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Fabrication and Degradation of Hierarchical PLA Structures via Electrospinning and Fused Filament Fabrication

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Abstract

In the present work, we developed unique structures from poly lactic acid (PLA) by combining electrospinning and fused filament fabrication (FFF). The thin layers of fiber mats were used as interleaves between printed infill layers, and hence, we obtained a multi-level porous structure. Due to the known favorable characteristics of the electrospun mats for cell adhesion and growth, these structures may be used as scaffolds in the future. The aim of this study was to test the processing, the structure, and the hydrolytic degradation at a fundamental level. Samples were immersed into phosphate-buffered saline (PBS) solution and incubated at 37°C for 1, 3, 7, 15, 30 and 60 days. Our findings show that adding 0.15 wt% electrospun fibers results in a significantly higher degree of crystallinity. We found that the embedded fiber mats promoted heterogeneous nucleation, thus improving mechanical properties significantly. Scanning electron microscopy confirmed that fibers fused with the FFF grid *in situ*, resulting in increased tensile strength and elongation at break. Additionally, the hierarchical structures exhibit better mechanical performance at the potential application temperature (37 °C) than the neat 3D printed samples.

Keywords: Electrospinning, FFF 3D printing, Hydrolytic degradation, Multi-level structure, Poly lactic acid

Introduction

Processing customized products for biomedical applications, such as scaffolds, requires advanced techniques and new approaches. A combination of multiple techniques and creating complex, detailed structures can fulfill the complex set of requirements.

On one hand, electrospinning is a widely used practice of nanofiber fabrication, based on the effect of an electric field on a fluid jet. It has gained considerable attention for its varied material selection, controllable properties and wide range of applications, such as filtering [1-3], sensors [4,5], drug delivery systems [6-8], and wound healing [9,10]. Electrospun nanofibers are also used in biomedical research, since their high surface-to-volume ratio promotes a native environment for cell cultures and supports cell growth. The main drawback is that electrospinning is not directly capable of producing 3D objects. Modified methods still do not produce decent dimensional precision.

On the other hand, additive manufacturing builds up custom 3D geometries layer-by-layer [11]. Its main advantage lies in its design freedom and customizability, especially as demonstrated by 3D printed models constructed of medical imaging data (CT, MRI, PET) images, which have significantly advanced medical technology [12]. 3D printing, such as electrospinning, also holds great potential as an innovative approach in personalized medicine [13]. However, the functionalization is not easy because processing may damage the additives, and because the surface area and details of the product are limited.

A combination of these two techniques would be greatly beneficial because a porous 3D printed scaffold can be easily generated with the desired geometry, while nanofibers add another layer of complexity [14]. The printed porous structure protects the fiber layers, while nanofibers render an extra layer of functionality to the product, *e.g.*, nanoporosity, drug elution, and promote cell adhesion and proliferation.

Biomedical applications, including scaffold fabrication, impose high requirements on the material used. In addition to naturally occurring biological polymers (*e.g.*, hyaluronic acid, collagen, chitin), synthetic biopolymers such as polylactic acid (PLA) provide a promising alternative for biomedical applications. PLA is a bioplastic that has attracted considerable attention in recent years due to its biocompatibility and biodegradability. It metabolizes into harmless byproducts, and it can be processed in various ways, including electrospinning and 3D printing. Consequently, PLA is an ideal candidate for producing bimodal, self-reinforced scaffold structures using ES and FFF.

For biodegradable porous scaffold materials, the degradation rate is a key factor, and recording the changes in mechanical properties with decomposition is necessary. It has been reported that PLA can exhibit early-stage physical aging effects, which may lead to a temporary increase in stiffness due to enthalpy relaxation processes [15].

Numerous studies have explored the degradation behavior of bulk PLA specimens and PLA nanofibers/nanoparticles separately. Duek *et al.* [16] investigated the degradation mechanism of injection-molded PLLA specimens with varying degrees of crystallinity (χ), and they observed an overall increase in χ until the end of the degradation period. While χ fluctuated in less crystalline samples, it steadily increased in more crystalline specimens. Signs of volume and surface degradation were detected after week 12. Another study conducted by Zhou *et al.* [17] showed that the crystallinity of bulk PLLA specimens increased until week 16 but declined by week 20. They related the rise in crystallinity to degradation occurring primarily in the amorphous regions, as evidenced by the absence of new peaks in the X-ray diffraction (XRD) patterns during the decomposition study. Additionally, they reported lower melting temperature (T_m) with degradation time, as newly formed crystalline parts were imperfect. Similarly, Deroiné *et al.* [18] examined hydrothermal aging of injection-molded PLA across water environments: distilled water, filtered and renewed seawater, and natural seawater, all at 25–50 °C. They noted a gradual decline in molecular weight, especially at elevated temperatures, due to hydrolytic chain scission and changes in crystallinity. Their results also showed that water absorption, plasticization, and hydrolysis can occur simultaneously during aging. This indicates that several degradation processes can occur simultaneously in PLA aging.

Woo and Wee [19] performed accelerated decomposition tests at elevated temperatures (50, 60, 70 °C) on compression-molded sheets. Fourier-transform infrared (FTIR) spectroscopy results revealed a growing peak associated with -OH groups. They suggest that in the aqueous medium, polymer backbone degrades, which leads to an increased number of hydroxyl groups. Leones *et al.* [20] demonstrated that PLA polymer chain scission in phosphate-buffered saline (PBS) solution at 37 °C starts right in the first week, according to the FTIR analysis. Spectral data showed a reduction in carbonyl group intensity.

The decomposition of fibrous PLA structures was also investigated in the literature. Yuan *et al.* [21] studied the degradation of PLLA mats in different media (PBS and NaOH solution) under accelerated degradation conditions. Although crystallinity rose with degradation, a decrease in structural order of crystallites may occur, as the melting temperature dropped during the decomposition process. According to mechanical studies, the tensile strength decreased during the degradation process. The number of entanglements decreased due to chain scissions, which enhanced the mobility of (the shortened) polymer chains. Furthermore, the broken macromolecular chains could easily form new crystalline domains, hence the degree of crystallinity increased.

Other publications also report similar results, stating that the degree of crystallinity increases with degradation [22,23]. On the other hand, You *et al.* [24] found that the crystallinity of PGA and PLA nanofiber mats increased in the first phase of the *in vitro* degradation. The crystallinity of the samples decreased after the third and twelfth day, respectively. After that, the crystalline phases degraded.

Microcracks and nanofiber breakage are reported in various publications, which affect mechanical properties [21,25,26]. Yuan *et al.* [21] observed axial microcracks on the surface of nanofibers. In addition to molecular weight loss, these factors contributed to the reduction of tensile strength after 5 days. Araque-Monrós *et al.* [27] conducted a degradation study in NaOH. SEM images showed nanofibers with a smooth surface; however, from day 30 onward, the surface became porous.

To meet the requirements of various medical applications, mixing and copolymerization techniques are commonly used to develop PLA composites [28]. Structural modifications allow for control over the degradation rate and improve the mechanical properties of the materials. Mixing PDLA with L-lactide inhibits crystallization within the polymer matrix, thus accelerating degradation [29]. Similarly, starch promotes degradation through its hydrophilizing effect. In both cases, reduced crystallinity leads to decreased tensile strength and modulus [28,29]. Incorporating carbon nanotubes (CNTs) and hydroxyapatite can increase crystallinity, thereby slowing degradation and improving mechanical strength [30,31].

Overall, the nanofibers exhibit different degradation kinetics compared to the bulk PLA material, which is important when combining them in a single scaffold. The degradation rate of both components can be tailored.

Electrospinning and FFF 3D printing are both prominent technologies in scaffold development, and recent attempts have been made to integrate the two processes [32-35]. A suitable method is

to place nanofiber interleaves between the printed layers, which provides sufficient interfacial adhesion and allows control of fiber distribution without clogging the nozzle. Interleaving 3D-printed layers with nanofiber mats delivers promising mechanical performance, while the ultrafine nanofibers provide essential functional properties and porosity for tissue culture.

In this study, we hypothesize that inserting electrospun nanofiber mats between FFF-printed PLA layers enhances interfacial adhesion, mechanical properties, and degradation behavior. Using an integrated electrospinning and FFF method, we created multilevel PLA structures with nanofiber interleaves. We initially examined how printing temperature (190–230 °C) and nanofiber content (2.2%, 3.2%, and 5.5%) affect the structural, thermal, chemical, and mechanical properties, focusing particularly on morphology and crystallinity to evaluate how well the two techniques combine and under which conditions the fiber architecture stays intact. Additionally, we assessed the degradation behavior of the hierarchical structures under hydrolytic conditions through complementary chemical, thermal, morphological, and mechanical analyses. Collectively, these studies establish structure–property relationships and offer a fundamental basis for designing integrated electrospun–FFF scaffolds for future applications.

Results

The effect of process parameters on morphology

First, we tested the effect of printing temperature and nanofiber content to see how the hot melt affects the nanofibers' integrity (Figure 1 a-f). Based on the SEM images, the electrospun mats interposed between the printed layers remained attached with proper adhesion to the printed filaments. Therefore, although minor local alterations occur at elevated temperatures (*e.g.*, 210 °C), the nanofiber network as a whole is preserved, which supports the selection of 210 °C for subsequent degradation studies (Figure 1 d-f).

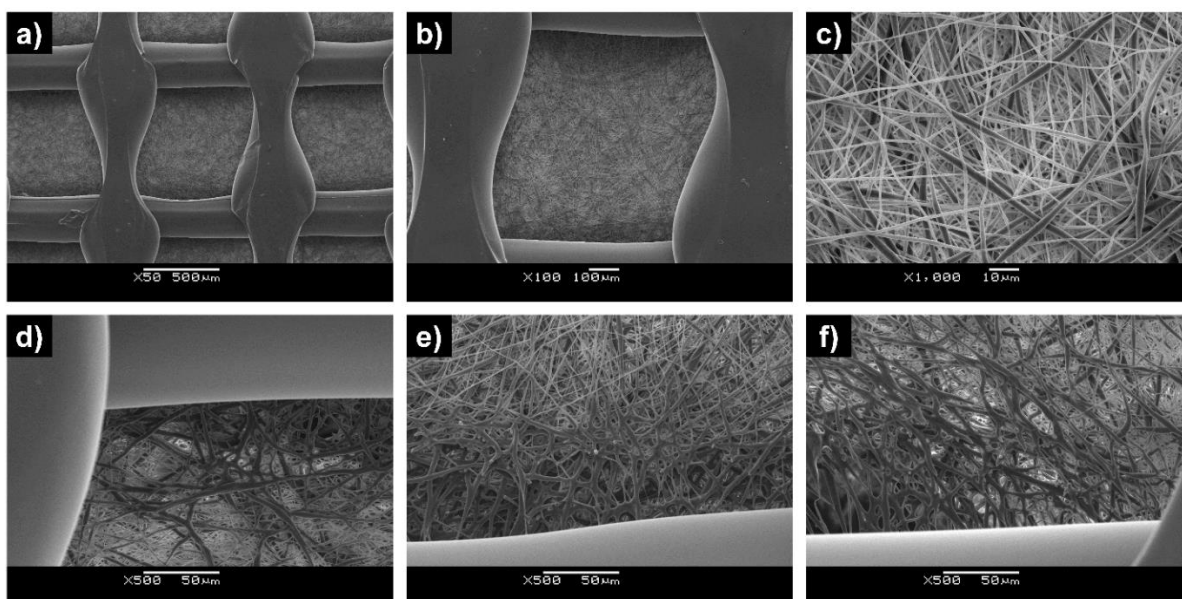


Figure 1. Representative SEM images showing the morphology and interface of electrospun nanofibers within the 3D-printed PLA structures at different printing conditions. a)-c): 200/3.2 sample structure, d)-f): molten nanofibers located near the FFF grid, d): 210/3.2, e): 210/5.5, f): 230/3.2.

In the DSC experiments, we determined the thermal properties of the 3D printed, nanofiber-containing samples fabricated with different parameters. Transition temperatures and degrees of crystallinity were calculated from the first heat cycle of the DSC curves (Figure 2). Results are listed in Table 1. DSC curves of the fiber mat and the references, printed at different temperatures, can be found in Figure S1; thermal properties are listed in Table S1 of the Supplementary Material.

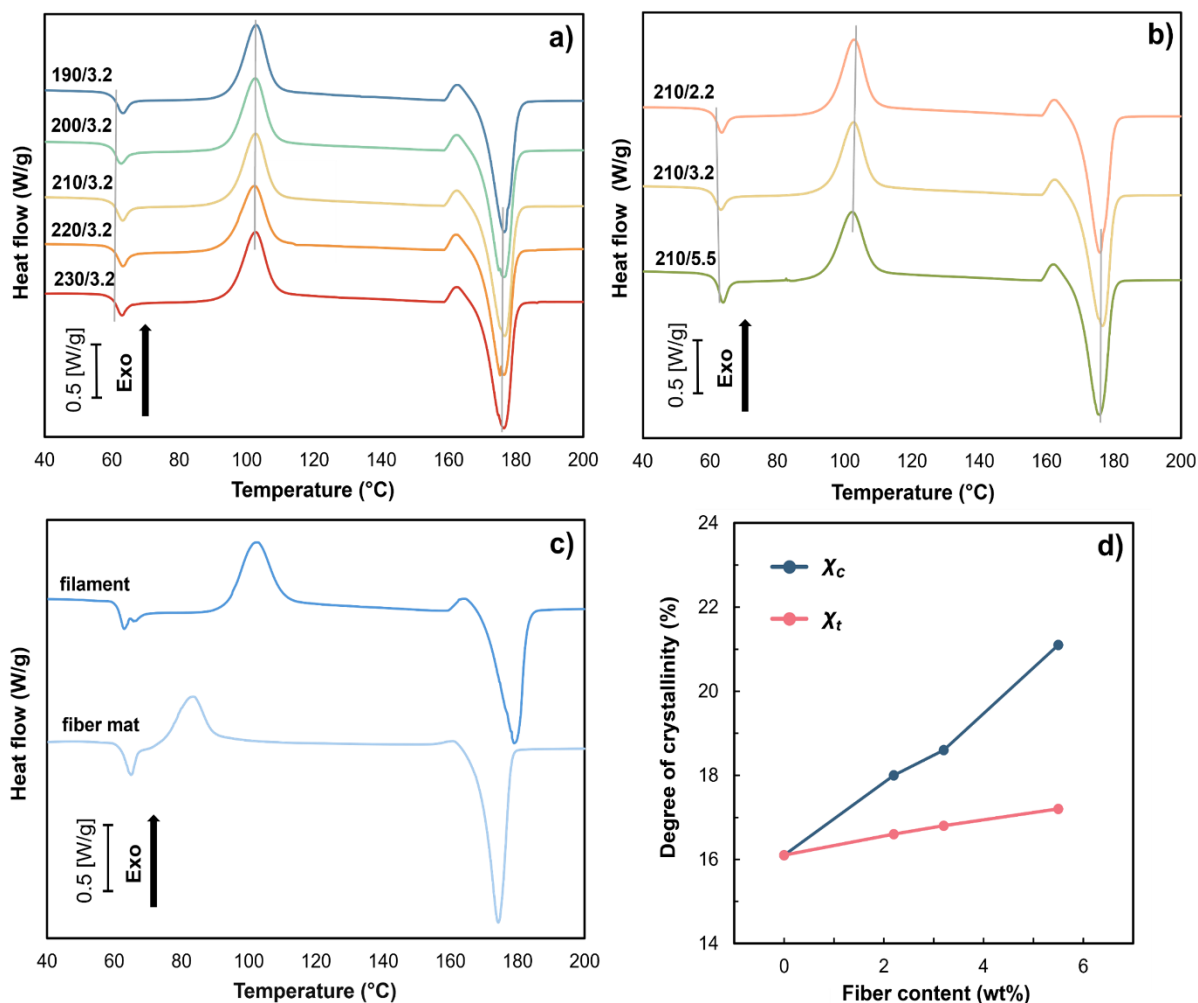


Figure 2. DSC analysis of PLA 3100HP samples with different nozzle temperatures and nanofiber contents, including comparison of experimental and theoretical crystallinity. a) samples made with different nozzle temperatures, b) samples with different nanofiber content, c) PLA 3100HP filament and nanofiber mat, d) comparison of crystallinity results, calculated with the rule of mixtures (X_t) and obtained from DSC (X_c).

For each sample, an exothermic peak was observed on the DSC curves around 170 °C, just before the crystalline melting. Above 160 °C, the disordered α' phase transforms into the stable, ordered α phase, which has the same conformation that releases heat. This results in the small exothermic peak before reaching the crystal melting temperature, where the newly formed α -phase melts [36].

Both nozzle temperature and fiber content affected the crystallinity of the samples. At elevated printing temperatures, the viscosity of the polymer melt decreased, enhancing flow and the

deposition of filament onto the printing tray and the previously laid material layers. Increasing the temperature also enhanced the adhesion between printed layers [37]. Since higher temperatures promoted the arrangement of ordered polymer chains, the 190/3.2 sample, printed at the lowest nozzle temperature, was the least crystalline (16.1%). Among the samples printed at different temperatures, 210/3.2 has the highest crystallinity (18.6%), thus, we printed the DMA and tensile specimens at this temperature.

Crystallinity results obtained from DSC measurements (χ_c) were compared with the theoretical crystallinity (χ_t) calculated with the rule of mixtures (Figure 4d). Nanofibers, with their huge surface area, act as nucleation agents for the printed layers. Therefore, the degree of crystallinity can be further enhanced by increasing the fiber content, reaching more than 21% in the case of the 210/5.5 sample.

Table 1. Thermal properties determined using DSC from the first heating cycle.

Sample name	T_g (°C)	T_{cc} (°C)	T_m (°C)	ΔH_{cc} (J/g)	ΔH_p (J/g)	ΔH_m (J/g)	χ_c (%)
190/3.2	61.7	102.7	176.5	31.7	4.0	50.7	16.1
200/3.2	60.9	102.4	176.5	31.2	3.5	51.8	18.5
210/3.2	61.6	102.6	176.6	31.0	3.6	51.8	18.6
220/3.2	61.7	102.3	175.3	30.5	3.6	45.5	16.9
230/3.2	61.5	102.5	176.4	30.6	3.6	50.0	16.9
210/2.2	62.2	102.7	175.9	31.6	3.6	51.9	18.0
210/3.2	61.6	102.6	176.6	31.0	3.6	51.8	18.6
210/5.5	62.2	102.2	175.8	30.0	3.5	53.1	21.1
filament	61.7	101.9	178.9	30.6	2.8	47.2	14.8
fiber mat	62.9	82.8	174.2	17.4	0.5	52.0	36.8

Decomposition study – fiber diameters

Based on our previous findings, we selected 210 °C for printing and a low nanofiber content to produce specimens for decomposition studies. SEM images of 3D, 3D-NF, and NF samples were taken during hydrolytic degradation. Images of the 3D printed grid indicate that the surface of the

printed component of 3D and 3D-NF samples did not change even after being exposed to the hydrolytic environment for 60 days (Figure S2 is presented in the Supplementary Material.) However, a major difference can be seen in fiber morphology between the neat nanofiber samples and when these were used as interleaves in the 3D-NF samples. While the NF samples had a porous surface (Figure 3 a-e), the fibers' surface in the 3D-NF sample was grooved (Figure 4 a)-e)).

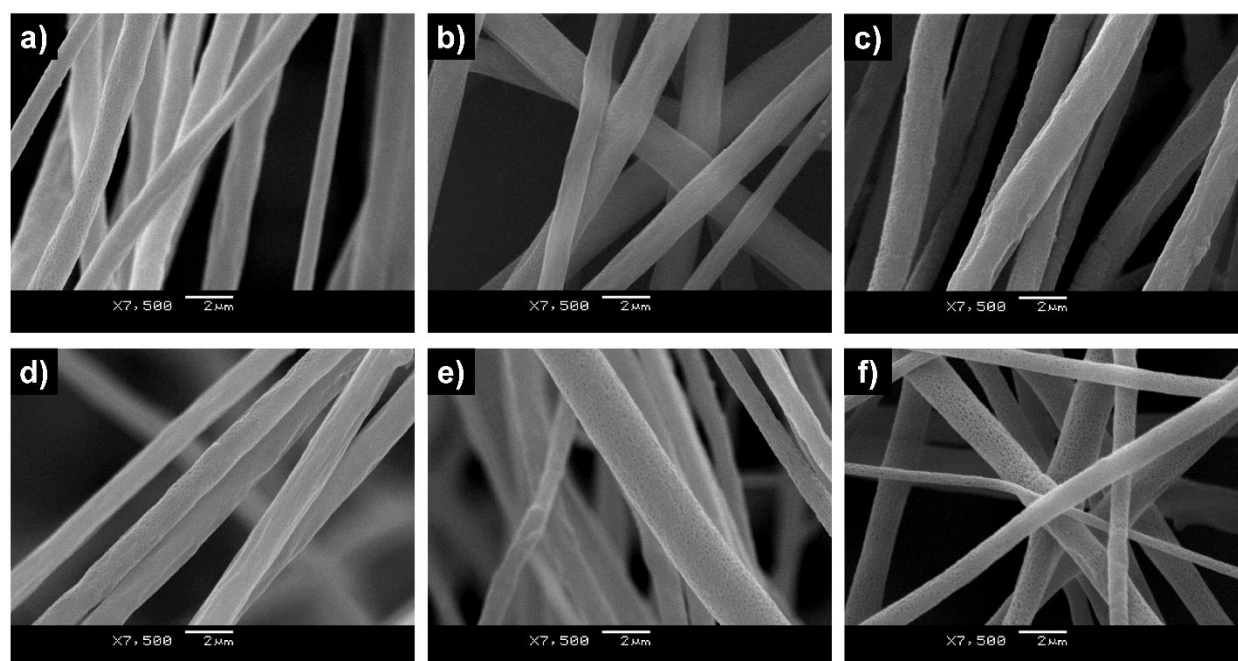


Figure 3. SEM analysis of fiber morphology during hydrolytic degradation. a) NF-0, b) NF-3, c) NF-7, d) NF-15, e) NF-30, f) NF-60.

According to the literature [38], porous fiber morphology is often caused by volatile solvents. The process of fiber formation is endothermic due to the evaporating solvent. This results in condensed water vapor at the interface between the liquid jet and the air. The charged jet attracts the tiny polar water molecules, which leave an imprint on the surface (Figure 5). The difference in fiber morphology between the two groups of samples is due to the evaporation mechanism. The printing temperature of 210 °C heated the fibers and stretched the circular pores into grooves.

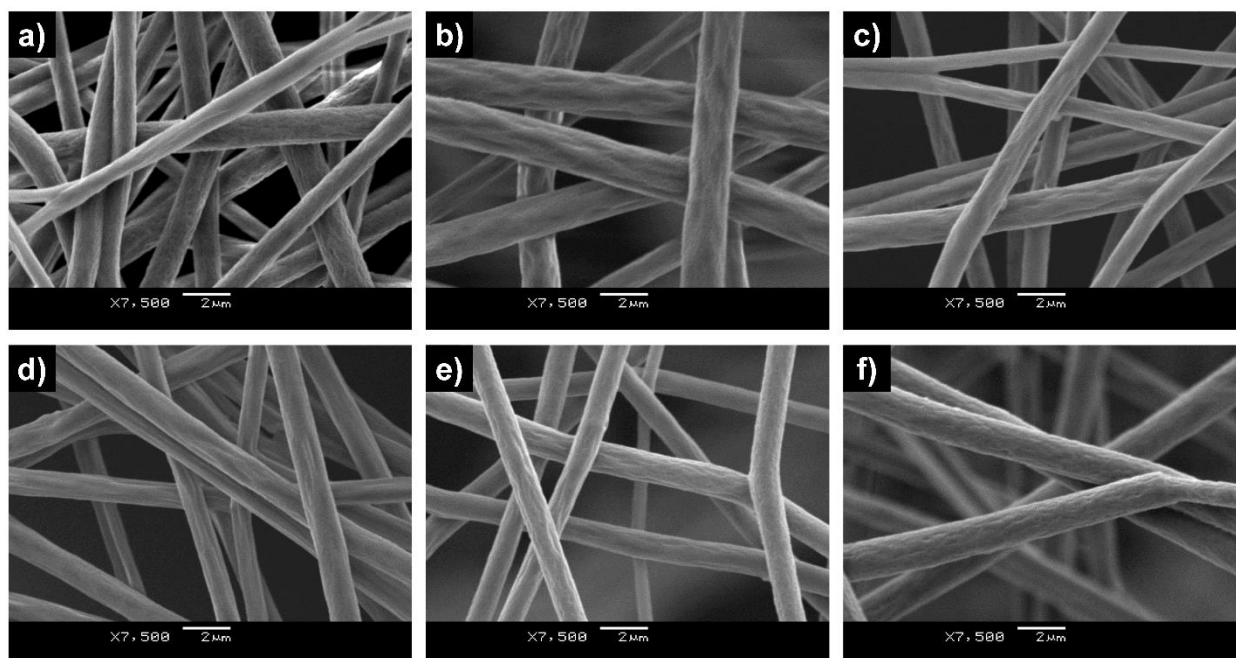


Figure 4. SEM images showing the morphology of the nanofiber component in 3D-printed nanofiber interleaved samples with varying nanofiber content. a) 3D-NF-0, b) 3D-NF-3, c) 3D-NF-7, d) 3D-NF-15, e) 3D-NF-30, f) 3D-NF-60 samples.

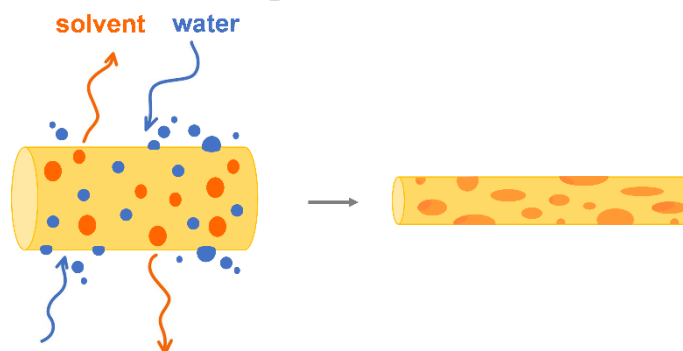


Figure 5. Solvent leaching and environmental water penetration drive the development of the fiber surface architecture. Schematic diagram of the formation of fibers with a porous, grooved surface.

We determined the average fiber diameter of each NF sample throughout the decomposition study using ImageJ software (Table 2). The fibers turned out to be no actual nanofibers, as their diameter was approximately 1 micron. The average fiber diameter steadily decreased over time, showing a 33% reduction after 60 days. This suggests that surface degradation occurred on the ultrafine fibers due to their high surface-to-volume ratio.

Table 2. Average fiber diameter of NF samples.

Sample name	Fiber diameter (nm)
NF-0	1170 $\pm$ 240
NF-1	1135 $\pm$ 227
NF-3	1014 $\pm$ 302
NF-7	968 $\pm$ 197
NF-15	952 $\pm$ 171
NF-30	837 $\pm$ 199
NF-60	780 $\pm$ 160

Comparative DSC analysis during degradation

DSC curves of degraded samples are shown in Figure 6 (numerical results are presented in Table S2 of the Supplementary Material). Among the samples, which were not immersed in the PBS solution, the NF-0 nanofiber mat had the highest degree of crystallinity (39.5%). However, by the end of the degradation study, the fiber mat lost some of its crystallinity (from 39.5% to 34.9%), while the crystallinity of 3D and 3D-NF samples increased from the initial 17.6% to 25.7% and from 20% to 29.2% respectively (Figure 7 a).

Because of its high surface-to-volume ratio, the fiber mat degraded faster than the solid, 3D and 3D-NF samples with lower specific surface area. While in the NF samples, degradation could also affect crystalline parts, in the case of the 3D and 3D-NF specimens, primarily the amorphous regions degraded.

Only 0.15 wt% of fiber content promoted crystallization. Before the degradation study (day 0), the nanofiber-containing sample (3D-NF-0) had a higher degree of crystallinity than the reference 3D printed material (3D-0). Throughout the 60-day degradation period, the crystallinity increased for both samples. The increase in crystallinity over time suggests that hydrolytic cleavage of polymer chains (chain scission) occurred, as shorter chains have greater mobility and can reorganize into new crystalline phases [39].

The T_g of all three sample types shifted to higher temperatures over degradation time, as depicted in Figure 7b. Although hydrolytic chain scission typically reduces molecular weight, the increase

in crystallinity during degradation restricts the mobility of the amorphous phase. As a result, the observed T_g shift reflects the combined effect of chain scission and recrystallization, with crystallinity being the dominant factor in this semi-crystalline PLA system. The decrease in cold crystallization temperature of 3D and 3D-NF samples is due to slower chain relaxation and indicates increased crystallinity. The enthalpy of cold crystallization (ΔH_{cc}) also decreased with degradation due to the formation of shorter molecular chains, which require less energy to develop crystalline regions. The smaller fragments likely facilitated recrystallization and physical reorganization of the material, contributing to the observed increase in crystallinity.

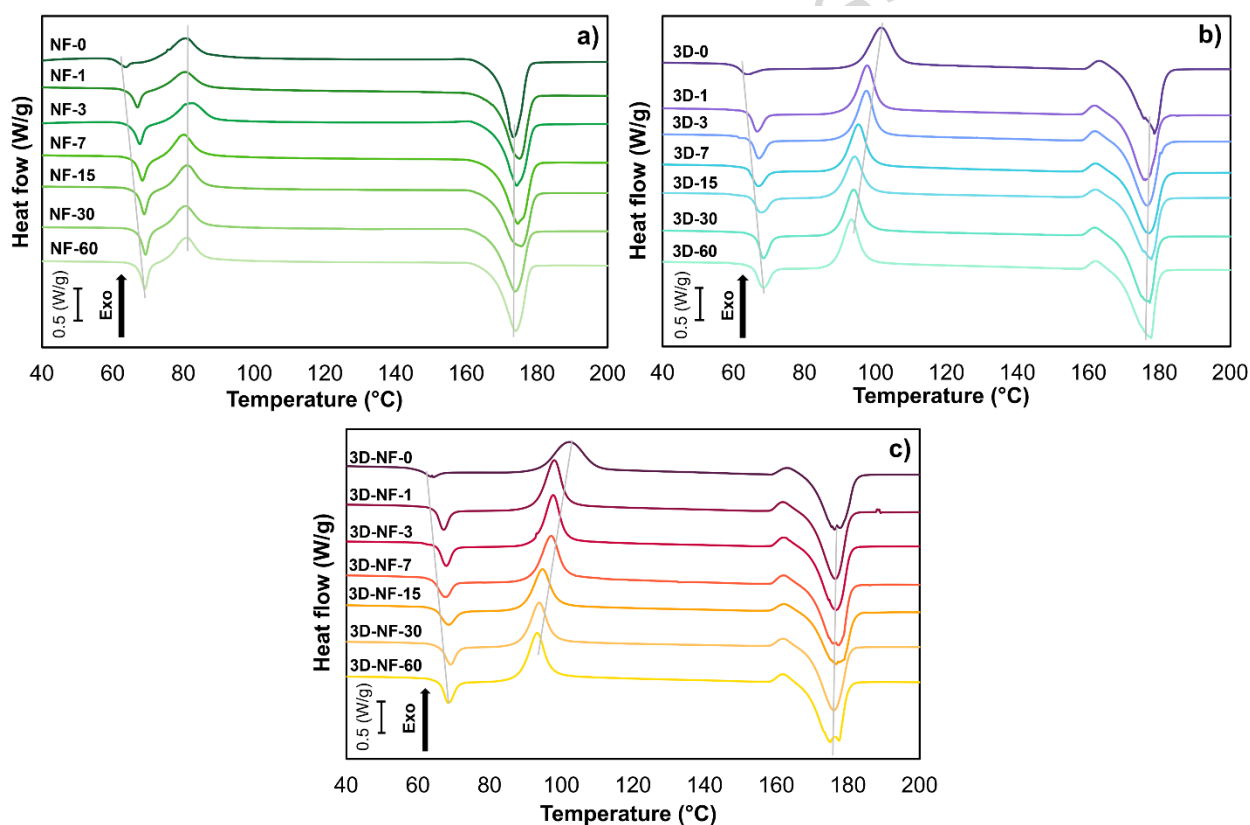


Figure 6. DSC profiles reveal structural changes and shift in crystallinity in the nanofiber and printed samples over the degradation time. a) NF b) 3D c) 3D-NF samples exposed to hydrolytic degradation.

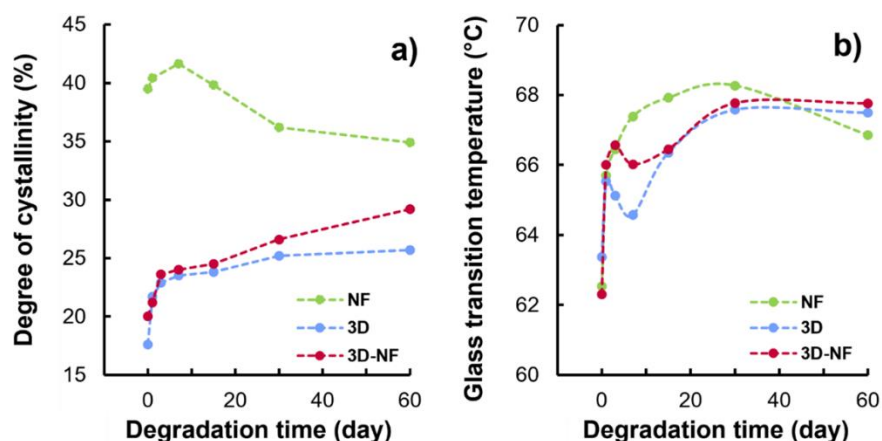


Figure 7. **Hydrolytic degradation induces divergent, time-dependent changes in the crystallinity and glass transition temperatures of nanofiber and 3D-printed samples.** DSC results plotted as a function of degradation time up to 60 days: a) degree of crystallinity and b) glass transition temperature as a function of degradation time.

Changes in molecular structure during decomposition

We carried out FTIR-ATR on 3D and 3D-NF samples to find out how the absorbances changed at PLA-specific wavenumbers as the materials broke down. The C=O carbonyl bending vibration associated with the characteristic ester bonding of PLA molecules appears as an intense peak at $\sim 1747\text{ cm}^{-1}$ in the spectrum (Figure 8a-b). The peak at $\sim 1453\text{ cm}^{-1}$ is related to the asymmetric CH_3 bending vibration. The peaks at ~ 1180 and $\sim 1080\text{ cm}^{-1}$ are associated with ester bonding and correspond to symmetric and asymmetric C–O stretching vibrations, respectively, and the peak at $\sim 866\text{ cm}^{-1}$ represents the amorphous regions. (Numerical results are presented in Table S3 of the Supplementary Material).

The curves were normalized to the intensity value at 1453 cm^{-1} , as the CH_3 methyl group on the PLA chain remains unaffected by hydrolytic degradation [40]. According to the literature, absorbance at approximately 1450 cm^{-1} is considered a good practice for PLA and is appropriate for normalizing results [41].

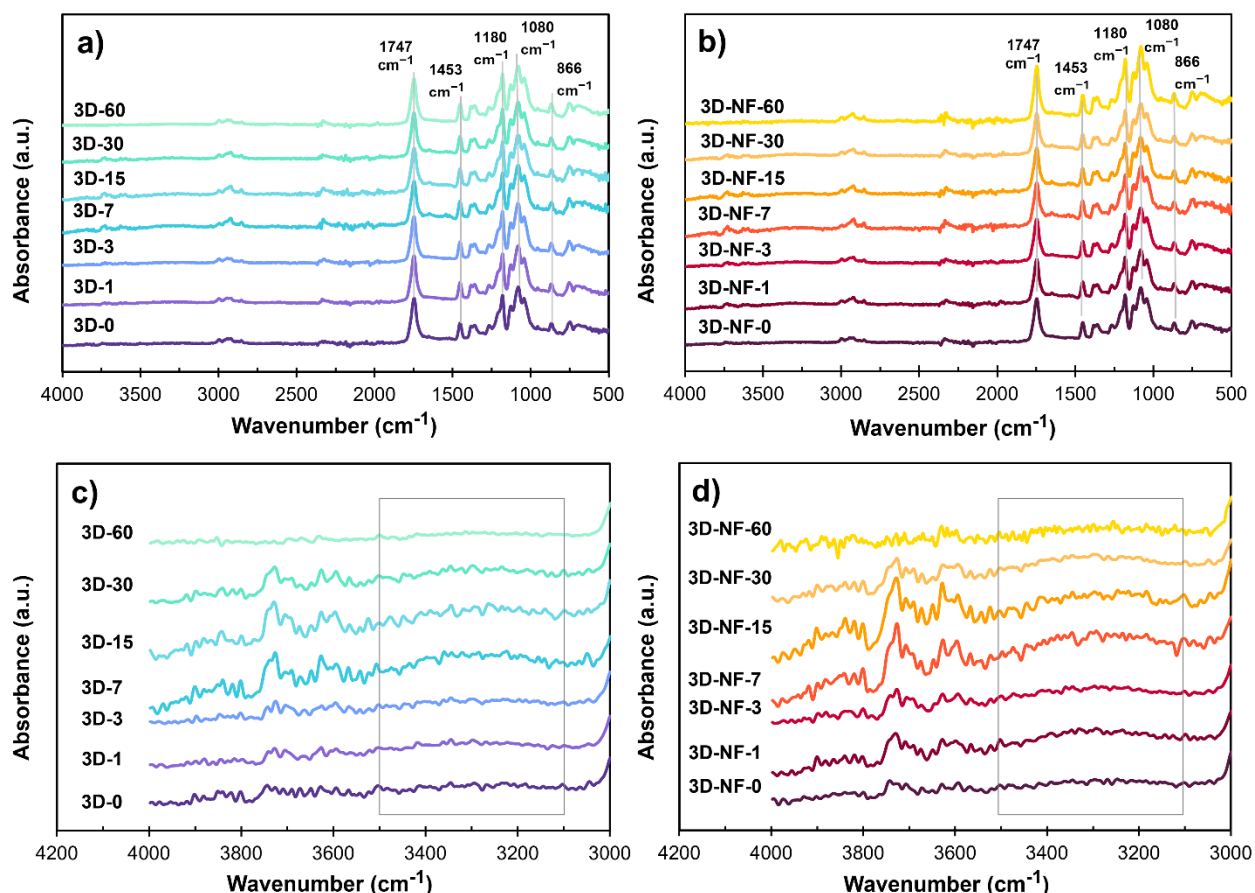


Figure 8. FTIR-ATR spectra track changes in the characteristic chemical bonds of 3D and 3D-NF samples during hydrolytic degradation. a)-b) whole spectra of 3D and 3D-NF samples, c)-d) detailed spectra of 3D and 3D-NF samples between 3000-4000 cm^{-1} .

The decline in absorbance at $\sim 860 \text{ cm}^{-1}$ indicates that the proportion of amorphous regions decreased with incubation. This finding aligns with the DSC results discussed in the previous section, confirming that hydrolytic degradation increased the degree of crystallinity in the structures.

The decrease in the intensities at ~ 1180 and $\sim 1080 \text{ cm}^{-1}$ indicates that hydrolysis led to the breakdown of ester bonds, as these peaks are related to the cleavage of PLA chains. Hydrolytic degradation of PLA proceeds through random cleavage of ester bonds, resulting in a gradual decrease in molecular weight. Similar findings are documented in the literature [18], showing that molecular weight decreases with aqueous aging, particularly above 30°C , because of hydrolytic chain scission of ester bonds. As the polymer chains become shorter, chain mobility increases and the fragmented chains can reorganize into more ordered crystalline regions [39]. This

interpretation is consistent with the DSC results, which showed increasing crystallinity during degradation.

During the degradation, a notable change was observed in the 3000-4000 cm^{-1} wavelength range (Figure 8 c-d). The intensity of the broad peak became stronger until day 30, which confirms the formation of –OH groups due to hydrolytic degradation. However, by day 60, the absorbance at 1080 and 1180 cm^{-1} for ester bonds increased again, while the intensity of the broad –OH peak diminished. This suggests that the fragmented chains may have undergone partial reorganization or recrystallization, thereby altering the relative intensities of the ester- and hydroxyl-related bands.

DMA test results

Based on the volume and mass of 3D-0 and 3D-NF-0 DMA samples, we calculated their densities, which were 0.948 g/cm^3 for 3D and 0.710 g/cm^3 for 3D-NF. We normalized each data series with its own density value, which provides a better relative comparison of the properties of 3D and 3D-NF samples.

The storage modulus (E') values were then normalized by density and plotted as a function of temperature (Figure 9 a-c). Based on our results, below 65 °C, the 3D-NF curves consistently run above the reference 3D curves, indicating that the nanofiber mat enhances the storage modulus, especially at lower temperatures. This suggests that nanofibers in 3D-NF samples improve mechanical strength, also at the typical application temperature (37 °C) for scaffolds.

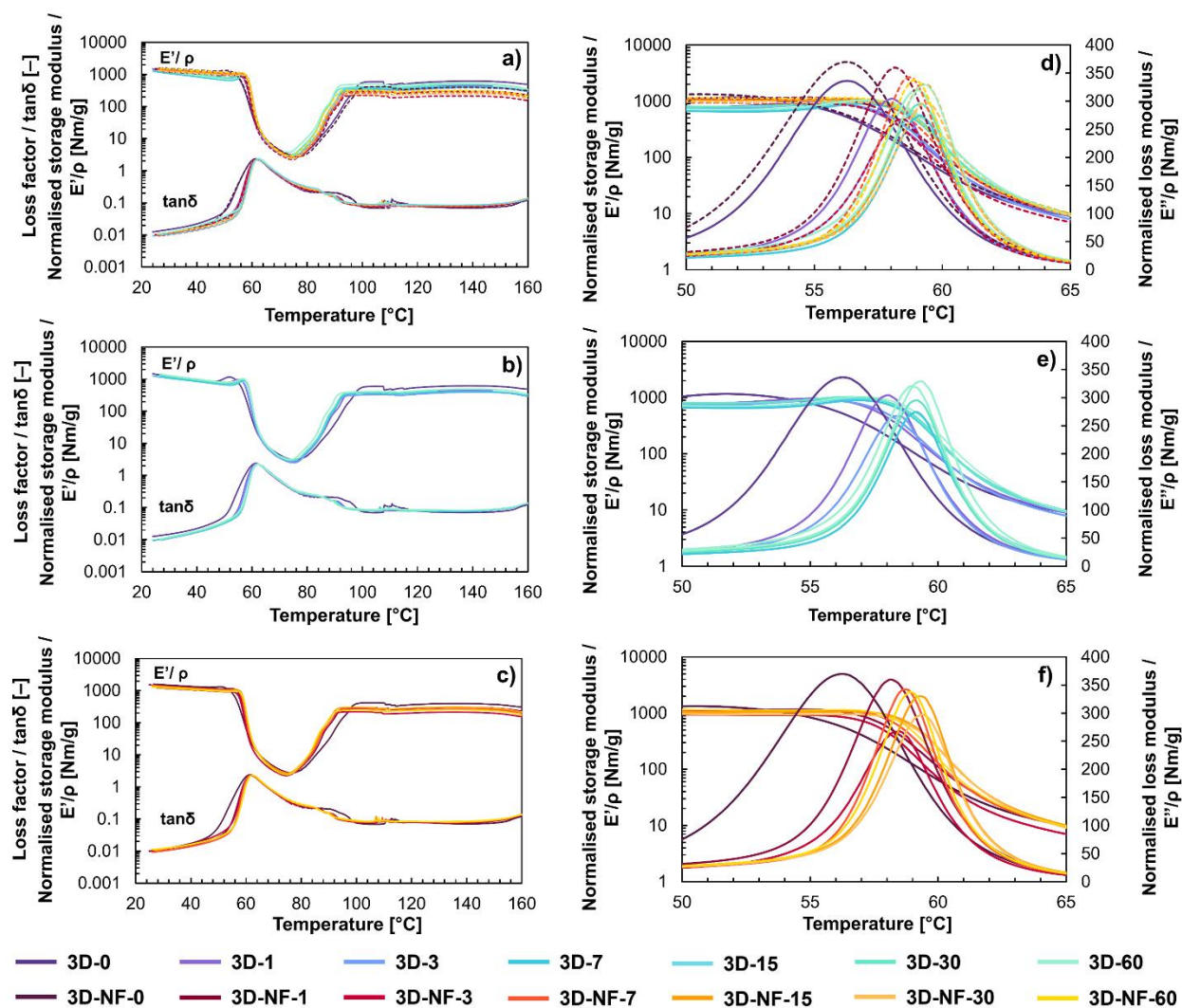


Figure 9. Density-normalized DMA curves compare the mechanical properties of 3D and 3D-NF samples during thermal testing. Normalized DMA curves a)-c) in the range of 20-160 °C, d)-f) detailed curves around T_g (50-65 °C).

The peak of the loss factor ($\tan\delta_{max}$) corresponds to the α -relaxation processes and the T_g . At this temperature range, the amorphous phase of PLA transitions from a brittle, glassy state to a lower-modulus, rubbery state, and the material absorbs energy due to the mechanically induced mobility of the chain segments.

T_g values obtained from $\tan\delta_{max}$, DMA measurements (E''), and DSC analysis (compared in Figure 10 a) show a similar trend over degradation time. DMA measurements are in good agreement with the results obtained from DSC, which show that hydrolytic degradation enhances crystallinity. (Numerical results are presented in Table S4 of the Supplementary Material).

Figure 9 d)-f) shows the normalized E' and E'' as functions of temperature (50–65 °C), where the E'' , also the glass transition, shifts toward higher temperatures with degradation. Additionally, E' curves shift to the right as degradation progresses. Thus, the onset of glass transition shifts towards higher temperatures. As crystallinity (χ) increases, a higher proportion of crystalline regions restricts amorphous segment motion, thus raising T_g .

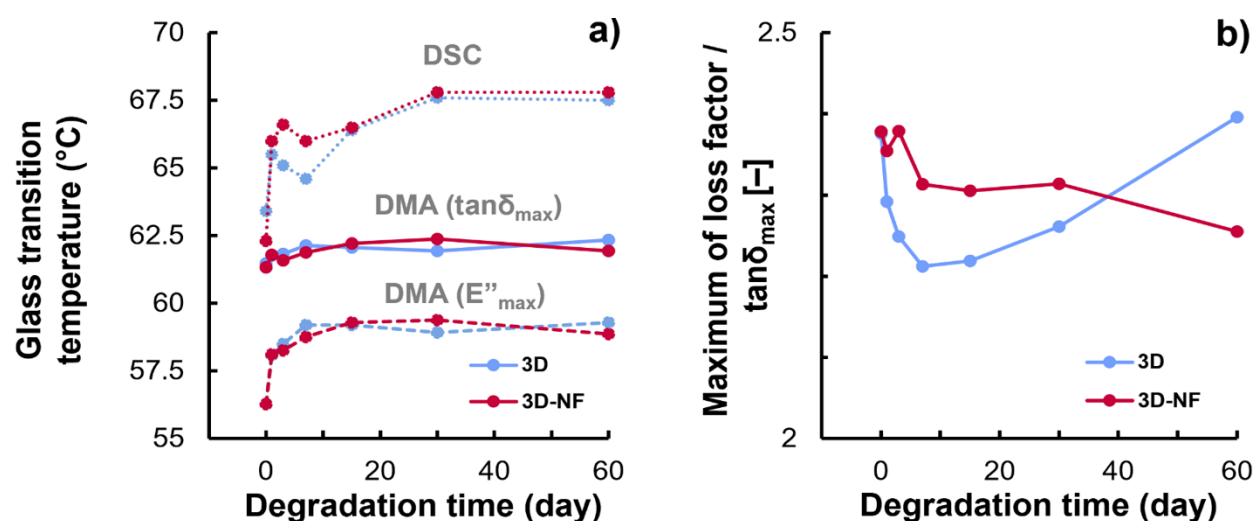


Figure 10. **Thermal and mechanical properties measured by different methods as a function of degradation time.** a) comparable glass transition temperature evolution determined by three methods, b) variation in $\tan\delta_{\max}$ throughout the degradation period.

The change of mechanical properties during degradation

In the case of the tensile test, we had to take into account that the actual cross-section of the specimens was smaller than the rectangular area defined by the program. Additionally, the specimens were not fully filled, and the 3D-NF specimens were thicker than the reference samples due to printing with a raised print head. However, during the fabrication of fiber-interleaved 3D printed samples, only the distance between printed layers was increased, while the amount of extruded filament remained unchanged. Furthermore, the thickness of the nanofiber mats is negligible. As a result, the software overestimated the cross-section of the fiber-containing 3D printed specimens compared to the neat samples based on the input parameters: specimen thickness and specimen width. Since both sets of samples have effectively the same cross-section, the tensile results of 3D-NF specimens – originally based on an overestimated cross-section – were

normalized for comparability. We adjusted the tensile curves of 3D-NF, using the ratio of their average cross-sections ($\bar{A}_{3D+NF}/\bar{A}_{3D}$). The typical stress-strain curves are presented in Figure 11. We determined the average tensile strength, elongation at break, and Young's modulus of each sample set over degradation time (Figure 12). (Numerical results are presented in Table S5 of the Supplementary Material).

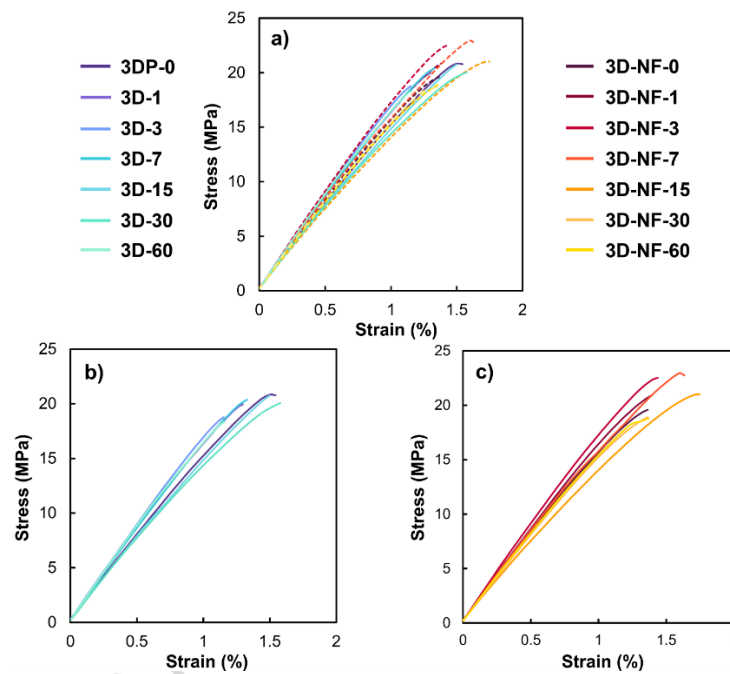


Figure 11. Typical mechanical stress-strain behavior of the specimens within degradation period. a) comparison of reference and nanofiber-containing specimens, b) reference specimens, and c) nanofiber-containing specimens

Initially, 3D and 3D-NF specimens had similar tensile strength. After 3 days in the PBS solution, the tensile strength of 3D-NF showed a gradual increase (from 19.28 MPa to 22.94 MPa), reaching its maximum. From day 7, this value started to decrease, likely due to the faster degradation rate of the electrospun fibers that connect the printed layers. However, the strength of 3D samples also reduced from day 15 at a slower rate. This may be attributed to the larger specific surface area of the fiber-containing printed structures, which were more exposed to the PBS solution. Furthermore, the ultrafine fibers, being more susceptible to hydrolytic degradation, could have accelerated the structural degradation process. Since degradation may have also affected the

adhesion between the FFF grid and the nanofibers, the load transfer between the two components likely weakened by day 30 and continued to decline by day 60.

The elongation at break of the 3D and 3D-NF samples followed different trends over the 60-day study period. While the 3D samples showed an increase in elongation only until day 1, the elongation at break of the 3D-NF samples increased until day 15 (from 1.37% to 1.68%), with a 22% relative growth. However, by the end of the degradation period, the elongation at break of both samples dropped below their initial, 0-day values.

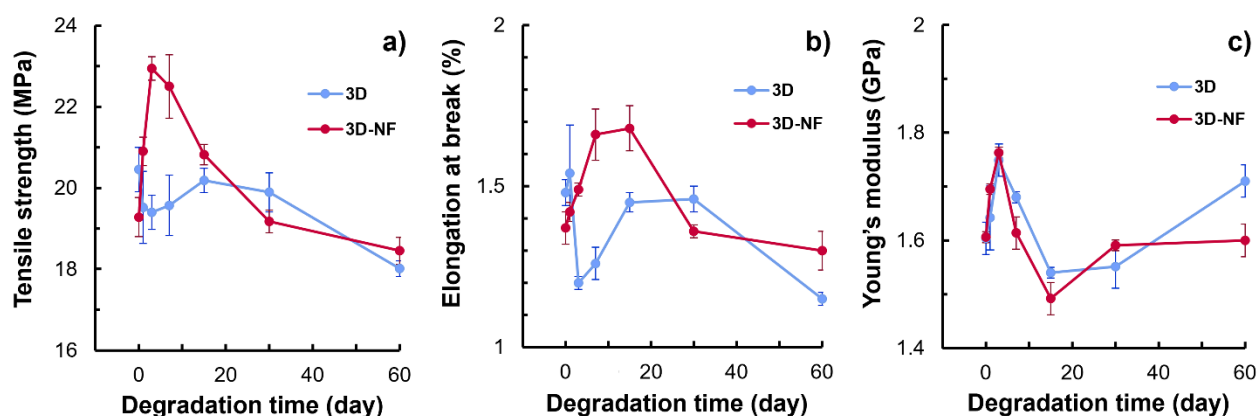


Figure 12. *Tensile properties of samples as a function of hydrolytic degradation time. The effect of hydrolytic decomposition on a) tensile strength, b) elongation at break, and c) Young's modulus.*

There was no significant difference in the elastic modulus between 3D-0 and 3D-NF-0 samples. By day 3 of hydrolytic degradation, the modulus of both 3D and 3D-NF samples increased, likely due to increased crystallinity. As crystallinity increased, the molecular chains within the structures became more constrained. By day 7, both samples began annealing, and their modulus continued to decline by day 15.

We performed statistical analysis, using a set of F-tests and t-tests to determine whether the properties of the 3D and 3D-NF samples differed significantly at the end of each incubation period. (The results are summarized in Table S6 of the Supplementary Material).

Based on the obtained p-values, the nanofiber mat placed between the printed layers was statistically proven to enhance the tensile strength of the structures after 3 and 7 days of incubation at a 95% significance level. Additionally, statistical calculations confirm that the fiber-containing

structures subjected to 3, 7, and 15 days of degradation exhibited greater elongation at break than the 3D samples incubated for the same duration.

Fracture morphology of the degraded samples

The fracture surfaces of the tensile test specimens were examined by SEM (*Figure 13 a-d*). Tiny voids were observed on the fracture surfaces of the 3D-printed components, and their number increased with degradation time in both the 3D and 3D-NF sample groups. These findings align with literature reports stating that hydrolytic degradation affects not only the outer surface of the material but also its internal structure [42]. While hydrolytic degradation proceeded through surface erosion for the nanofibers, bulk degradation occurred in the FFF printed component.

In the aqueous medium, water molecules penetrating the printed structure of the samples contributed to the degradation of the 3D printed component. By days 30 and 60, the numerous voids formed within the printed grid likely weakened the structure. The appearance of these microstructural defects explains the reduction in tensile strength detected during the tensile tests.

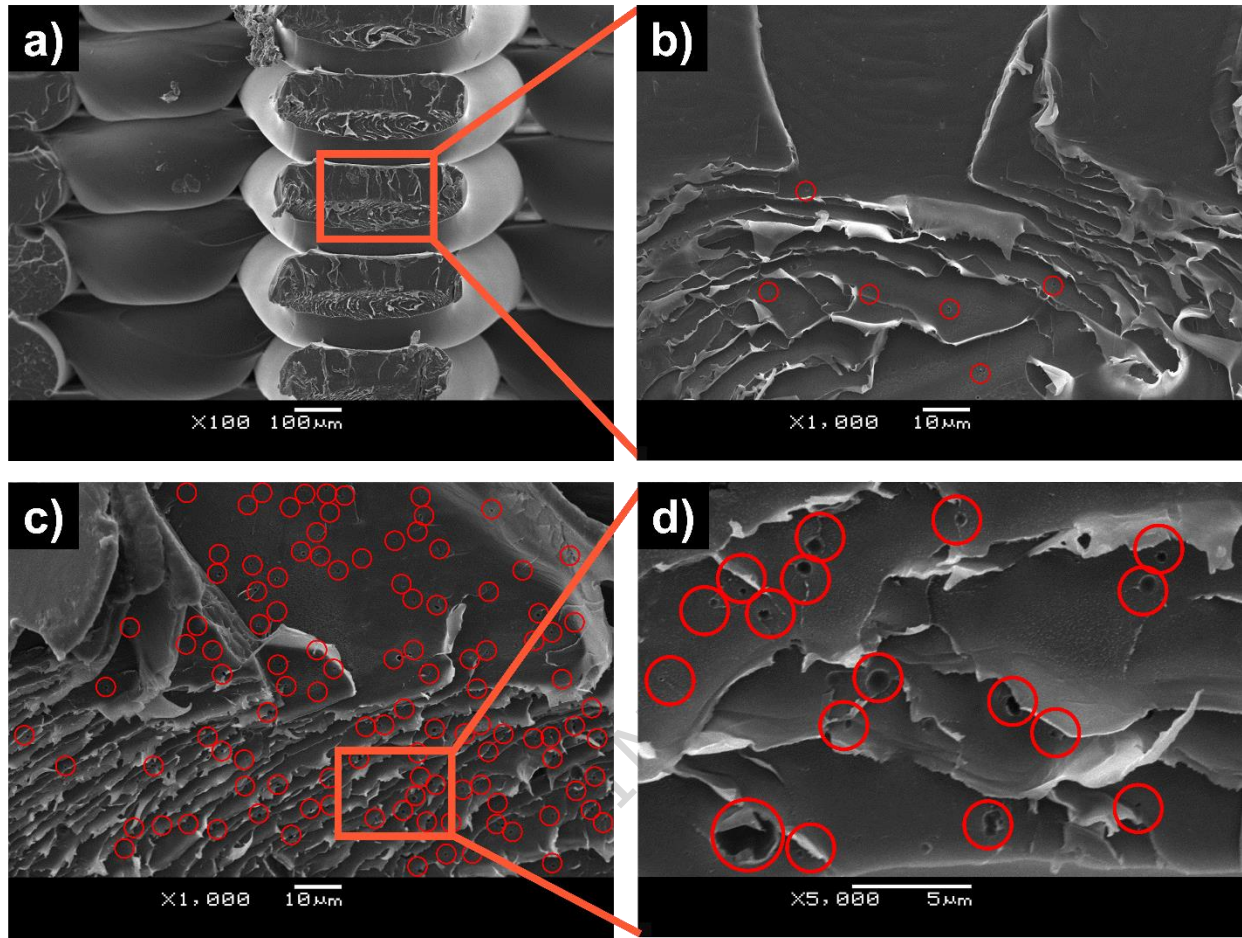


Figure 13. SEM images of fracture morphology of the degraded samples. Microvoids on the fracture surface, a) fracture surface of the FFF grid, b) 3D-NF-0, c)-d): 3D-NF-60 at different magnifications. Red circles indicate microvoids, while red rectangles highlight the specific areas chosen for closer magnification.

Figure 14 a-d shows the interface between the fractured nanofibers and the 3D printed infill grid on the fracture surfaces. The electrospun fiber mats did not detach from the printed structure under load but were able to transfer stress from the printed matrix, demonstrating their reinforcing effect [32]. The high surface area of the nanofibers likely enhanced interfacial contact and mechanical interlocking between neighboring printed layers beyond what filament self-fusion alone could achieve.

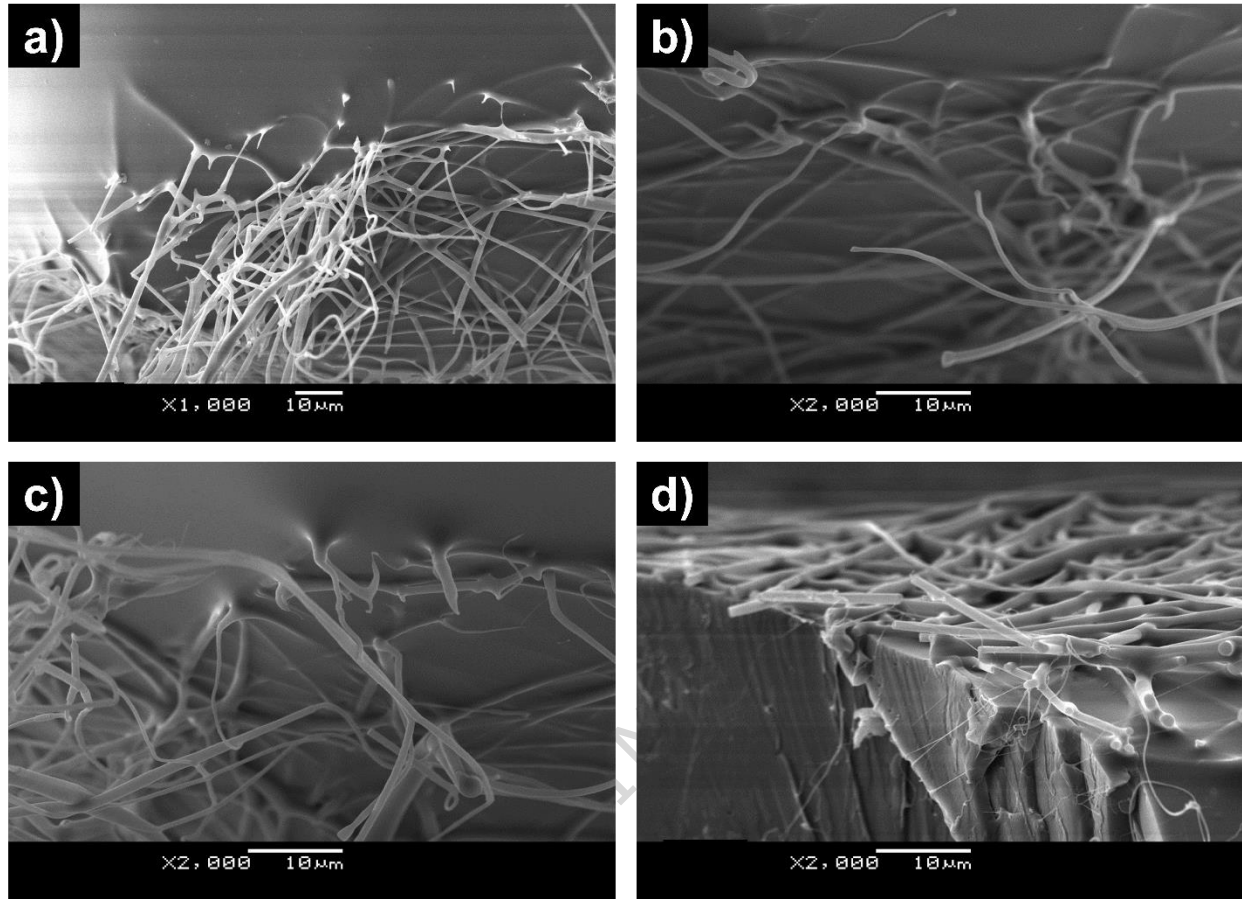


Figure 14. SEM images of the interface between the fractured nanofibers and the 3D printed infill grid on the fracture surfaces. a)-d) Interfacial fusion between the nanofibers and the FFF grid.

Discussion

In this study, we successfully fabricated a hierarchical PLA scaffold by combining the free-form geometry of FFF 3D printing with the high surface area of electrospun nanofiber mats. Our results demonstrate that nozzle temperature is a critical parameter governing the successful integration of these two components. The scaffold exhibited a distinct, multi-stage degradation profile, characterized by rapid nanofiber surface erosion and microvoid formation in the printed grid. Throughout degradation, the electrospun fiber mats directly influenced the hierarchical structure's mechanical and thermal properties. In the early stages of immersion, an increase in T_g and crystallinity was observed, indicating that, in addition to hydrolytic effects, structural

rearrangements, including cold crystallization. These processes temporarily counteract hydrolytic chain scission, resulting in an initial increase in stiffness and strength before degradation becomes dominant at longer exposure times. Although direct measurements of molecular weight, such as steric exclusion chromatography or gel-permeation chromatography, were not performed in this study, molecular weight changes could not be directly quantified. Nonetheless, results from FTIR, DSC, DMA, and mechanical testing suggest that hydrolytic degradation caused polymer chain scission and a reduction in molecular weight during incubation. These promising results open exciting avenues for future work, including the incorporation of stimuli-responsive polymers for 4D printing and the introduction of shape-memory effects. Such advanced approaches could enable the creation of intelligent hybrid scaffolds with precisely tailored degradation profiles, mechanical properties, and dynamic functionality, enhancing their adaptability to environmental stimuli.

Methods

Materials used and electrospinning

In this study, we used polylactic acid (PLA) (3100HP, $M_w=140,000$ g/mol) from NatureWorks LLC (Plymouth, MN, USA) for sample preparation. The pellets were dissolved in the mixture of chloroform and N,N-dimethylformamide (DMF) (Molar Chemicals Kft., Halásztelek, Hungary) at a ratio of 9:1 to prepare a 10 wt% solution for electrospinning [32]. The solution was stirred at 50 °C for 10 hours by a magnetic stirrer for homogenization.

To prepare the nanofiber mat, we used a custom-built, single-needle, horizontal electrospinning setup, consisting of a high-voltage power supply, syringe pump, and grounded collector, similar to the system described by Abdullah and Molnár [43]. We filled a 20 ml syringe with the polymer solution, then placed it into a syringe pump (Aitecs SEP-10S plus, Vilnius, Lithuania), providing a steady flow rate of 0.3 ml/h. The solution was fed through a silicone tube to the tip of a needle with an inner diameter of 0.51 mm. High voltage of 25 kV was applied to the system by a DC power supply (MA2000 NT 35/P, Nagykanizsa, Hungary) with the positive electrode connected to the needle and the collector grounded. Electrospinning was performed at 25 °C and 40–50% relative humidity.

We collected nanofibers by two different collector systems: a plate and a slow-rotating drum. The collector was covered by parchment paper (non-sticky baking paper), and the collection distance was 200 mm from the tip of needle to the collector surface in both cases.

In the case of the plate collector, we collected nanofibers for 15, 30 and 60 minutes to investigate the effect of different fiber mat thicknesses. In the case of the drum collector, we collected the fibers for 40 minutes. These samples were bigger and much thinner due to the 160 mm diameter of the collector (strip length approx. 500 mm), but the rotation made the thickness more homogeneous. We chose a slow speed of 135 rpm that did not orient the fibers. At this speed, the tangential velocity of the collector surface remains substantially lower than the typical flight speed of the electrospun jet, preventing mechanical drawing and alignment of the fibers during deposition. These veils were used as interleaves in 3D printed structures. The nanofiber-3D printed hierarchical structures were tested for hydrolytic degradation in detail.

Filament preparation

We prepared a 1.75 mm filament for FFF printing from the same PLA 3100HP grade pellets, which were preliminarily dried in a vacuum dryer (Binder VD 53, Germany) at 80 °C for one hour before processing. We used a Precision 450 type (3Devo, Utrecht, Netherlands) filament extruder for the filament production. The extruder zone temperatures were 170, 185, 185 and 170 °C from the hopper to the die, while the extruder screw speed was set to 3 rpm. Upon exiting the die, the filament was air-cooled at ambient temperature using a controlled air flow system to ensure gradual solidification and dimensional stability.

Sample preparation for investigating the effect of temperature and fiber content

We produced complex electrospun-3D-printed PLA structures by interleaving nanofiber layers between the printed infill grids during 3D printing. The porous nanofiber veils, therefore, fill the macropores of the printed infill layers, and a hierarchical structure is produced. The effect of process parameters, nanofiber layer thickness, and hydrolytic degradation was investigated. The specimens contained varying amounts of nanofibers and were printed on a glass bed under variable conditions using a CraftBot Plus 3D printer (CraftUnique, Budapest, Hungary) with a 0.4 mm nozzle diameter and the previously described filament. Each $20 \times 20 \times 0.6$ mm sample consisted

of three 0.2 mm printed layers with two nanofiber mats between the first and second, as well as between the second and third layers. We used PrusaSlicer software to do the slicing of the model. We chose three nanofiber contents (2.2%, 3.2%, and 5.5%) corresponding to the electrospinning collection times of 15, 30 and 60 minutes and five nozzle temperature settings (190 °C, 200 °C, 210 °C, 220 °C, and 230 °C) to study their effects on crystallinity, transition temperatures and morphology. We also used these different temperatures and thicknesses to see under which circumstances the fibers remain intact. In the sample names, the first number denotes the printing temperature, and the second represents the fiber content. For example, 210/5.5 denotes a nozzle temperature of 210 °C and a nanofiber content of 5.5%.

We modified the G-code of the printing process to enable placing nanofiber mats between the printed layers. Sending the printhead to the home position and pausing the printing allowed access to the sample at the required layers. During the pause, a nanofiber mat was carefully placed on the printed layers. Instead of the preset 0.2 mm layer height, we positioned the print head 0.1 mm higher, 0.3 mm above the previous printed layer, to avoid damaging the ultra-fine fiber mat. The next layer was printed on top of the nanofiber mat, which welded the layers as they fused together, but without damaging the nanofiber mats in the printed macropores. The infill density was set to 80%, resulting in a mechanically resistant, yet scaffold-like mesh structure (Figure 15). The bed temperature was maintained at 60 °C, and the printing speed remained 25 mm/s throughout the entire process.

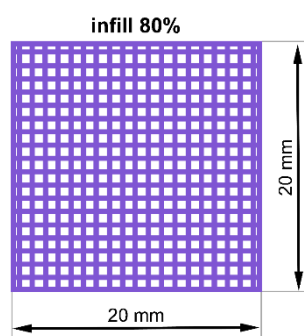


Figure 15. Schematic representation of the 3D-printed mesh structure and grid configuration. Graphic of the FFF infill grid showing the pattern design used to produce the 80% infill density scaffold specimens.

Sample preparation for hydrolytic degradation study

We fabricated two types of specimens for our hydrolytic degradation experiments. Dumbbell specimens (overall length 50 mm, end width 8.5 mm, gauge width 4.5 mm, thickness 1.2 mm) and rectangular ($60 \times 10 \times 1.2$ mm) samples. The samples composed of six printed layers with three nanofiber interleaves (3D-NF). Both specimen types were used to investigate the thermal, mechanical and morphological properties as a function of degradation time after being exposed to a hydrolytic environment (Figure 16). Besides hierarchical structures, we also tested neat 3D printed samples (3D) and electrospun nanofiber mats (NF). The experimental design is summarized in Table 3.

We used Ultimaker Cura software for slicing. To facilitate gentler removal of the thin specimens without damage, the printer was subsequently changed. The PLA filament was processed with an Ender 3 V3 SE at a nozzle temperature of 210 °C, as the experiments showed (3.1.1.), indicating that this printing temperature resulted in the highest degree of crystallinity. We replaced the original factory printing bed, which was coated with polyetherimide (PEI) powder, with masking tape to enable easier removal of the relatively thin samples without causing damage. All other printing parameters remained unchanged from the initial setup, and the G-code was modified only to accommodate the change in the bed surface. Therefore, the variation introduced by the printer change is considered negligible.

Due to the negligible thickness of the nanofiber mat and the additional thickness resulting from the offset of the print head in the z direction, the density of the nanofiber-containing structures was lower than that of the neat 3D printed samples. Since the nanofibers were collected on a rotating drum, they were distributed along the lateral surface rather than being concentrated in a single, specific spot, as observed with a plate collector. Therefore, the 3D-NF samples containing three layers of nanofiber mats had a fiber content of only 0.15 wt%.

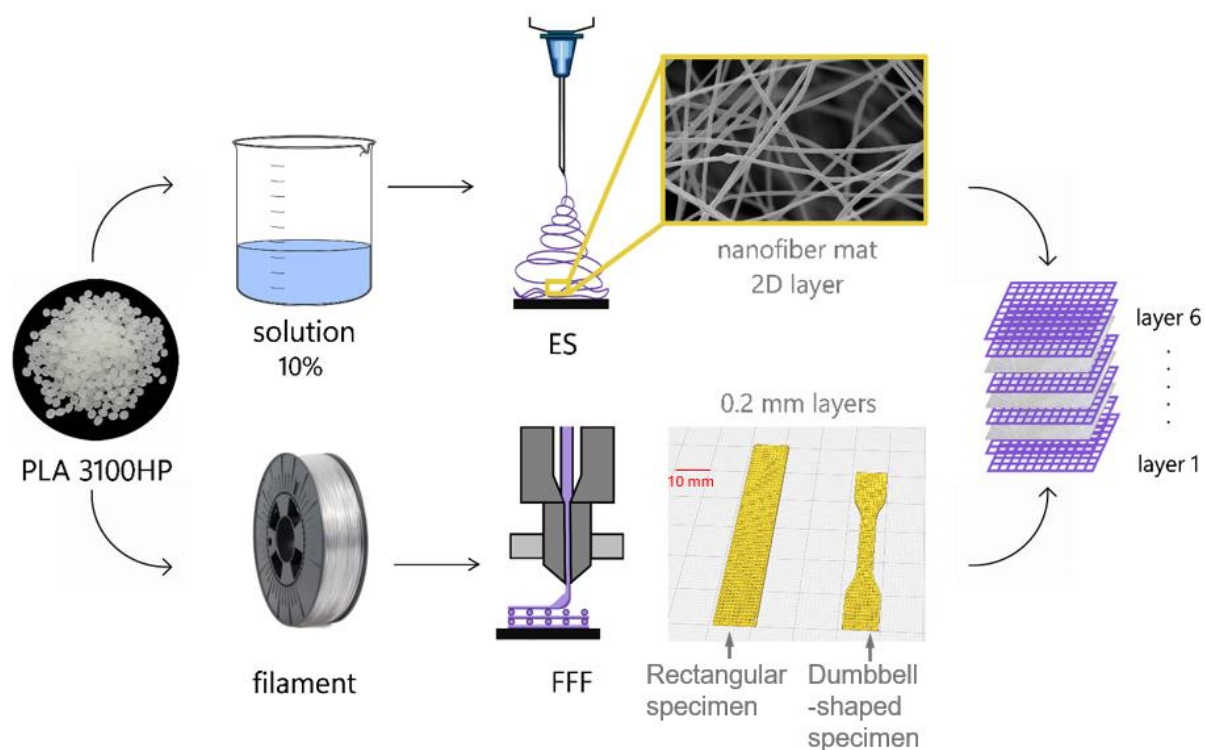


Figure 16. Schematic diagram of sample preparation, combining electrospinning and 3D printing for hydrolytic degradation. The diagram illustrates the fabrication process using PLA material, detailing the electrospinning and FFF printing steps to assemble the multi-layered structures.

Table 3. Neat 3D printed (3D), nanofiber containing 3D printed samples (3D-NF) and nanofiber mats (NF) exposed to hydrolytic degradation.

Sample names	Duration of hydrolytic degradation (day)	Number of tensile specimens (–)	Number of DMA specimens (–)
3D-0 / 3D-NF-0 / NF-0	0	7 / 7 / 0 each	2 / 2 / 0 each
3D-1 / 3D-NF-1 / NF-1	1	7 / 7 / 0 each	2 / 2 / 0 each
3D-3 / 3D-NF-3 / NF-3	3	7 / 7 / 0 each	2 / 2 / 0 each
3D-7 / 3D-NF-7 / NF-7	7	7 / 7 / 0 each	2 / 2 / 0 each
3D-15 / 3D-NF-15 / NF-15	15	7 / 7 / 0 each	2 / 2 / 0 each

3D-30 / 3D-NF-30 / NF-30	30	7 / 7 / 0 each	2 / 2 / 0 each
3D-60 / 3D-NF-60 / NF-60	60	7 / 7 / 0 each	2 / 2 / 0 each

Hydrolytic degradation examination

Nanofibers collected with the rotating collector (NF), neat 3D printed references (3D), and fiber-containing printed structures (3D-NF) were subjected to hydrolytic degradation under controlled pH and temperature conditions. To prepare a phosphate-buffered saline (PBS) solution (pH 7.4), we dissolved salt tablets (P4417 - Sigma-Aldrich, USA) in distilled water according to the manufacturer's instructions. The specimens were immersed in the saline solution for the degradation testing and sealed in 120 ml propylene containers. Each container was fully filled with PBS solution, ensuring complete immersion of the specimens. We changed the PBS solution once a week to prevent a decrease in pH caused by the acidic degradation products of PLA. The containers were placed in an incubator (IN-36DDI, Berlin, Germany) at 37 °C to simulate physiological conditions. Hydrolytic degradation times for each sample group were 1, 3, 7, 15, 30, and 60 days. Following each degradation period, the samples were removed from the PBS solution, rinsed three times with distilled water and dried in a vacuum dryer (Binder VD 53, Germany) at 37 °C for 24 hours before characterization.

Scanning electron microscopy

Scanning electron microscopy (SEM, Jeol 6380 LA, Japan) was used to study the interface of the printed grid and electrospun fibers. We examined whether hydrolytic degradation results in any changes in the microstructure of the samples. The samples produced with different nanofiber contents and different nozzle temperatures were investigated.

Furthermore, we investigated the surface of the nanofibers (NF), printed layers (3D) and also the structures of their combinations (3D-NF) exposed to degradation conditions for various periods, as well as cross-sections after tensile testing. All the samples were sputter-coated with a thin layer of gold prior to microscopy. SEM imaging was performed at an accelerating voltage of 10 kV. SEM images were taken, and 100 fibers were randomly selected per sample to measure their diameters using ImageJ software (version 1.54g, National Institutes of Health, Bethesda, MD, USA). The number in each sample designation (NF-0 – NF-60) indicates the days spent in PBS solution.

Differential scanning calorimetry

We determined the thermal properties of samples by differential scanning calorimetry (DSC-Q2000, TA Instruments, USA). We investigated the effect of different fabrication parameters (fiber content and nozzle temperature), as well as 3D, 3D-NF and NF specimens exposed to hydrolytic degradation. Specimens were randomly cut from various regions of each sample, with vertical cuts through the entire thickness to include all layers and maintain the representative nanofiber/3D-printed ratio. We cut each specimen into approximately 1–2 mm sections, weighed and placed 3–7 mg of each sample into an aluminum pan, then conducted the measurement from 25 °C to 210 °C under a nitrogen gas flow of 50 mL/min. The samples were subjected to a heat–cool–heat cycle from 25 °C to 210 °C at a heating and cooling rate of 10 °C/min. The thermal properties were determined from the first heating cycle. In addition to transition temperatures, we determined the degree of crystallinity of the specimens (χ_d):

$$\chi_d(\%) = \frac{\Delta H_m - \Delta H_{cc} - \Delta H_p}{\Delta H_{m0}} \times 100 \quad (1)$$

where ΔH_m is the melting enthalpy, ΔH_{cc} is the cold crystallization enthalpy and ΔH_p is the enthalpy of crystal phase transition. ΔH_{m0} denotes the melting enthalpy of the perfect PLA crystal with 100% crystallinity ($\Delta H_{m0} = 93$ J/g).

We assumed that the density of the nanofibers and 3D printed material is approximately the same and calculated the theoretical degree of crystallinity (χ_t) using the rule of mixtures:

$$\chi_t = m_{NF} \times \chi_{NF} + (1 - m_{NF}) \times \chi_{3D} \quad (2)$$

where m_{NF} is the mass of the nanofiber content, χ_{NF} is the crystallinity of the nanofiber mat and χ_{3D} is the crystallinity of the 3D printed grid.

FT-IR

We monitored the changes in chemical structural and functional groups of 3D and 3D-NF samples at each stage of the degradation process, using Fourier transform infrared spectroscopy (FTIR, Bruker Tensor II, USA). The FTIR measurement was performed between 400 and 4000 cm^{-1} in attenuated total reflectance mode (ATR) with a resolution of 4 cm^{-1} . We compared the intensity values measured at the wavenumbers associated with the degradation of PLA.

Dynamic mechanical analysis

Dynamic mechanical analysis (DMA, Q800 TA Instruments, USA) was used to examine the thermomechanical properties of 3D and 3D-NF specimens for each period of the degradation process, following the ISO 6721 standard. DMA measurements were performed in dual cantilever mode using rectangular specimens (as described in the Sample preparation for hydrolytic degradation study chapter) with a free length of 35 mm. The tests were conducted from room temperature up to 160 °C at a heating rate of 2 °C/min, a frequency of 1 Hz, and a strain amplitude of 0.05%.

Tensile tests

We used a Zwick Z005 (Zwick Roell, Germany) tensile testing machine equipped with a 5 kN high-precision load cell to evaluate the tensile properties of neat 3D printed PLA specimens and nanofiber-containing complex structures. All specimens were conditioned at 25 °C and 35 ± 5% relative humidity. Tensile tests were performed with testXpert II test software. The test speed was set to 5 mm/min, and the gripping distance was 30 mm. Five dumbbell specimens were tested for each degradation period, including both 3D printed (3D) and combined (3D-NF) sets. We determined the average tensile strength, elongation at break, and Young's modulus. Statistical analysis was conducted to assess whether there were significant differences in the mechanical properties of the 3D printed and the hierarchical bimodal sample groups.

Data availability

The data supporting the findings of this study are presented within the article and in the supplementary materials. Additional data are available from the corresponding author upon reasonable request.

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Author Contributions

All authors have read and approved the manuscript. **Kata Lipkovics:** Writing – original draft, Data curation, Investigation, Visualization, Formal analysis, **Kardo Khalid Abdullah:** Methodology, Investigation, Writing – review & editing, **Kolos Molnár:** Conceptualization, Supervision, Writing – review & editing, Methodology, Project administration, Resources, Funding acquisition.

Competing interests

The authors declare no competing financial or non-financial interests.

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