≥ 10 wt.% in PLA derived from food waste.

Interestingly, when biochar derived from walnut shells via high-temperature pyrolysis (700 °C) was used, a notable increase in PLA crystallization kinetics was already evident at just 2 wt.% loading. Given the comparable particle size and distribution of both biochars, this difference can be ascribed to their distinct porosity and specific surface area. At 10 wt.% loading of the high-temperature biochar, however, a reduction in structural order relative to neat PLA was detected. This behaviour may result from increased particle–matrix contact and steric hindrance associated with the high surface area of B700. Together, these effects may restrict chain mobility. A comparable trend was observed by Arrigo et al.⁴² for biochar derived from spent coffee grounds, who reported reduced crystallinity at biochar loadings above 2.5 wt.%. Haeldermans et al.⁴⁷ likewise documented decreased crystallinity at higher biochar concentrations (20–30 wt.%). Collectively, these

Fig. 11 | Tensile modulus of neat PLA and PLA/biochar films. PLA denotes polylactic acid. Error bars represent standard deviations.

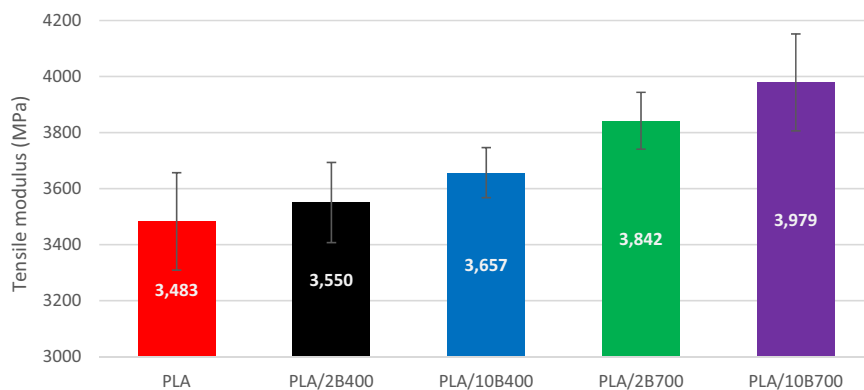


Table 2 | Melt volume-flow index of PLA films with biochar

	PLA	PLA/ 2B400	PLA/ 10B400	PLA/ 2B700	PLA/ 10B700
MVR (cm ³ 10 min)	11.8 ± 0.5	9.9 ± 0.2	19.0 ± 0.4	10.5 ± 0.1	63.8 ± 5.3

B400 and B700, walnut-shell biochar produced at 400 °C and 700 °C, respectively. Values are expressed in cm³ 10 min⁻¹ and are reported as mean ± standard deviation.

PLA polylactic acid, MVR melt volume-flow rate.

results demonstrate that, aside from influencing biodegradation, the production method of biochar plays a decisive role in the structural organization of PLA biocomposites.

No significant differences in glass transition (T_g) or melting temperature (T_m) were detected among the analyzed samples. Even though pronounced chain scission might be expected at 10 wt.% of high-surface-area biochar, T_g and T_m remained essentially unchanged. Similar observations were reported by Zouari et al.⁴⁰, Arrigo et al.⁴², Mozrall et al.³⁹, and Kane et al.⁴⁶ for biochar loadings below 10 wt.%. At higher concentrations, the literature remains inconsistent, likely due to distinct interfacial interactions between specific biochars and the PLA matrix. While Hernandez-Charpak et al.⁴⁸ observed no changes even at high loadings, Kane et al.⁴⁶ reported marked decreases in both T_g and T_m at 10–20 wt.%. Chen et al.⁴⁹ attributed similar decreases to reduced interfacial adhesion. In the present study, the unchanged transition temperatures at 10 wt.% is consistent with the combined effects of the high-surface-area filler, altered chain mobility and particle–matrix contact with the PLA matrix, counteracting the expected thermal shift despite chain scission.

No statistically significant differences in glass-transition temperature (T_g) or melting temperature (T_m) were detected among the as-produced films. This result indicates that, within the investigated formulation range, biochar incorporation did not measurably alter the principal thermal-transition temperatures of the PLA phase. Similar retention of T_g and T_m has been reported for PLA/biochar composites at low and moderate biochar contents by Zouari et al.⁴⁰, Arrigo et al.⁴², Mozrall et al.³⁹, and Kane et al.⁴⁶. At higher biochar loadings, the reported behaviour is less consistent. Hernandez-Charpak et al.⁴⁸ observed no appreciable changes in the transition temperatures. In contrast, Kane et al.⁴⁶ reported decreases in both T_g and T_m at 10–20 wt.% biochar, while Chen et al.⁴⁹ related similar decreases to reduced interfacial adhesion. The present results therefore fall within the range of previously reported behaviour and show that the higher MVR observed for PLA10B700 was not accompanied by a resolvable shift in T_g or T_m .

During the first 15 days of thermophilic composting, the glass-transition and melting temperatures remained broadly similar to those of the as-produced films. In contrast, pronounced changes were detected in the directly measured DSC enthalpies. In all formulations, the cold-crystallisation peak observed in the as-produced films disappeared after

15 days, while the melting enthalpy increased. For example, the melting enthalpy of neat PLA increased from 35.9 ± 0.5 to 54.3 ± 0.5 J g⁻¹, whereas that of PLA10B700 increased from 32.4 ± 0.4 to 41.5 ± 0.4 J g⁻¹. The absence of cold crystallisation upon reheating indicates that the material remaining after compost exposure had already undergone substantial structural reorganisation before DSC analysis. The simultaneous increase in melting enthalpy is consistent with an enrichment of ordered PLA domains during thermophilic exposure. This interpretation is consistent with the hydrolytic degradation mechanism described by Elsayy et al.⁵⁰, who reported preferential chain cleavage in the amorphous regions of PLA, resulting in an apparent increase in the crystallinity of the remaining material. A similar increase in structural order during the early stage of PLA hydrolysis was reported by Li et al.⁵¹. This behaviour can result from preferential modification and depletion of the less ordered amorphous fraction. Increased mobility of shorter PLA chains may also promote structural reorganisation during composting. The calculated X_c values support this comparative trend; however, the interpretation is based primarily on the directly measured enthalpy changes.

The kinetics and extent of this structural evolution differed among formulations. At day 15, the 10 wt.% biochar-filled films retained a distinct pre-melt crystallisation transition, with ΔH values of 5.3 ± 0.2 J g⁻¹ for PLA10B400 and 4.6 ± 0.5 J g⁻¹ for PLA10B700. In contrast, this transition was absent or almost negligible in neat PLA and in the formulations containing 2 wt.% biochar. The persistence of pre-melt crystallisation indicates that a fraction of the PLA chains in the 10 wt.% formulations remained insufficiently ordered before reaching the melting region. This is consistent with slower or more constrained structural reorganisation during the early stage of composting. By day 30, ΔH_{pc} had decreased to 1.7 ± 0.4 J g⁻¹ for PLA10B400 and 0.6 ± 0.5 J g⁻¹ for PLA10B700, indicating that this difference gradually diminished with continued exposure.

After 30 days, neat PLA and the formulations containing 2 wt.% biochar displayed double melting peaks, whereas the 10 wt.% biochar-filled films retained a single melting peak. The double-melting behaviour is consistent with the presence of crystal populations of different thermal stability and/or melt–recrystallisation processes occurring during heating. Yasuniwa et al.⁵² and Pan et al.⁵³ similarly attributed double melting peaks in PLA to melting–recrystallisation processes and to the coexistence of crystal populations with different structural perfection. Therefore, it provides evidence of a more advanced reorganisation of the crystalline morphology in neat PLA and the 2 wt.% biochar formulations. In all samples, the melting transition shifted towards lower temperatures with exposure time. This decrease in T_m , combined with the increasing melting enthalpy, indicates the formation or enrichment of ordered domains with lower thermal stability, which is consistent with progressive degradation and structural reorganisation of PLA during thermophilic composting.

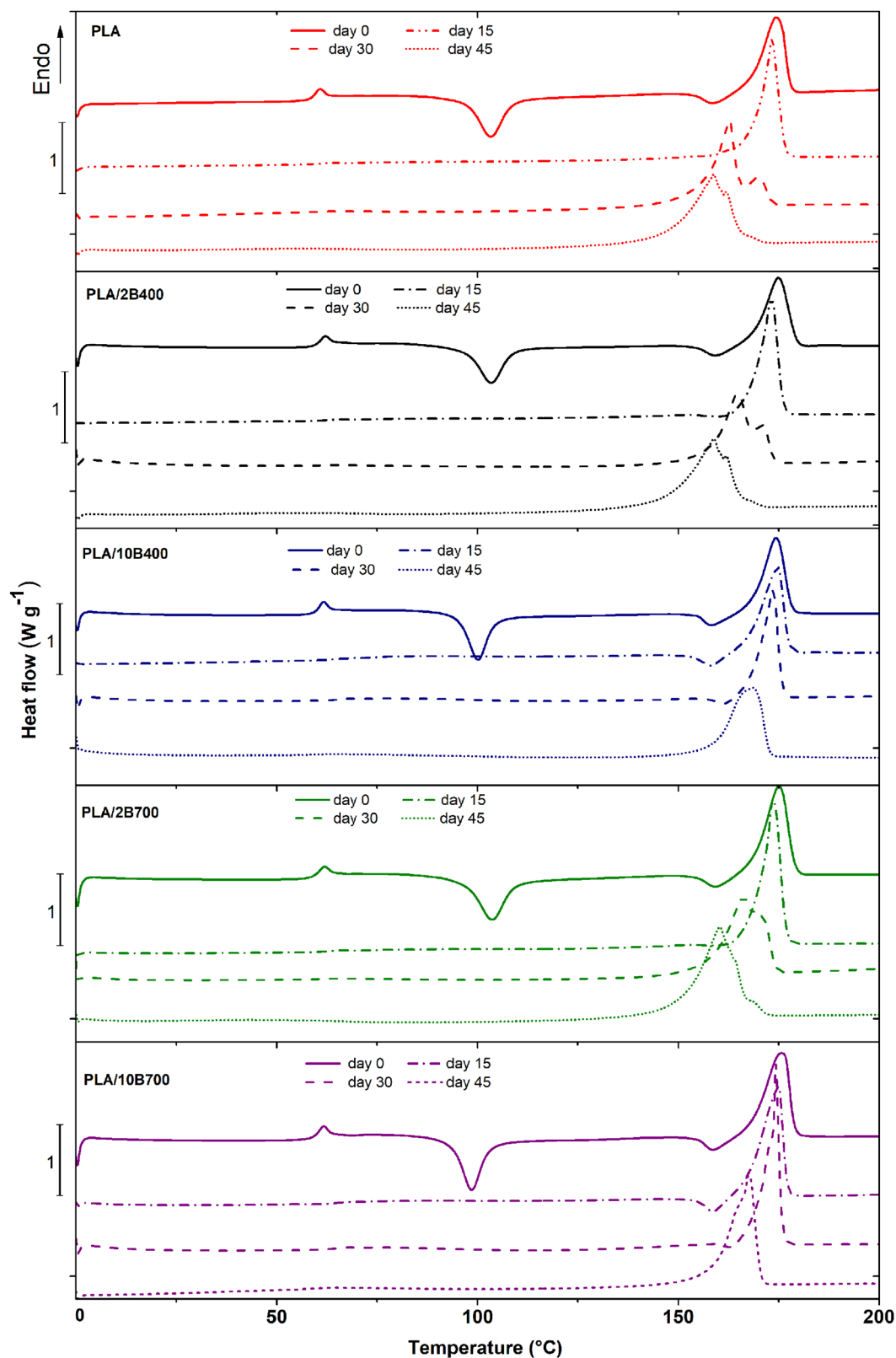


Fig. 12 | First-heating DSC curves of PLA and PLA/biochar films before and during thermophilic composting. DSC denotes differential scanning calorimetry. Day 0 denotes as-produced films. In the sample designations, 2 and 10 denote

biochar contents of 2 wt.% and 10 wt.%, respectively, whereas B400 and B700 denote walnut-shell biochar produced at 400 °C and 700 °C, respectively. Error bars represent standard deviations.

Table 3 | Thermal properties of PLA films before and after composting obtained from DSC analysis

Sample	Exposure time	T _g (°C)	T _{sc} (°C)	ΔH _{sc} (J·g ⁻¹)	T _{pc} (°C)	ΔH _{pc} (J·g ⁻¹)	T _{ma} (°C)	T _m (°C)	ΔH _m (J·g ⁻¹)	X _c (%)
PLA	Day 0	60.4 ± 0.5	103.3 ± 0.3	28.1 ± 0.6	158.8 ± 0.4	4.8 ± 0.6	-	174.9 ± 0.5	35.9 ± 0.5	3.2 ± 0.5
	Day 15	58.7 ± 0.4	-	-	-	-	-	173.3	54.3 ± 0.5	58.3 ± 0.4
	Day 30	54.2 ± 0.5	-	-	-	-	162.7 ± 0.6	170.0 ± 0.6	64.1 ± 0.8	68.9 ± 0.8
	Day 45	-	-	-	-	-	158.6 ± 0.5	161.9 ± 0.8	69.2 ± 0.6	74.3 ± 0.5
PLA/ 2B400	Day 0	60.9 ± 0.5	100.1 ± 0.5	24.1 ± 0.6	158.3 ± 0.4	5.4 ± 0.4	-	175.5 ± 0.5	33.4 ± 0.5	4.3 ± 0.5
	Day 15	59.9 ± 0.7	-	-	160.8 ± 0.5	0.8 ± 0.6	-	173.3 ± 0.6	49.7 ± 0.5	53.6 ± 0.6
	Day 30	-	-	-	-	-	164.7 ± 0.9	170.9 ± 0.6	58.7 ± 0.6	64.3 ± 0.5
	Day 45	-	-	-	-	-	-	162.1 ± 0.5	66.8 ± 0.7	73.2 ± 0.7
PLA/ 10B400	Day 0	60.2 ± 0.5	98.4 ± 0.4	23.5 ± 0.7	158.8 ± 0.6	4.8 ± 0.6	-	175.8 ± 0.8	35.0 ± 0.4	8.0 ± 0.5
	Day 15	-	-	-	162.6 ± 0.8	5.3 ± 0.2	-	174.8 ± 0.5	40.4 ± 0.6	41.9 ± 0.5
	Day 30	-	-	-	161.2 ± 0.7	1.7 ± 0.4	-	172.9 ± 0.4	41.8 ± 0.5	47.9 ± 0.5
	Day 45	-	-	-	-	-	-	168.8 ± 0.7	56.3 ± 0.8	67.2 ± 0.7
PLA/ 2B700	Day 0	61.2 ± 0.4	103.6 ± 0.4	24.7 ± 0.5	159.2 ± 0.5	4.4 ± 0.3	-	175.2 ± 0.7	34.8 ± 0.6	6.2 ± 0.9
	Day 15	60.4 ± 0.5	-	-	161.9 ± 0.6	0.2 ± 0.4	-	173.7 ± 0.5	50.8 ± 0.5	55.5 ± 0.5
	Day 30	-	-	-	-	-	166.2 ± 0.8	169.6 ± 0.6	56.0 ± 0.5	61.4 ± 0.5
	Day 45	-	-	-	-	-	-	160.3 ± 1.2	67.3 ± 1.2	73.8 ± 0.5
PLA/ 10B700	Day 0	60.6 ± 0.5	103.4 ± 0.6	25.6 ± 0.3	159.2 ± 0.5	5.1 ± 0.4	-	174.9 ± 0.5	32.4 ± 0.4	2.0 ± 0.4
	Day 15	-	-	-	162.7 ± 0.5	4.6 ± 0.5	-	175.0 ± 0.7	41.5 ± 0.4	44.0 ± 0.5
	Day 30	-	-	-	162.5 ± 0.7	0.6 ± 0.5	-	172.6 ± 0.8	43.7 ± 0.5	51.4 ± 0.6
	Day 45	-	-	-	-	-	-	167.4 ± 0.9	53.8 ± 0.9	64.2 ± 0.5

The degree of crystallinity (X_c) was calculated according to Eq. (4) using the nominal PLA mass fraction of each formulation. Because disintegration of the biocomposites remained low during the 45-day exposure period (0.4–2.2 wt.%; Table 5), a possible change in PLA mass fraction due to biochar release has a negligible effect on the relative X_c trends. PLA, polylactic acid; B400 and B700, walnut-shell biochar produced at 400 °C and 700 °C, respectively; T_g, glass-transition temperature; T_{sc} and H_{sc}, cold-crystallisation temperature and enthalpy; T_{pc} and H_{pc}, pre-melt crystallisation temperature and enthalpy; T_m and H_m, melting temperature and enthalpy; X_c, degree of crystallinity. Day 0 denotes as-produced films. Values are reported as mean ± standard deviation.

Thermogravimetric analysis (TGA) of PLA films

The TGA curves of the investigated PLA-based films are presented in Fig. 13, and the corresponding characteristic degradation temperatures are summarised in Table 4.

The addition of 2 wt.% biochar caused only a minor reduction in the onset degradation temperature, T_{5%}, relative to neat PLA. In contrast, the 10 wt.% biochar-filled films exhibited a more pronounced reduction in thermal stability. The T_{5%} value decreased from 323.9 ± 1.1 °C for neat PLA to 313.1 ± 1.1 °C for PLA10B400 and 306.2 ± 1.2 °C for PLA10B700. A similar decrease in thermal stability with increasing biochar content was reported by Kane et al.⁴⁶, who observed deterioration in the thermal degradation behaviour of PLA at higher biochar loadings. Zouari et al.⁴⁰ likewise reported progressively lower degradation temperatures for PLA composites containing 5, 10 and 20 wt.% biochar. Consistently, Haeldermans et al.⁴⁷ observed a decrease in both the onset degradation temperature and the temperature of maximum mass-loss rate with increasing biochar concentration.

Several mechanisms may contribute to the reduction in T_{5%}. According to Moustafa et al.⁵⁴ and Arrigo et al.⁴², a decrease in the thermal degradation temperature of biocomposites can be associated with catalytic effects of inorganic constituents, particularly potassium-containing ash fractions. Elnour et al.³¹ reported that ash and potassium contents can increase with pyrolysis temperature. However, the walnut-shell biochars used in the present work contained only low ash contents (1.8 and 2.6 wt.% for B400 and B700, respectively) and low potassium contents (0.22 and 0.15 wt.%, respectively). Therefore, catalytic effects of inorganic ash constituents cannot be excluded, but they are unlikely to represent the sole cause of the observed reduction in thermal stability. Liu et al.⁴⁴ reported that melt blending of PLA with particulate inorganic fillers decreased the molecular weight of the PLA matrix and was accompanied by a reduction in the onset degradation temperature. They attributed the lower thermal stability

primarily to molecular-weight reduction during melt mixing. Although the filler type and processing conditions in that study differ from the present system, the reported behaviour is consistent with the simultaneous increase in MVR and decrease in T_{5%} observed here, particularly for PLA10B700.

The literature further indicates that filler characteristics, including particle size, particle-size distribution, surface chemistry, and the available polymer–filler interfacial area, can modify the thermal and processing behaviour of PLA-based composites. In the present study, B400 and B700 had broadly comparable particle sizes and particle-size distributions, whereas their surface characteristics were markedly different. B700 exhibited a specific surface area of 356 m² g⁻¹ and a total pore volume of 0.505 cm³ g⁻¹, compared with 2.1 m² g⁻¹ and 0.102 cm³ g⁻¹, respectively, for B400. The substantially larger available surface of B700 may therefore have modified the local flow and interfacial conditions during compounding and film extrusion, increasing the susceptibility of the PLA phase to thermo-mechanical degradation.

The TGA results provide a thermal perspective on the processing-related changes identified by the rheological measurements and their consequences for the mechanical response. At 10 wt.% biochar loading, PLA10B700 exhibited a markedly higher MVR (63.8 ± 5.3 cm³ 10 min⁻¹) than PLA10B400 (19.0 ± 0.4 cm³ 10 min⁻¹), demonstrating a substantially lower apparent melt viscosity. Together with the lower T_{5%} of PLA10B700, this result is consistent with more extensive processing-induced chain scission in the PLA phase of the B700-filled composite. Nevertheless, the increased MVR and lower T_{5%} of PLA10B700 were not accompanied by a statistically significant additional decrease in tensile strength or elongation at break relative to PLA10B400.

This apparent discrepancy can be explained by the fact that, at the identical 10 wt.% filler loading, tensile failure is controlled not only by the molecular state of the PLA matrix but also by filler-related effects. Both 10 wt.% biocomposites contained comparable particle sizes and particle-size

Table 4 | Thermal degradation properties of PLA films before and after composting obtained from TGA analysis

Sample	Exposure time							
	Day 0		Day 15		Day 30		Day 45	
	T _{5%} (°C)	T _{50%} (°C)	T _{5%} (°C)	T _{50%} (°C)	T _{5%} (°C)	T _{50%} (°C)	T _{5%} (°C)	T _{50%} (°C)
PLA	323.9 ± 1.1	349.4 ± 1.2	306.4 ± 1.6	339.8 ± 1.4	268.2 ± 1.3	327.6 ± 1.5	259.8 ± 2.0	302.6 ± 2.3
PLA/2B400	322.8 ± 0.9	346.9 ± 0.9	304.8 ± 1.4	336.8 ± 1.2	287.2 ± 1.9	331.5 ± 1.6	260.9 ± 1.8	321.9 ± 1.9
PLA/10B400	313.1 ± 1.1	341.8 ± 1.4	311.8 ± 1.8	348.1 ± 1.6	310.6 ± 2.1	337.7 ± 1.9	286.8 ± 2.1	341.4 ± 2.0
PLA/2B700	318.5 ± 1.2	347.0 ± 1.1	308.0 ± 1.6	347.4 ± 1.8	288.7 ± 1.8	341.6 ± 1.6	275.9 ± 2.3	335.3 ± 2.7
PLA/10B700	306.2 ± 1.2	344.8 ± 1.3	290.2 ± 2.0	337.6 ± 1.9	285.2 ± 1.5	336.4 ± 1.7	280.8 ± 1.9	336.7 ± 2.4

PLA polylactic acid. B400 and B700, walnut-shell biochar produced at 400 °C and 700 °C, respectively; T_{5%} and T_{50%}, temperatures at 5% and 50% mass loss, respectively. Day 0 denotes as-produced films. Values are expressed in °C and are reported as mean ± standard deviation.

PLA polylactic acid.

distributions and were therefore similarly affected by stress concentrations, possible particle agglomeration, interfacial debonding, and a reduction in the effective load-bearing cross-section of PLA. These filler- and defect-related factors can dominate tensile failure and mask the effect of different matrix chain lengths on tensile strength and elongation at break. Conversely, the high specific surface area and pore volume of B700 may promote mechanical interlocking and more effective stress transfer at the PLA–biochar interface, partially compensating for the detrimental effect of chain scission. This interpretation is consistent with the higher tensile modulus recorded for PLA10B700.

The onset degradation temperature, T_{5%}, decreased after 15 days of thermophilic composting for all formulations except PLA10B400. For this material system, a more pronounced reduction in degradation temperatures is observed only after 45 days. In contrast, the kinetics of changes in thermal degradation temperatures for the other material variants are considerably faster. When comparing the reductions in initial degradation temperature after 45 days of exposure, the largest changes are found for neat PLA films and PLA films containing 2 wt.% biochar produced at 400 °C, which also exhibit the fastest disintegration kinetics.

Fourier transform infrared spectroscopy (FT-IR) of PLA films

ATR-FTIR spectra of the as-produced neat PLA and PLA/biochar films are provided in Supplementary Fig. S5 because no new absorption bands or unambiguous shifts of the characteristic PLA bands were detected after biochar incorporation. This result is consistent with the findings of Kane et al.⁴⁶, Bajwa et al.²³, and Haeldermans et al.⁴⁷, who reported no substantial FTIR changes in PLA/biochar composites even at biochar contents of up to 20 wt.%. The present spectra therefore indicate that biochar incorporation did not cause a detectable chemical modification of the PLA backbone or the formation of new covalent PLA–biochar bonds. However, conventional one-dimensional ATR-FTIR does not permit an unambiguous assignment of the dominant non-covalent interaction at the particle–matrix interface.

Differences in the absolute intensity of the characteristic PLA bands were nevertheless observed with increasing biochar content and during thermophilic composting. In particle-filled films, these intensity changes may reflect several factors. These include the relative PLA content within the ATR-probed volume, absorption and scattering by carbonaceous particles, surface roughness, sample–crystal contact and possible changes in the chemical environment of the PLA surface layer. The observed spectral changes are therefore considered qualitative indicators of changes in the material surface and are interpreted together with the DSC, TGA and SEM results, rather than as independent evidence of a specific interfacial interaction or of the extent of chain scission.

During thermophilic composting, neat PLA exhibited a visible reduction in the intensity of characteristic PLA bands after 15 days, whereas the changes in the biochar-containing films developed more gradually. After 45 days, the PLA/biochar films generally showed lower band intensities, with PLA/10B400 showing the smallest change. This qualitative spectral trend is consistent with the slower evolution of PLA/10B400 observed in the preceding thermal analyses: this formulation showed the smallest change in

the DSC enthalpy profile during the early exposure period and the most delayed reduction in onset degradation temperature, T_{5%}, during composting. In contrast, the substantially higher MVR and lower initial T_{5%} of PLA/10B700 indicate that the B700-filled formulation underwent more pronounced processing-induced changes before composting.

Biochar was incorporated partly because its wettability and porosity can influence water access to PLA and thereby modify the hydrolytic component of degradation. The evolution of the O–H stretching region around 3400 cm^{−1} during thermophilic composting is shown in Fig. 14. In our previous studies^{10,55}, the emergence or growth of this broad band was associated with the formation of hydroxyl-containing products during PLA hydrolysis. In the present study, no resolvable increase in the O–H region was observed for any formulation during the first 45 days of exposure. This result shows that hydroxyl-containing degradation products did not accumulate to a detectable extent within the ATR-probed surface layer during this early stage of composting.

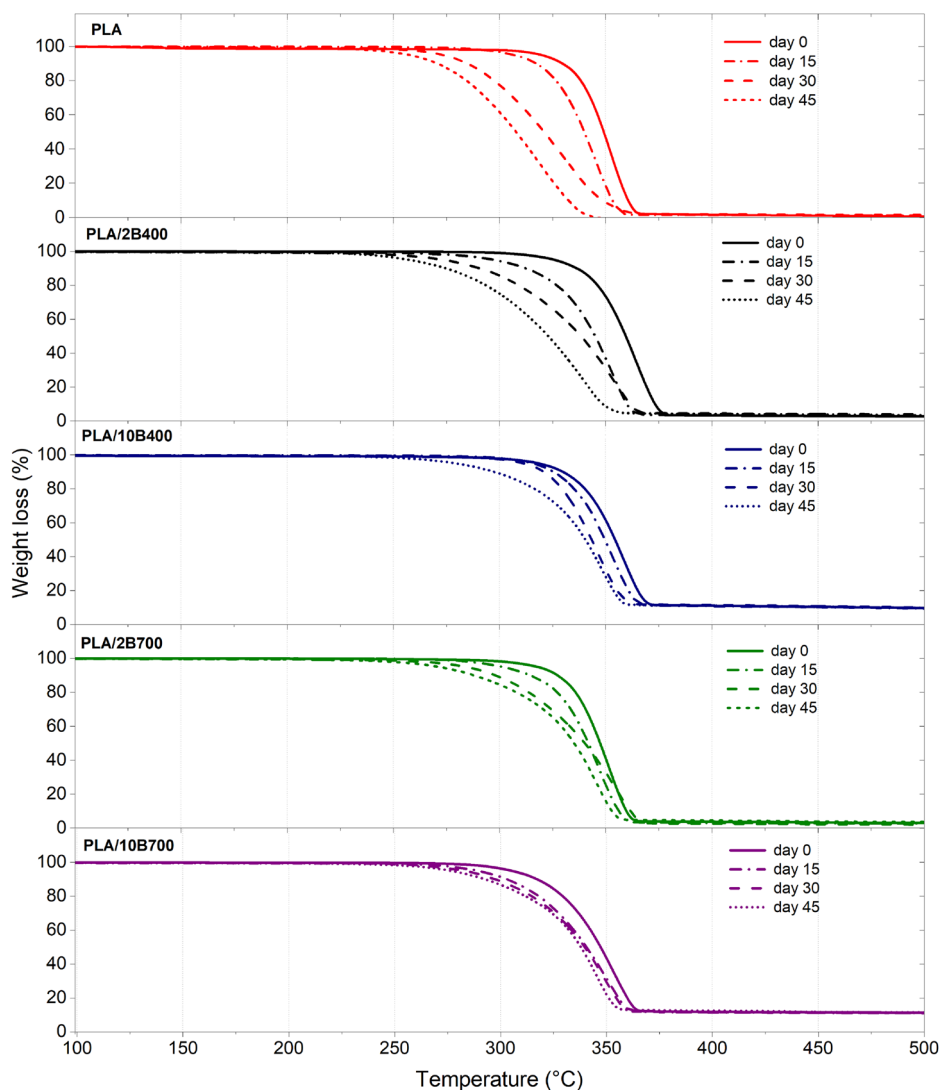
The O–H region contains contributions from terminal hydroxyl and carboxylic-acid groups formed by ester-bond cleavage, adsorbed water, residual oxygen-containing groups on biochar and, after compost exposure, surface-associated biological material. The absence of a resolved intensity increase therefore does not rule out hydrolytic chain scission; rather, it indicates that any newly formed products were below the detection limit of the measurement, overlapped with the existing broad absorption, or were removed from the analysed surface layer. Bajwa et al.²³ likewise reported no significant evolution of the O–H region in PLA/biochar composites, even at a biochar loading of 20 wt.%.

The FTIR results thus complement the thermal and morphological analyses by showing that the early changes detected by DSC and TGA were not accompanied by a measurable accumulation of O–H-containing species at the film surface. This finding is consistent with the low disintegration degrees observed within the first 45 days. The contribution of biochar-controlled water uptake may become more evident at later stages of composting, when fragmentation increases the accessible surface area and enhances contact between the polymer, moisture and microorganisms.

Scanning electron microscopy (SEM) analysis of PLA films

No discernible surface changes were detected after 15 days of thermophilic composting for any formulation. Therefore, only representative micrographs of the as-produced films and films exposed for 30 and 45 days are presented in Figs. 15–18. The corresponding images of PLA/2B700 are provided in Supplementary Fig. S6 because this formulation likewise showed no distinctive surface changes during the early exposure period. Biochar incorporation increased the initial surface roughness, particularly at 10 wt.% loading, which may facilitate local water access and microbial attachment. Castro-Aguirre et al.⁵⁶ reported that PLA-film degradation under simulated composting proceeds through hydrolytic chain scission followed by surface erosion and microbial assimilation. In a related biochar-containing PLA-based system, Musiol et al.⁵⁷ also observed that the surface morphology after composting depended strongly on biochar loading.

Fig. 13 | TGA curves of PLA and PLA/biochar films before and during thermophilic composting. TGA denotes thermogravimetric analysis. Day 0 denotes as-produced films. In the sample designations, 2 and 10 denote biochar contents of 2 wt.% and 10 wt.%, respectively, whereas B400 and B700 denote walnut-shell biochar produced at 400 °C and 700 °C, respectively. Error bars represent standard deviations.



After 30 days of exposure, initiation zones of surface damage were visible on the neat PLA films and evolved into pronounced surface fragmentation by day 45 of composting. PLA films containing 2 wt.% biochar produced at 400 °C likewise exhibited clearly distinguishable crack formation after 30 days, and fungal hyphae were observed on their surfaces. In contrast, PLA biocomposite films containing 10 wt.% B400 showed no visible signs of microbial interaction or incipient fragmentation, even after 45 days, consistent with the slower evolution observed in the DSC and TGA results. PLA/2B700 did not exhibit surface damage or fungal growth comparable to that observed for PLA/2B400. However, increasing the content of the high-specific-surface-area B700 biochar to 10 wt.% resulted in more pronounced surface microbial colonisation, consistent with its faster biodegradation relative to PLA/10B400.

The SEM observations further show that neat PLA films underwent the most pronounced physical fragmentation during the 45-day exposure period. However, the resulting fragments remained relatively large and distinguishable in the compost; therefore, this observation alone cannot be interpreted as evidence of complete disintegration or microbial assimilation.

Degree of disintegration of composted PLA films

The evaluated mass loss (disintegration) over 45 days of thermophilic composting is summarized in Table 5. During the first 15 days of exposure, virtually no change in film mass was observed. A further 15 days of composting likewise did not result in substantial differences. Only neat PLA

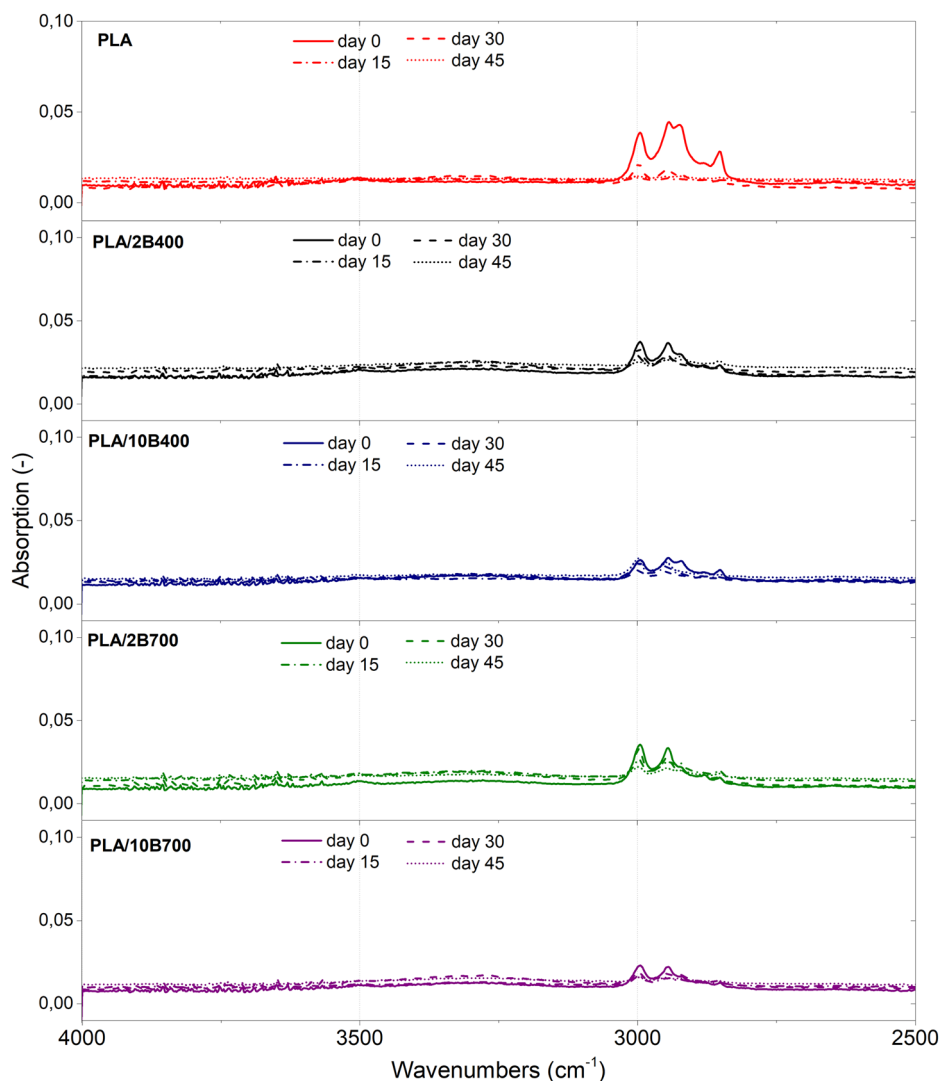
films and PLA biocomposite films containing 2 wt.% biochar produced at 400 °C showed a slight increase in disintegration. After 45 days of composting, the neat PLA films became highly brittle and fragmented extensively during sampling. This prevented a reliable determination of their disintegration degree. Nevertheless, the film fragments remained clearly distinguishable in the compost, and their complete disintegration therefore cannot be asserted. A delayed increase in disintegration under thermophilic composting conditions was likewise reported by de la Rosa-Ramírez et al.⁵⁸ for PLA-based materials. One-way ANOVA applied to the disintegration degree at day 45 did not reveal statistically significant differences among the remaining formulations ($p > 0.05$), reflecting the overall low extent of mass loss within the investigated exposure period.

Biodegradability of PLA films under thermophilic composting

The biodegradation kinetics of PLA films containing walnut-shell biochar produced at low (400 °C) and high (700 °C) pyrolysis temperatures are shown in Fig. 19. The validity of the test was verified in accordance with EN ISO 14855-1. The positive reference material, microcrystalline cellulose, reached 78% biodegradation after 45 days, and the microbial activity of the compost reached 68 mg CO₂ per gram of volatile solids within 10 days. The test conditions therefore fulfilled the validity criteria.

The CO₂-evolution profiles show that substantial mineralisation occurred predominantly after the first 45 days of exposure. Consistent with this delayed mineralisation, the parallel disintegration experiment showed

Fig. 14 | ATR-FTIR spectra of PLA and PLA/biochar films before and during thermophilic composting. ATR-FTIR denotes attenuated total reflectance Fourier-transform infrared spectroscopy.



only limited mass loss of the biochar-containing films after 45 days, ranging from 0.4% for PLA/10B400 to 2.2% for PLA/2B400 (Table 5). The progressive changes detected by DSC, TGA and SEM during this initial exposure period indicate that structural, thermal and morphological modification of the films had already begun. However, the extent of these early changes may not yet have been sufficient to promote extensive fragmentation, the release of low-molecular-weight degradation products and subsequent microbial mineralisation. The observed sequence is consistent with the established degradation pathway of PLA, in which hydrolytic chain scission precedes the microbial assimilation and mineralisation of lower-molecular-weight products⁵⁹.

The highest biodegradation degree after 16 weeks was observed for PLA/2B400, reaching 77.2%, which was significantly higher than for the other PLA-based formulations ($p < 0.001$). This value is within the range reported for PLA-based materials under thermophilic composting conditions. Lors et al.⁶⁰ summarised that biodegradation degrees of approximately 70–90% are commonly obtained at temperatures close to 58 °C, depending on the material formulation and test conditions. In addition, Melitou et al.⁶¹ reported substantial variability in the biodegradation behaviour of different commercially available PLA-based products under thermophilic aerobic laboratory conditions. This formulation also exhibited visible surface cracking and fungal hyphae after 30 days of thermophilic composting. PLA/10B400 exhibited the slowest biodegradation kinetics and showed no visible microbial colonisation during the initial 45-day exposure period. PLA/10B700 showed more pronounced microbial colonisation and faster

biodegradation than PLA/10B400, whereas PLA/2B700 exhibited a slower response than PLA/2B400 and did not show similarly pronounced surface damage or microbial growth during the early stage of composting.

The differences in biodegradation kinetics cannot be attributed to a single material parameter. PLA degradation in thermophilic compost proceeds through several coupled stages. These include water access to the polymer phase, hydrolytic cleavage of ester bonds, progressive shortening of polymer chains, and the formation and release of low-molecular-weight products. The released products can subsequently undergo microbial assimilation and mineralisation. A comparable non-monotonic effect of biochar loading on degradation was reported by Musioł et al.⁶¹ for PLA-containing biochar composites. They attributed accelerated degradation at moderate biochar contents to the porous filler structure and reduced polymer structural order. At high filler loading, however, degradation of the PLA component was delayed. This behaviour was associated with polymer entrapment and the hydrophobic character of the filler. Krähenbühl et al.⁶² similarly concluded that the effect of biochar on the degradation of biodegradable polymer systems depends on the balance between water accommodation, filler loading and physical hindrance within the polymer matrix. The parameters investigated in this study influence different stages of this sequence. The extent of structural ordering and the nature of particle–matrix contact mainly affect the accessibility of the amorphous phase to water. Processing-induced chain shortening may facilitate later formation of low-molecular-weight products. The wettability, porosity and surface morphology of biochar can influence water access and microbial

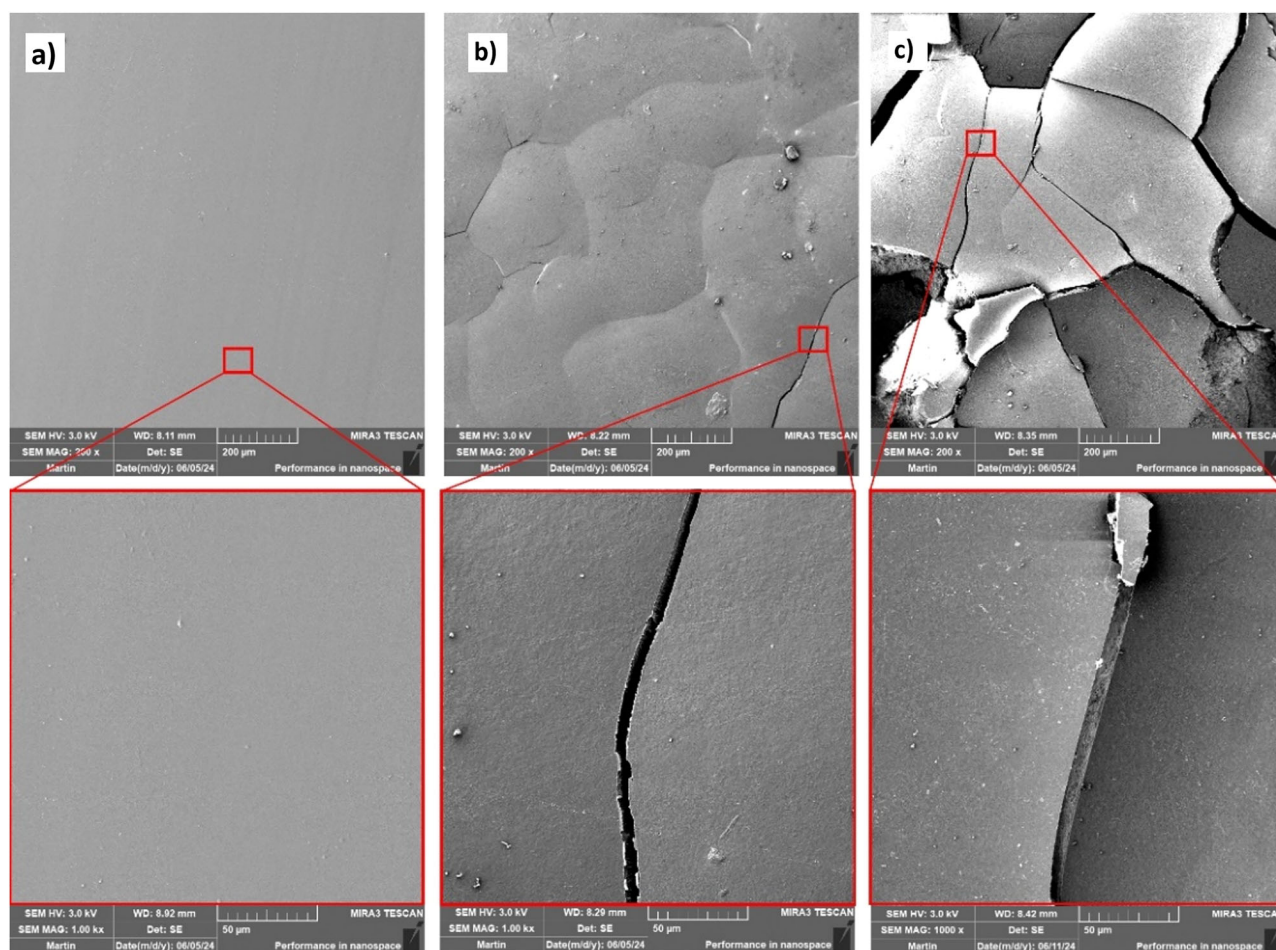


Fig. 15 | SEM micrographs of neat PLA films before and during thermophilic composting. a As-produced film. **b** Film after 30 days. **c** Film after 45 days.

colonisation. These contributions can act synergistically or competitively, depending on the filler loading and its properties.

The transport-related effects discussed above should be understood as differences in the local water environment at the PLA–biochar regions and in the accessibility of hydrolysable amorphous PLA domains. For unfilled PLA films approximately 400 μm thick, water has been reported to reach a homogeneous concentration within approximately 2 h at 50–58 $^{\circ}\text{C}$ ⁶³. Although biochar incorporation may modify the local distribution of water, this characteristic timescale remains substantially shorter than the 45-day disintegration period and the 16-week biodegradation test used in the present study. The present results therefore do not support interpreting the observed biodegradation differences solely in terms of the rate of water penetration through the whole film. Instead, they are discussed as the coupled effects of filler wettability and pore architecture, PLA structural ordering, particle–matrix contact and the resulting local accessibility of hydrolysable amorphous domains⁶⁴.

A qualitative summary of these competing contributions for each formulation is provided in Table 6. The assignments describe qualitative tendencies in local water availability and in the accessibility of the amorphous PLA phase, inferred from the measured filler wettability, pore architecture and film structure. They do not represent directly measured water uptake or effective diffusion coefficients of the composite films.

At 2 wt.% loading, the particles can be regarded as predominantly isolated within the PLA matrix. Consequently, their effect is local and is associated mainly with particle–matrix contact and changes in structural ordering. PLA/2B400 exhibited a lower apparent structural order than PLA/2B700 and contained the low-surface-area B400 filler. The lower apparent structural order of PLA/2B400, as indicated by the DSC enthalpy balance,

implies a larger proportion of hydrolysis-susceptible amorphous PLA domains. Hydrolytic degradation of PLA has been reported to proceed preferentially in the amorphous phase because water access to the more densely packed crystalline regions is restricted⁵⁰. This structural characteristic may therefore have contributed to the earlier crack formation and faster biodegradation response of PLA/2B400. At this low filler loading, the hydrophobicity of B400 did not impose an effective barrier to water transport through the whole film. In addition, the limited effective particle–matrix contact may have provided local interfacial regions favourable for water ingress and microbial attachment. These contributions are consistent with the rapid degradation response of PLA/2B400.

In contrast, PLA/2B700 showed a higher apparent structural order, as indicated by the DSC enthalpy balance, despite containing the high-surface-area porous B700 filler. At the low filler loading of 2 wt.%, the B700 particles were dispersed as isolated inclusions and were predominantly surrounded by the continuous PLA matrix. Water transport through the film was therefore expected to be governed mainly by the PLA phase rather than by the intrinsic wettability and porosity of the embedded biochar particles. The higher apparent structural order of PLA/2B700 is consistent with a lower accessibility of amorphous PLA domains to hydrolytic attack and may therefore have contributed to its slower degradation response. Although B700 exhibited a more hydrophilic character than B400, this local filler-related contribution did not outweigh the structural effect at 2 wt.% loading. The different response of PLA/2B400 and PLA/2B700 therefore demonstrates that the wettability of biochar alone cannot explain the degradation behaviour.

At 10 wt.% loading, the balance of controlling factors changed. The larger number of particles increased the influence of the filler phase on water

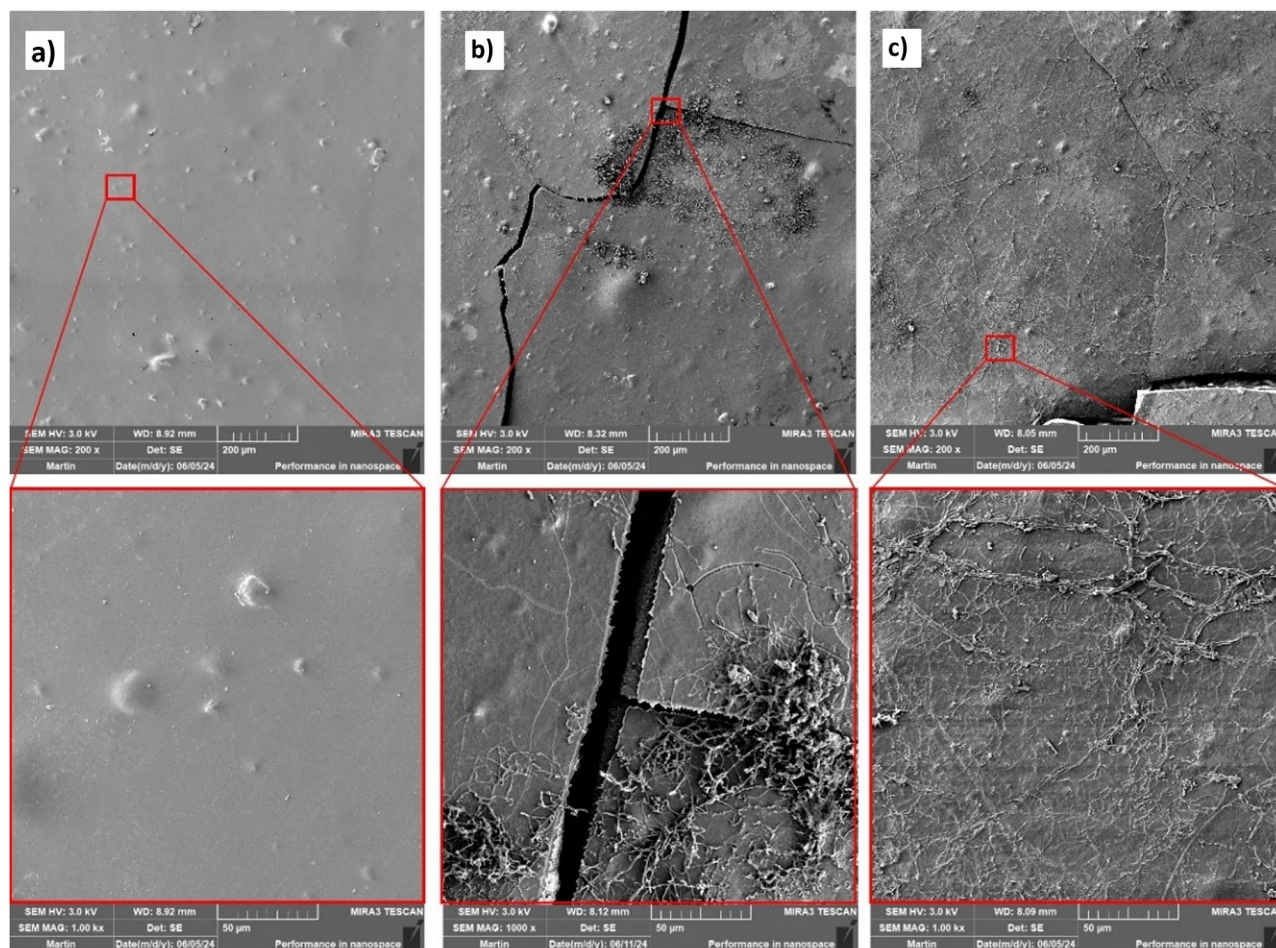


Fig. 16 | SEM micrographs of PLA films containing 2 wt.% biochar pyrolyzed at 400 °C. **a** As-produced, **b** after 30 days of thermophilic composting, **c** after 45 days of thermophilic composting.

transport, surface accessibility and the formation of local heterogeneities. PLA/10B400 combined a relatively high apparent structural order with the hydrophobic and low-porosity character of B400. These factors are consistent with restricted water access to the amorphous PLA phase and thus delayed hydrolytic degradation. Although rheological and TGA data indicated processing-induced chain shortening in this formulation, this effect did not outweigh the restricted water access during the early exposure period. This competitive balance is consistent with the slowest biodegradation kinetics, the smallest changes in thermal stability during composting and the absence of visible microbial colonisation.

PLA/10B700 exhibited the opposite balance of factors. This formulation showed the lowest apparent structural order among the investigated films, together with the highest MVR and the lowest initial $T_{5\%}$, indicating the most extensive processing-induced changes in the PLA matrix. The hydrophilic character and markedly higher pore volume of B700 may further facilitate water access, while the increased surface roughness can promote microbial attachment. These factors act synergistically to accelerate the hydrolytic and biological stages of degradation. However, the larger potential particle–matrix contact area associated with the high-surface-area B700 filler may reduce interfacial debonding and therefore counteract the accelerating effects. The net result was faster biodegradation of PLA/10B700 than PLA/10B400, but not a higher biodegradation degree than that observed for PLA/2B400.

Overall, the data reveal a loading-dependent change in the balance of degradation-controlling mechanisms. Greater structural ordering and more continuous particle–matrix contact tend to retard water access and hydrolysis. In contrast, low structural ordering, processing-induced chain

shortening, hydrophilic and porous biochar, and increased surface roughness tend to promote water access, structural deterioration and microbial colonisation. The observed biodegradation kinetics are therefore the net result of coupled structural, interfacial and transport-related effects, rather than the consequence of a single biochar property. This conclusion is consistent with the findings of Musioł et al.⁵⁷ and Krähenbühl et al.⁶², who likewise showed that biochar may either accelerate or retard the degradation of PLA-based materials depending on filler loading, porosity, water accessibility and polymer–filler morphology.

Discussion

This study demonstrates that the effect of walnut-shell biochar on the behaviour and biodegradation of PLA films is governed by the combined effect of pyrolysis temperature and filler content. Increasing the pyrolysis temperature from 400 to 700 °C transformed the biochar from a hydrophobic, low-surface-area filler into a hydrophilic and highly porous material, increasing its specific surface area from 2.1 to 356 m² g⁻¹ and total pore volume from 0.102 to 0.505 cm³ g⁻¹. These changes modified the particle–matrix contact, structural ordering and thermal stability of the PLA films.

Biochar incorporation affected the mechanical, rheological and thermal behaviour of PLA in a loading-dependent manner. At 2 wt.% loading, the influence of the filler on tensile properties, melt flow and thermal transitions was limited. At 10 wt.% loading, the two biochars produced contrasting structural responses: B400 increased the initial degree of crystallinity to 8.0%, whereas B700 reduced it to 2.0%, compared with 3.2% for neat PLA. Both biochars reduced tensile strength and elongation at break.

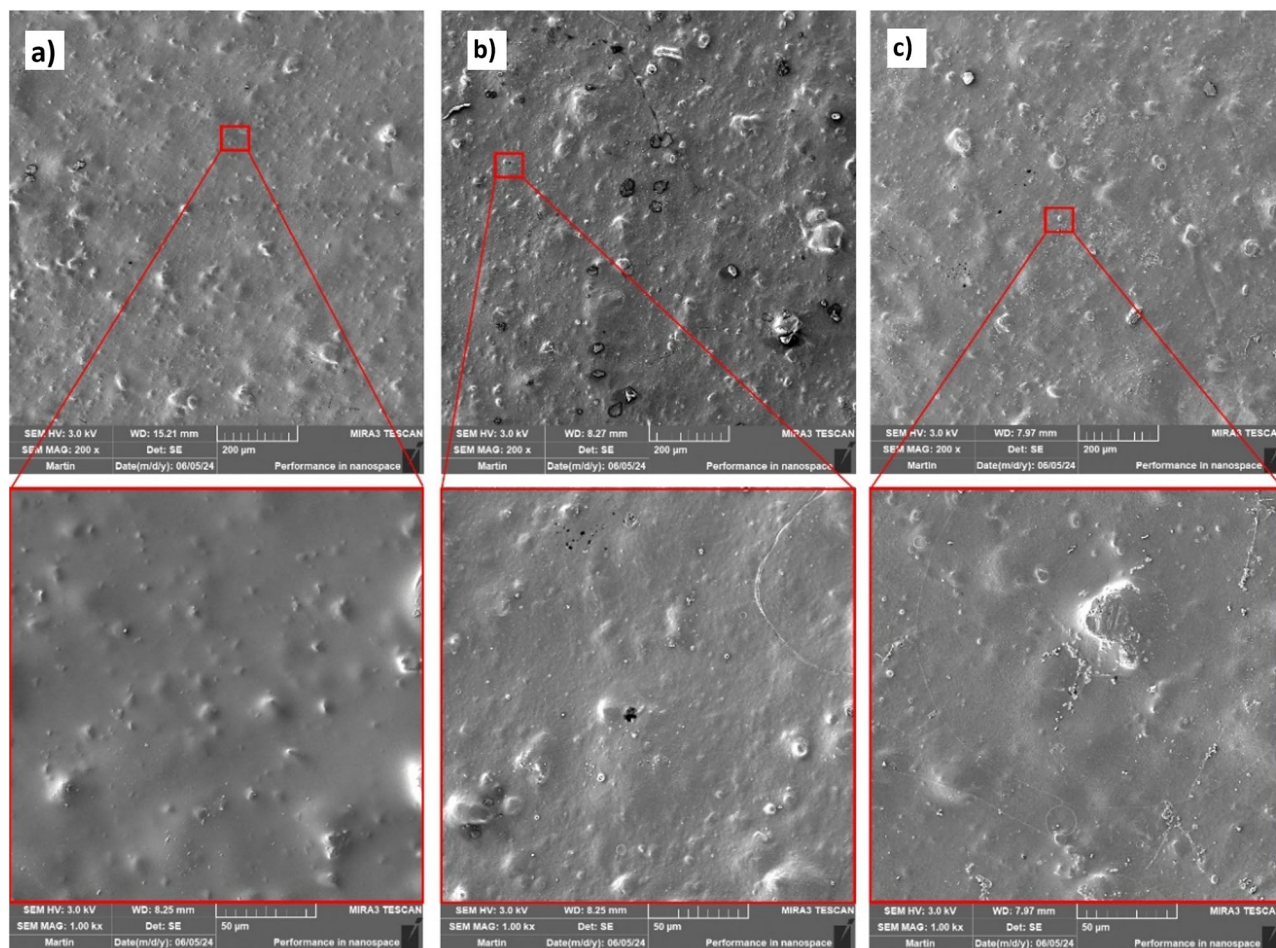


Fig. 17 | SEM micrographs of PLA films containing 10 wt.% biochar pyrolyzed at 400 °C. a As-produced, **b** after 30 days of thermophilic composting, **c** after 45 days of thermophilic composting.

However, the high-surface-area B700 biochar produced the largest increase in MVR and the greatest reduction in initial thermal stability. These results are consistent with more pronounced processing-induced changes in the PLA matrix at high B700 loading.

The biodegradation response was governed by the combined effects of biochar pyrolysis temperature and filler content. Pyrolysis at 700 °C generated a more hydrophilic and porous biochar than pyrolysis at 400 °C, whereas the corresponding PLA films differed in structural ordering, particle–matrix contact and processing-induced changes. At 2 wt.% loading, the low-temperature biochar produced the fastest biodegradation response, reaching 77.2% after 16 weeks of thermophilic composting. Its lower apparent structural order, limited particle–matrix contact, early surface cracking and microbial colonisation were consistent with enhanced local accessibility of the PLA phase to water and microorganisms. In contrast, at 10 wt.% loading, the hydrophobic, low-porosity B400 filler was associated with the slowest biodegradation behaviour.

The effect of pyrolysis temperature became particularly evident at 10 wt.% loading. Films containing the more hydrophilic and porous B700 biochar biodegraded faster than those containing B400. This response was consistent with the lower apparent structural order, increased surface roughness and more extensive processing-induced changes observed for the B700-filled films. Thus, the pyrolysis-controlled wettability and pore architecture of biochar are important factors influencing PLA biodegradation, acting together with filler content, particle–matrix morphology and PLA structural ordering.

Overall, walnut-shell biochar can be used to tune the performance and biodegradation behaviour of PLA films, but its effect depends jointly on

pyrolysis conditions, filler content and the resulting particle–matrix morphology. Within the investigated PLA film system and thermophilic composting conditions, 2 wt.% biochar produced at 400 °C provided the fastest biodegradation response, whereas 10 wt.% of the same biochar retarded biodegradation. At 10 wt.% loading, the more hydrophilic and porous biochar produced at 700 °C resulted in faster biodegradation than biochar produced at 400 °C. Therefore, the selection of biochar for PLA composites should consider the intended end-of-life scenario rather than biodegradation alone. Although low-temperature biochar at low loading promoted PLA biodegradation in the present system, the more hydrophilic and porous high-temperature biochar may be advantageous where water retention after compost application is also required. Future work should evaluate biodegradation and the water-retention performance of the resulting compost–biochar mixture in relevant soils. It should also assess water uptake, molecular-weight evolution and microbial colonisation of the PLA/biochar composites.

Methods

Biochar production

The biochar was produced in laboratory conditions using a CLASIC VRO 04 vacuum furnace (Clasic s.r.o., Czech Republic). The vacuum continuously removed all pyrolysis by-products (syngas, bio-oil) from the thermally degrading surface. To assess the effect of pyrolysis temperature on biochar properties, walnut shells were heated at 10 °C min^{−1} to two target temperatures, 400 °C and 700 °C. The samples were held at each target temperature for 90 min. To assess the thermal degradation processes of pyrolysis, TGA analysis of walnut shell degradation was also performed on a

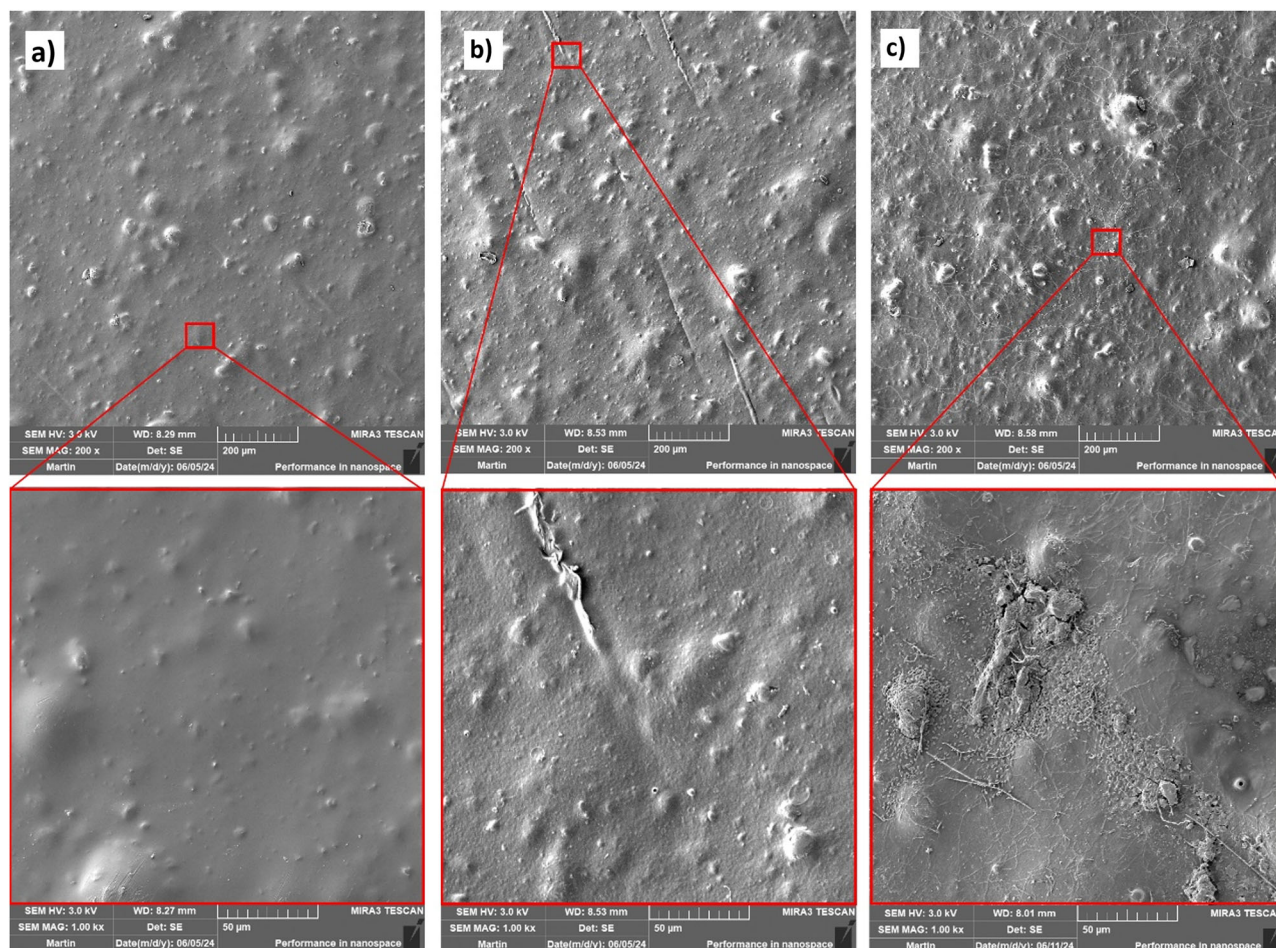


Fig. 18 | SEM micrographs of PLA films containing 10 wt.% biochar pyrolyzed at 700 °C. a As-produced, **b** after 30 days of thermophilic composting, **c** after 45 days of thermophilic composting.

Table 5 | Disintegration of PLA films

Sample	Day 15	Day 30	Day 45
PLA	0.6 ± 0.3%	1.8 ± 0.2%	-
PLA/2B400	0.3 ± 0.1%	1.2 ± 0.1%	2.2% ± 0.3%
PLA/10B400	0.1 ± 0.1%	0.2% ± 0.1%	0.4% ± 0.1%
PLA/2B700	0.2 ± 0.1%	0.4% ± 0.2%	0.7% ± 0.1%
PLA/10B700	0.3 ± 0.1%	0.5% ± 0.2%	1.1% ± 0.2%

B400 and B700, walnut-shell biochar produced at 400 °C and 700 °C, respectively. Values indicate the degree of disintegration and are expressed in %. Values are reported as mean ± standard deviation.

PLA polylactic acid.

TGA2 device (Mettler Toledo, Switzerland) using the same process settings. To enable the use of biochar as a particulate filler in PLA-based biocomposites, a grinding step was introduced to adjust its particle size. Biochar was ground using an Ultra-Centrifugal Mill ZM 200 (Retsch GmbH, Germany) equipped with a 0.2 mm sieve at a rotor speed of 12,000 min⁻¹ operation.

Biochar characterisation

Nitrogen and carbon contents were determined using a PRIMACS analyser with non-dispersive infrared and thermal-conductivity detection (Skalar, Netherlands). Mercury content was determined by thermal decomposition, amalgamation and atomic-absorption spectrometry using an AMA 254 instrument (Altec, Czech Republic). The remaining elements were

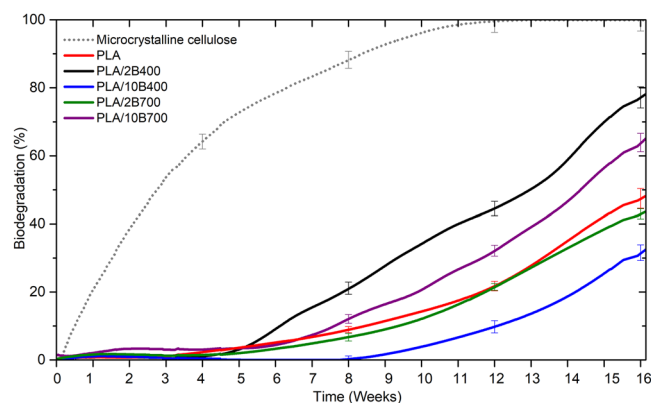


Fig. 19 | Biodegradation curves of neat PLA and PLA/biochar films under controlled thermophilic composting conditions. Error bars represent standard deviations. In the sample designations, 2 and 10 denote biochar contents of 2 wt.% and 10 wt.%, respectively, whereas B400 and B700 denote walnut-shell biochar produced at 400 °C and 700 °C, respectively. Error bars represent standard deviations.

determined after aqua regia digestion using an Agilent ICP-OES 5900 SVDV optical-emission spectrometer (Agilent, Santa Clara, USA). The structural stability of both biochar samples after grinding was observed using an FE-SEM TESCAN MIRA 3 (Tescan, Brno, Czech Republic)

Table 6 | Qualitative summary of competing factors affecting biodegradation of PLA/biochar films under thermophilic composting conditions

Formulation	Factors tending to retard biodegradation	Factors tending to promote biodegradation	Observed net response
PLA/2B400	Hydrophobic B400	Lower apparent structural order; limited particle–matrix contact; local interfacial defects; early cracking and microbial colonisation	Fastest; 77.2% after 16 weeks
PLA/2B700	Higher apparent structural order; more continuous particle–matrix contact	Hydrophilic and porous B700	Slower than PLA/2B400
PLA/10B400	Higher apparent structural order; hydrophobic low-porosity filler phase; restricted water access	Processing-induced chain shortening	Slowest
PLA/10B700	More continuous particle–matrix contact	Lower apparent structural order; hydrophilic porous B700; higher surface roughness; most extensive chain shortening; microbial colonisation	Faster than PLA/10B400, but slower than PLA/2B400

B400 and B700, walnut-shell biochar produced at 400 °C and 700 °C, respectively. The assignments are qualitative interpretations based on the measured biochar and film characteristics and do not represent directly measured water-uptake or diffusion-coefficient values.

PLA polylactic acid.

Table 7 | Sample compositions

Sample designation	Composition (wt.%)		
	PLA	Biochar produced at 400 °C	Biochar produced at 700 °C
PLA	100	-	-
PLA/2B400	98	2	-
PLA/10B400	90	10	-
PLA/2B700	98	-	2
PLA/10B700	90	-	10

instrument with an accelerated voltage of 10 kV. Prior to analysis, the samples were coated with 6 nm of platinum/palladium (Pt/Pd) alloy (80/20) using a Leica EM ACE200 sputter coater (Leica Microsystems, Wetzlar, Germany). Furthermore, the average particle size was determined using a LA-920 laser diffraction analyzer (Horiba, Japan) and subsequently verified from the SEM images. Porosity and specific surface area were determined using the BET (Brunauer–Emmett–Teller) method of gas-molecule physisorption on the surface of the tested material under reduced pressure with an Autosorb iQ MP from Quantachrome (Boynton Beach, Florida, USA). Further, the hydrophobic/hydrophilic properties of biochar were determined by measuring the contact angle between the biochar surface and a water droplet. The procedure was adapted from Usevičiūtė et al.³⁸. A 0.5 µL droplet of distilled water was released onto a continuous, flat biochar surface from a height of 1 cm using a Pipet4u Pro micropipette (AHN Bio-technologie GmbH, Germany). The contact angle was recorded using an optical system supplied by AdvEX Instruments (Brno, Czech Republic). The measurements were repeated on five samples.

Preparation of PLA biocomposites

Luminy L175 from Total Energies Corbion was used to determine the effect of biochar on the kinetics of PLA biodegradation. It is a homopolymer with a molar mass of 226,000 g·mol⁻¹, with a minimum content of 99 wt. % L-isomer in the chain. It has a melting point of 175 °C, a glass transition temperature of 60 °C, and a mean melt mass-flow rate (MFR) of 3 g 10 min⁻¹ at 190 °C under a load of 2.16 kg (determined in accordance with EN ISO 1133, procedure A). Before the PLA compounding process with the produced biochar, all material components were dried in a VD53 vacuum dryer at 50 °C for 12 h. Biochar loadings between 1 and 20 wt.% have been most commonly reported for PLA-based composites^{42,65–69}. In the present study, the selection of the biochar concentration also considered potential effects on biodegradability. The maximum loading was set at 10 wt.% because higher contents were expected to cause a substantial deterioration in mechanical properties and could exceed the production limits of the MC

15HT extruder (Xplore, Netherlands). To determine the effect of biochar amount on biodegradation kinetics, PLA biocomposites were also compounded with 2 wt. % of this component. The compositions and designations of all prepared PLA/biochar formulations are listed in Table 7. All material variants were compounded using the same MC 15HT extruder settings, with a constant screw chamber temperature profile of 185 °C and screw speed of 100 rpm. As before, the compounding process was followed by drying in a VD53 vacuum dryer at 50 °C for 12 h. This was followed by film extrusion using an MC 15HT extruder through a wide-slot die with a nominal size of 0.4 mm. For film extrusion, a constant temperature profile of 190 °C was used in the screw chamber, with an extrusion head temperature of 215 °C, screw speed of 100 rpm, and a draw roller speed ratio of 1.1. The extruded films had an average width of 51 ± 0.5 mm and a thickness of 0.43 ± 0.08 mm. Representative macroscopic photographs of the as-produced neat PLA and PLA/biochar films are provided in Supplementary Fig. S7.

Mechanical testing of PLA composites

The tensile properties were measured according to EN ISO 527-3 using a TiraTest machine (Labortech, Opava, Czech Republic) with an MFX 500-B extensometer (Mess & Feinwerktechnik GmbH, Velbert, Germany). Prior to testing, PLA films were cut to a width of 15 ± 0.2 mm and a length of 160 ± 2 mm, in accordance with EN ISO 527-3 and conditioned for 240 h in a climatic chamber at 25 °C and 50% relative humidity. The tensile modulus (E_t) was determined at a crosshead speed of 1 mm min⁻¹, and the tensile strength (σ_m) and elongation at break (ϵ_{tb}) were measured at a crosshead speed of 5 mm min⁻¹ as the average of 10 measurements.

Rheological testing of PLA composites

The rheological properties of the produced PLA films were assessed by determining the melt volume-flow rate (MVR) in accordance with EN ISO 1133-1 at 190 °C under a load of 2.16 kg using a CEAST 7028 instrument. Before the measurements, the films were dried in a VD53 vacuum dryer at 50 °C for 12 h. The results were evaluated based on five measurements.

Analysis of biodegradability under thermophilic composting

The biodegradation kinetics of PLA films under thermophilic composting conditions (58 °C) were studied using a method derived from ISO 14855-1. This approach monitors the evolution of carbon dioxide as an indicator of microbial degradation activity. The generated CO₂ was recorded by a spirometer (ECHO, ECHO d.o.o., Slovenske Konjice, Slovenia). According to the standard procedure, 10 g of PLA film was cut into fragments approximately 1 × 1 cm and placed into 2.8 L cylindrical hermetic vessels filled with 150 g of compost. The compost used in this experiment was supplied by AGRO CS (Říkov, Czech Republic) and exhibited a pH of 5.2, as measured with a Volcraft PH-100ATC pH meter (Conrad Electronic s.r.o., Praha, Czech Republic).

Table 8 | The individual proportions of total organic carbon of components

Sample designation	Proportions (%)
PLA	50
B400	76.2
B700	74.4

Prior to testing, the compost moisture content was adjusted to 50% using a Mettler Toledo™ HX204 halogen moisture analyzer (Mettler Toledo, Columbus, OH, USA), and particles larger than 2 mm were removed by sieving. To validate microbial activity, parallel vessels containing microcrystalline cellulose (Sigma-Aldrich, Saint-Quentin-Falavier, France) served as positive reference materials. All vessels were incubated in darkness and opened weekly for manual mixing to ensure uniform moisture distribution. Each biodegradation trial was conducted in triplicate, and the degree of biodegradation was calculated according to the following equation:

$$D_t = \frac{(\text{CO}_2)_T - (\text{CO}_2)_B}{T_{\text{hCO}_2}} \cdot 100 [\%] \quad (1)$$

where $(\text{CO}_2)_T$ represents the cumulative amount of carbon dioxide evolved in the composting reactor containing the tested material, $(\text{CO}_2)_B$ denotes the average cumulative amount of carbon dioxide released from the blank (reference) vessels, and (T_{hCO_2}) corresponds to the theoretical quantity of carbon dioxide that can be generated by complete oxidation of the test material (all values expressed in g per vessel).

The theoretical amount of carbon dioxide can be determined via the following equation:

$$T_{\text{hCO}_2} = m_{\text{TOT}} \cdot C_{\text{TOT}} \cdot \frac{44}{12} [\text{g}] \quad (2)$$

where m_{TOT} is the total dry mass of the test material introduced into the composting vessel at the beginning of the experiment (in g), C_{TOT} is the fraction of total organic carbon within the dry solids of the test material (expressed in g of carbon per g of dry solids), while 44 and 12 refer to the molecular weight of carbon dioxide and the atomic weight of carbon, respectively. The specific total organic carbon contents for the PLA films are summarised in Table 8.

Due to the evolving organic carbon content, no additional analyses could be performed directly on samples during the respirometric biodegradation test. Therefore, a parallel disintegration experiment was conducted in which PLA films (100 mm × 40 mm) were exposed to the same compost under identical thermophilic conditions. At 15-day intervals, films were retrieved, rinsed with demineralized water, and conditioned at 25 °C and 50% relative humidity for 240 h in a climatic chamber (Tesesco, Czech Republic).

The degree of disintegration was then determined according to the following equation:

$$D = \frac{m_i - m_r}{m_i} \cdot 100 [\%] \quad (3)$$

where D , is degree of disintegration (in %), m_i is initial dry mass of the test PLA films (in g), m_r is the dry mass of the residual test material (in g)

Furthermore, changes in structural, thermal, and chemical properties, including surface morphology, were characterized by differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). Results represent mean values from three independent measurements.

Differential scanning calorimetry (DSC) of PLA composites

Thermal properties and structural changes of the produced (pristine) and biodegraded PLA films were analyzed using a DSC 1/700 calorimeter (Mettler Toledo, Greifensee, Switzerland). Approximately 5 mg of material, extracted from the film cross-section, was sealed in an aluminum pan and placed in the DSC cell under a constant nitrogen flow of 50 mL min⁻¹. The thermal program consisted of heating from 0 °C to 200 °C at 10 °C min⁻¹, followed by an isothermal hold at 200 °C for 180 s, and subsequent cooling at the same rate. The glass transition temperature (T_g), cold crystallisation temperature and enthalpy (T_{sc} , ΔH_{sc}), pre-melt crystallisation temperature and enthalpy (T_{pc} , ΔH_{pc}) and melting temperature and enthalpy (T_m , ΔH_m) were evaluated.

The degree of crystallinity (X_C) was determined according to the following equation:

$$X_C = \frac{\Delta H}{\Delta H_m^0 \cdot w_m} = \frac{\Delta H_m - \Delta H_{sc} - \Delta H_{pc}}{\Delta H_m^0 \cdot w_m} \cdot 100 [\%] \quad (4)$$

where ΔH_m^0 is the melting enthalpy of 100% crystalline PLA (93 J g⁻¹)⁷⁰, w_m is the mass fraction of PLA in the composites, and the ΔH is the enthalpy balance.

Fourier transform infrared spectroscopy (FT-IR) of PLA composites

Chemical changes in the PLA films were analyzed using a Nicolet iS10 infrared spectrometer (Thermo Scientific, Waltham, MA, USA) equipped with an ATR accessory and a diamond crystal. FTIR-ATR spectra were recorded over the range of 400–4000 cm⁻¹ by averaging 64 scans at a resolution of 4 cm⁻¹.

Thermogravimetric analysis (TGA) of PLA composites

Thermal stability was evaluated using a TGA2 instrument (Mettler Toledo, Greifensee, Switzerland). Samples (5 ± 0.5 mg) were extracted from the film cross-section following the same procedure as DSC analysis. Thermograms were obtained by heating from 50 °C to 600 °C at 10 °C min⁻¹ under nitrogen atmosphere, and decomposition temperatures at 5% weight loss ($T_{5\%}$) and 50% weight loss ($T_{50\%}$) were determined.

Scanning electron microscopy (SEM) analysis of PLA composites

The mechanism of degradation and surface changes were observed with field emission scanning electron microscopy (FE-SEM). For this purpose, a TESCAN MIRA 3 microscope (Tescan, Brno, Czech Republic) at an accelerated voltage of 3 kV was used. The test samples were, prior to analysis, coated with 1 nm of platinum using Q150R ES (Quorum Technologies, UK).

Statistical analysis

All mechanical test results are reported as mean ± standard deviation. The effect of biochar content and pyrolysis temperature on tensile strength, elongation at break, tensile modulus, and melt volume-flow rate (MVR), as well as on disintegration degree and biodegradation degree, was evaluated using one-way analysis of variance (ANOVA) with the formulation as a single factor. ANOVA was performed in Origin (OriginLab Corporation, Northampton, MA, USA) at a significance level of $\alpha = 0.05$.

Data availability

The datasets generated and/or analyzed during the current study are not publicly available because the raw experimental data and image files are retained by the authors and have not been deposited in a public repository but are available from the corresponding author on reasonable request.

Code availability

No custom code was generated or used in this study.

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Conceptualisation, P.B.; methodology, P.B.; validation, P.B., M.B. and M.J.; formal analysis, P.B. and J.G.-C.; investigation, P.B., M.B., J.G.-C.; data curation, P.B.; writing—original draft preparation, P.B.; writing—review and editing, P.B., J.G.-C.; visualisation, J.G.-C.; supervision, M.J.; project administration, P.B.; funding acquisition, P.B. All authors have read and agreed to the published version of the manuscript.

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Competing interests

The authors declare no competing interests.

Additional information

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