

ORIGINAL RESEARCH ARTICLE

Comparative study of process structure property relationships and melt flow behavior of CNT GO-reinforced PLA nanocomposites fabricated via fused granular fabrication and material extrusion

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Abstract

This study offers a systematic process structure property comparison of polylactic acid (PLA) nanocomposites reinforced with hybrid carbon nanotubes (CNT) and graphene oxide (GO), fabricated via pellet-fed fused granular fabrication (FGF) and conventional filament-based material extrusion (MEX). Nanocomposites were prepared via a dissolution assisted route to ensure homogeneous filler dispersion while mitigating thermal degradation. To bridge formulation and extrudability, the melt flow index (MFI) was introduced as a critical processability metric alongside standardized thermal (TGA/DSC) and mechanical (tensile/flexural) characterization. Hybrid reinforcement, through complementary CNT and GO mechanisms, significantly enhanced thermal stability, elevating the onset degradation temperature from 305.0 °C to 319.8 °C, and promoted crystallization, increasing the degree of crystallinity from ~7.5% to 21.5%. Tensile strength improved by 8–22% and elongation at break by up to 82%, despite a moderate reduction in elastic modulus (7–29%). Flexural modulus increased by up to 41% (MEX) and 28% (FGF), while FGF specimens exhibited markedly higher bending compliance and deformation capability, correlating with slightly higher interlayer porosity from FESEM. MFI decreased with nanofiller addition, with the MWCNT-rich formulation showing the largest viscosity increase, while FGF feedstocks exhibited higher MFI than MEX filaments due to reduced thermomechanical history. FGF achieved thermal, rheological, and mechanical performance comparable to MEX, with microstructural differences providing a beneficial stiffness-ductility trade-off. This work provides the first comparative dataset incorporating MFI for identical hybrid formulations across both processing routes, establishing pellet-fed FGF as a scalable, cost-effective, and environmentally friendlier alternative to filament-based MEX for high-performance additive manufacturing.

Keywords: Polylactic acid; Carbon nanotubes; Graphene oxide; Fused granular fabrication; Material extrusion; Melt flow index; Additive manufacturing; Nanocomposites

1. Introduction

Additive manufacturing (AM) has emerged as a transformative manufacturing technology capable of producing complex geometries with reduced material waste, shortened development cycles, and increased design freedom.^{1,2} Among polymer-based AM technologies, material extrusion processes are the most widely adopted because of their simplicity, affordability, and compatibility with a broad range of thermoplastic materials.^{3,4} Conventional material extrusion (MEX) relies on premanufactured polymer filaments as feedstock, whereas fused granular fabrication (FGF) directly processes polymer granules or pellets. By eliminating the filament production stage, FGF offers several practical advantages, including reduced material costs, increased feedstock flexibility, higher deposition rates, and improved scalability for industrial manufacturing applications.^{5,6} Consequently, pellet-fed extrusion systems are attracting increasing attention as a promising route for large-scale AM.⁷

Despite these advantages, concerns remain regarding the consistency and mechanical performance of pellet-fed printed components. Variations in thermal history, melt flow behavior, and extrusion stability can influence interlayer bonding and final part properties.⁸ Recent studies have demonstrated that FGF can achieve mechanical performance comparable to conventional filament-based MEX when processing conditions are appropriately optimized.^{9,10} For instance, Mohammed¹¹ showed that FGF achieved consistently higher tensile strength and stiffness across all build orientations compared to FDM, while FDM demonstrated superior ductility and toughness. Additionally, recent investigations have reported that FGF-processed polylactic acid (PLA) can reach tensile strengths up to 59.5 MPa, with proper parameter selection significantly reducing anisotropy and enhancing part reliability.^{12,13} Although these findings support the viability of FGF, systematic investigations involving advanced nanocomposite formulations processed through both manufacturing routes remain limited.

PLA is one of the most widely utilized thermoplastics in AM due to its biodegradability, renewable origin, ease of processing, thermal stability, and commercial availability.^{3,14} These characteristics have enabled its widespread use in packaging, biomedical devices, consumer products, engineering prototypes, and customized manufacturing applications.¹⁵ However, the relatively low thermal resistance, slow crystallization kinetics, and inherent brittleness of PLA restrict its application in demanding structural and functional components.¹⁶ Consequently, significant research efforts have focused on improving the thermo-mechanical performance of PLA through material

modification and reinforcement strategies.¹⁷

Among the available nanofillers, carbon nanotubes (CNTs) and graphene oxide (GO) have demonstrated considerable potential owing to their exceptional mechanical properties, high aspect ratios, and multifunctional characteristics.¹⁸⁻²⁰ CNTs provide one-dimensional reinforcement capable of enhancing stress transfer, crack bridging, and energy dissipation mechanisms within polymer matrices. In contrast, GO contributes two-dimensional reinforcement through its platelet morphology and oxygen-containing functional groups that promote interfacial interactions with the polymer matrix.²⁰ Previous studies have reported significant improvements in the mechanical, thermal, and functional properties of PLA through the incorporation of CNTs, GO, graphite, carbon fibers, and other carbon-based nanofillers.²¹⁻²⁶ For instance, Feng *et al.*²⁷ demonstrated that a GO-CNT nanohybrid (0.75 wt.%) endowed PLA scaffolds with remarkable increases in tensile strength (55.35%) and compressive strength (18.85%) compared to scaffolds containing only GO. Similarly, recent investigations on PLA scaffolds reinforced with GO and CNT showed that increasing nanofiller content from 0 wt.% to 0.4 wt.% led to improvements in compressive strength and elastic modulus of up to 79.3% and 165.9%, respectively.^{28,29} Furthermore, hybrid CNT-GO systems may provide complementary reinforcement mechanisms capable of producing enhanced performance relative to single-filler systems.²⁷ A comparative study by various researchers confirmed that PLA/GO composites exhibit superior tensile and degradation properties compared to PLA/CNTs and PLA/GNP composites.³⁰

The effectiveness of nanofiller reinforcement depends strongly on achieving homogeneous dispersion throughout the polymer matrix. Agglomeration can create stress concentration sites and significantly reduce the expected property improvements.^{31,32} Several approaches have therefore been investigated to improve nanofiller distribution, including melt blending, solution blending, ultrasonication, shear mixing, and *in situ* polymerization.^{19,33} Among these methods, dissolution-assisted processing has demonstrated considerable potential for promoting homogeneous dispersion while minimizing thermal degradation associated with repeated melt-processing cycles.^{33,34} In conventional AM workflows, nanocomposite feedstocks may be subjected to multiple thermal histories during compounding, filament extrusion, and printing. Repeated thermal exposure can induce thermo-oxidative degradation and molecular chain scission in PLA, resulting in reductions in molecular weight and deterioration of mechanical properties.³⁴ During preliminary investigations

conducted in the present study, repeated melt-processing operations produced similar effects on printability and mechanical performance. Consequently, a dissolution-assisted preparation method was adopted to promote nanofiller dispersion while preserving the molecular integrity of the PLA matrix prior to AM.

Extensive research has examined the influence of carbon-based nanofillers on PLA composites manufactured via filament-based material extrusion. Previous studies have investigated the effects of printing parameters, raster orientation, filler type, and reinforcement content on the thermal and mechanical performance of printed PLA components.^{35–38} However, relatively few studies have simultaneously considered hybrid CNT-GO reinforcement, dissolution-assisted feedstock preparation, and a direct comparison between filament-based MEX and pellet-fed FGF using identical material formulations. Moreover, the influence of these hybrid fillers on the melt flow behavior as a function of processing route (pellet vs. filament) has not been systematically quantified, despite its critical relevance to extrusion stability and print quality.^{39,40} The melt flow index (MFI) serves as a fundamental tool for controlling thermoplastic materials' flow qualities and determining whether they are within the required range for successful printing.^{29,41,42} Consequently, the combined influence of manufacturing route, hybrid nanofiller reinforcement, and melt rheology on the thermo-mechanical behavior of PLA nanocomposites remains insufficiently understood. Therefore, the objective of this study is to investigate the process-structure-property relationships of CNT-GO-reinforced PLA nanocomposites fabricated using both filament-based MEX and pellet-fed FGF. Particular emphasis is placed on evaluating whether FGF can achieve performance comparable to conventional MEX while benefiting from the economic and manufacturing advantages associated with direct pellet processing. Thermal stability, crystallization behavior, melt flow characteristics, and mechanical performance (tensile and flexural) are systematically characterized using thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), MFI measurements, and standardized mechanical testing. Additionally, microstructural and chemical analyses (FESEM and FTIR) are employed to elucidate the underlying reinforcement and deformation mechanisms. This comprehensive approach aims to establish whether pellet-fed FGF can serve as a scalable, cost-effective, and environmentally friendlier alternative to conventional filament-based MEX without compromising the structural integrity or performance of advanced PLA-based nanocomposites.

2. Materials and methods

CNT-GO-reinforced PLA nanocomposites were prepared using a dissolution-assisted compounding route and subsequently processed through two extrusion-based AM technologies: filament-based MEX and pellet-fed FGF. The experimental methodology was designed to isolate the influence of the manufacturing route while maintaining identical material formulations and printing parameters wherever possible. Thermal, rheological, morphological, and mechanical characterization was performed to evaluate the process-structure-property relationships of the fabricated nanocomposites.

2.1. Materials

This study utilizes PLA as the base polymer, combined with two types of nanofillers: multiwalled carbon nanotubes (MWCNTs) and GO. These fillers were incorporated into nanocomposites with varying compositions, as outlined in Table 1. Ethyl acetate ($\geq 99.5\%$ purity) was employed as the solvent for the dissolution-assisted preparation route. The PLA filament (ANYCUBIC, 1.75 mm diameter, standard general-purpose grade) was used as the base polymer. According to the manufacturer's specifications, this material has a tensile strength of ≥ 55 MPa, a density of $1.23\text{--}1.25\text{ g/cm}^3$, and a melt flow index of $\sim 9\text{ g/10 min}$ ($210^\circ\text{C}/2.16\text{ kg}$). The filament was mechanically granulated into small chips prior to dissolution to facilitate processing. MWCNTs (purity $> 95\%$, external diameter 30 nm, length 2 μm) and GO (purity $> 99.5\%$, platelet thickness 3.4–7 nm, average number of layers 6–10, specific surface area 500–1200 m^2/g) was supplied by US Research Nanomaterials.

Table 1. Composition and formulation of neat PLA and PLA-based nanocomposites

Test no.	Manufacturing method	Composite material composition (wt.%)		
		PLA	MWCNT	GO
1	MEX	100	0	0
2	FGF			
3	MEX	99.7	0.15	0.15
4	FGF			
5	MEX	99.7	0.2	0.1
6	FGF			
7	MEX	99.7	0.1	0.2
8	FGF			

Abbreviations: FGF: Fused granular fabrication; GO: Graphene oxide; MEX: Material extrusion; MWCNT: Multi-walled carbon nanotube; PLA: Polylactic acid.

2.2. Methods

This section begins with the preparation of nanocomposite granules. It then outlines the manufacturing process using two different printing techniques: MEX and FGF. Lastly, the section describes the procedures for conducting mechanical strength tests, including tensile, bending, and impact tests.

2.2.1. Preparation of PLA nanocomposite

To circumvent the thermo-mechanical degradation typically induced by repeated melt compounding—which adversely affects molecular weight and, consequently, melt flow characteristics—a dissolution-assisted route was employed for nanocomposite preparation. This method ensures that the subsequent AM processes (both FGF and MEX) receive feedstocks with preserved polymeric backbone integrity, allowing the MFI measurements to accurately reflect the influence of nanofillers rather than compounded thermal history.

The granulated PLA chips (obtained from the commercial filament) were dissolved in ethyl acetate under mild ultrasonic agitation (60 °C) to achieve a homogeneous polymer solution. Pre-weighed quantities of MWCNT and GO, corresponding to the formulations listed in Table 1, were gradually introduced into the solution. The mixture was subjected to continuous mechanical stirring to prevent filler agglomeration and to promote exfoliation of the nanofillers within the viscous medium. Good dispersion was visually confirmed by inspecting the suspension at multiple stages during preparation; field-emission scanning electron microscopy (FESEM) analysis at various magnifications ($\times 5,000$ to $\times 20,000$) further supported this observation, as discussed in Section 3.6.

The homogeneous suspension was cast into a flat-bottomed vessel and maintained under controlled stirring during solvent evaporation. Upon complete solidification, the resulting nanocomposite film was fragmented and subjected to vacuum drying at 70 °C for 12 hours to eliminate residual ethyl acetate (final solvent content < 0.5 wt.%). The dried material was subsequently mechanically ground into fine granules. A portion of these granules was retained for direct FGF processing, while the remainder was extruded into continuous 1.75 mm diameter filaments using a laboratory-scale single-screw extruder, serving as the feedstock for the MEX route (Figure 1).

The effectiveness of the vacuum-drying process was indirectly confirmed by TGA, which showed no significant weight loss below 200 °C, indicating that residual ethyl acetate was reduced to a level that does not affect the thermal or mechanical properties of the matrix.

2.2.2. Fabrication of test specimens by FGF and MEX

Tensile (ASTM D638) and flexural (ASTM D790) test specimens were fabricated using two extrusion-based AM platforms: a custom-built pellet-fed FGF system and a conventional filament-fed MEX printer. The digital manufacturing strategy (Gcode) and all physical deposition parameters—including layer height, nozzle diameter, infill density, raster orientation, and printing speed—were kept strictly identical across both platforms to enable a direct comparative analysis; detailed values are provided in Table 2.

While the deposition parameters were standardized, the extrusion temperatures were independently optimized for each feedstock form based on preliminary MFI assessments to maintain equivalent melt viscosity during printing. The FGF route employed a nozzle temperature of 200 °C for the directly compounded granules, whereas the MEX route required a higher nozzle temperature of 200 °C for the filament feedstock to achieve a comparable flow regime. Both processes were conducted within a thermally insulated build chamber maintained at approximately 60 °C to minimize warpage and enhance interlayer diffusion. The overall fabrication workflow for both routes is illustrated in Figure 2.

2.3. Characterization protocols

The characterization strategy was tailored to establish comprehensive process-structure-property correlations, with a specific emphasis on replacing dynamic impact resistance with rheological processability indicators.

2.3.1. Thermal transitions and stability

Thermogravimetric analysis (TGA) was performed on an SDT simultaneous thermal analyzer (TA Instruments) under nitrogen purge (50 mL/min). Samples (~8–10 mg) were heated from 25 °C to 600 °C at a rate of 10 °C/min to determine the onset degradation temperature ($T_{5\%}$) and maximum degradation rate temperature (T_{max}). Differential scanning calorimetry (DSC) was conducted in a heat-cool-heat protocol; data extracted from the second heating cycle provided the glass transition (T_g), cold crystallization (T_{cc}), and melting (T_m) temperatures. The PLA samples in this study predominantly exhibit the α crystalline form, as evidenced by the melting temperatures in the range of 169–170 °C (Table 3), which is characteristic of the α form. Accordingly, the widely accepted melting enthalpy for 100% crystalline α -form PLA, $\Delta H_m = 93.6$ J/g, was used for crystallinity calculations. The degree of crystallinity (X_c) was quantified using Equation 1, incorporating the PLA weight fraction (ϕ) correction:

$$X_c (\%) = [(\Delta H_m - \Delta H_{cc}) / (\Delta H_m \times \phi)] \times 100, \quad (1)$$

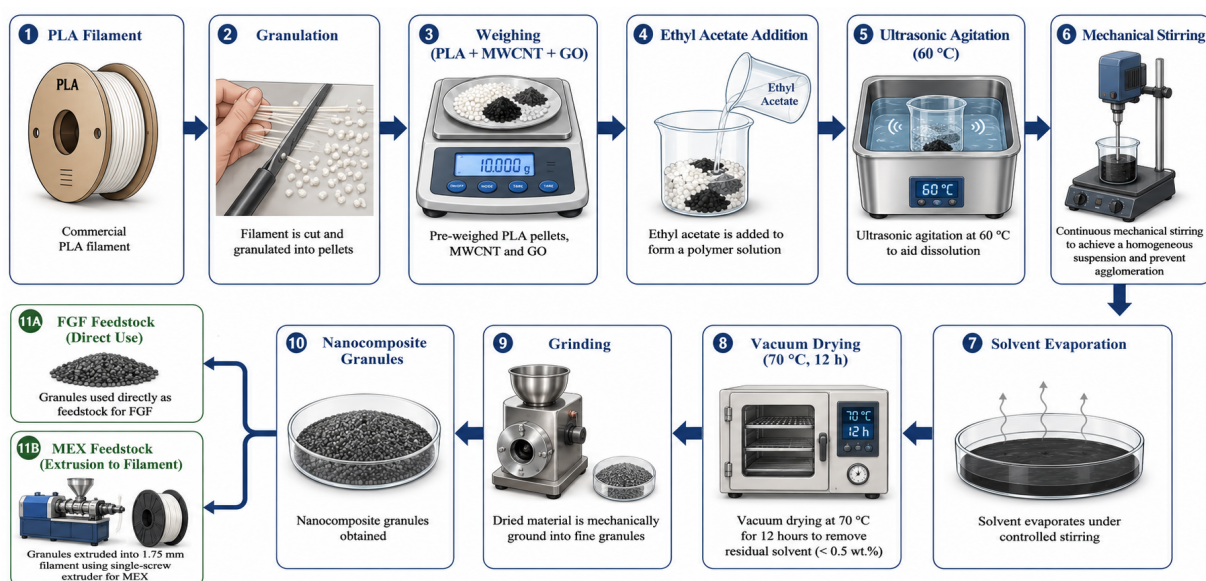


Figure 1. Chemical dissolution process and manufacturing of PLA nanocomposite granules

Abbreviations: FGF: Fused granular fabrication; GO: Graphene oxide; MEX: Material extrusion; MWCNT: Multi-walled carbon nanotube; PLA: Polylactic acid.

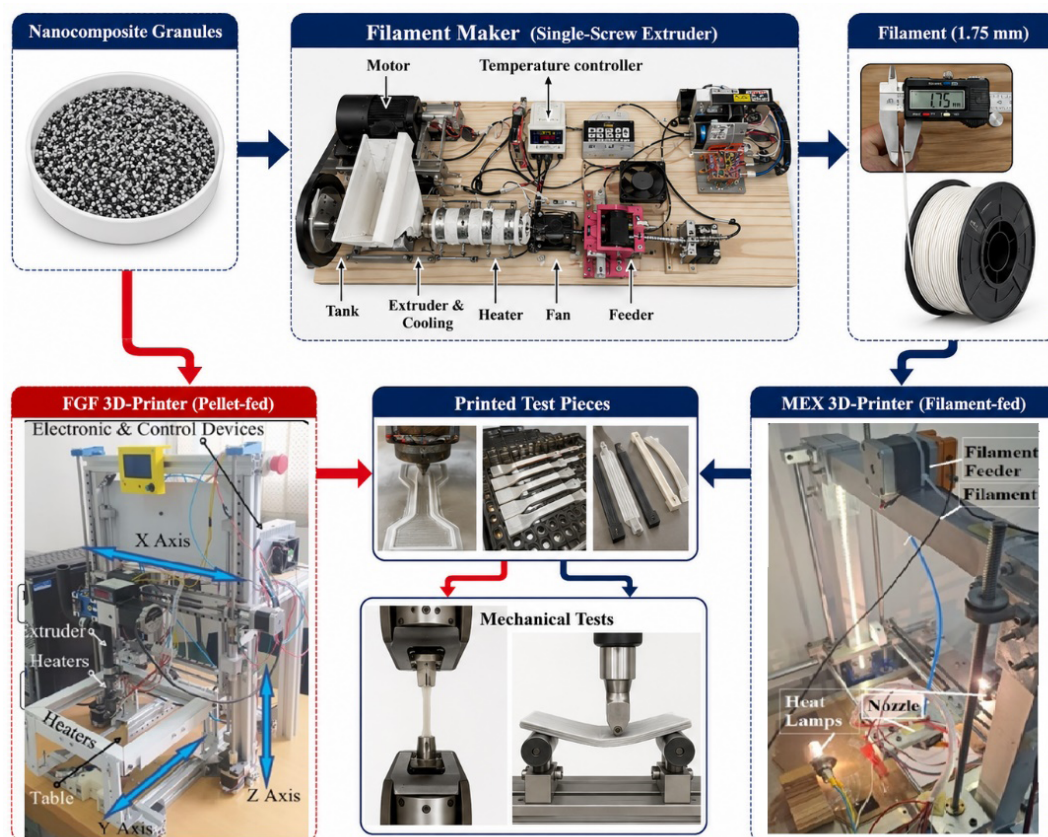


Figure 2. Steps for manufacturing parts using the FGF and MEX methods

Abbreviations: FGF: Fused granular fabrication; MEX: Material extrusion.

where $\Delta H_m = 93.6 \text{ J.g}^{-1}$ for fully crystalline PLA.

Table 2. Comparison of key printing parameters for FGF and MEX processes

Parameter	FGF	MEX
Feedstock	Nanocomposite granules	Nanocomposite filament (1.75 mm)
Extrusion method	Direct granule extrusion	Filament-based extrusion
Nozzle temperature	200 °C	200 °C
Ambient / chamber temperature	Controlled, 60 °C	Heated environment (~60 °C)
Feedstock preparation	Not required	Filament extrusion required
Comparative framework	Identical G-code and print settings	Identical G-code and print settings
Nozzle diameter	0.8 mm	0.8 mm
Layer height	0.4 mm	0.4 mm
Printing speed	15 mm/s	15 mm/s
Infill density	100%	100%
Infill pattern	Rectilinear	Rectilinear
Raster orientation	0°/90°	0°/90°
Cooling fan	on	on
Retraction distance	3 mm	3 mm
Calibration procedure	Dimensional measurement of the samples by the caliper and compensating in Simplify3D software	Dimensional measurement of the samples by the caliper and compensating in Simplify3D software

Abbreviations: FGF: Fused granular fabrication; MEX: Material extrusion.

2.3.2. Melt processability assessment

To quantify the effect of nanofiller incorporation and feedstock preparation history on extrudability, MFI measurements were carried out in strict accordance with ASTM D1238/ISO 1133 at 210 °C under a 2.16 kg piston load. This temperature was selected as the standard condition specified by the protocol to ensure comparability with the extensive literature on PLA processability. It is noted that the actual printing temperature used in this study was 200 °C for both MEX and FGF (while the filament

extrusion temperature was 170 °C); the 10 °C difference between the standardized test and the printing conditions is within the typical range for such assessments and does not affect the relative comparisons, as all feedstocks were tested under identical MFI conditions.

A critical methodological distinction was made in this study: MFI was evaluated on the final feedstock state immediately prior to printing. Specifically, measurements were conducted on the compounded granules for FGF and on the drawn filaments for MEX. This approach allowed for the decoupling of nanofiller-induced viscosity changes from viscosity alterations arising from the additional thermomechanical history of filament drawing. All specimens were tested in triplicate ($n = 3$) after vacuum drying at 80 °C for 4 hours to eliminate moisture interference.

2.3.3. Quasi-static mechanical performance (tensile and flexural)

The mechanical response under quasistatic loading was evaluated using a universal testing machine. Tensile properties, including elastic modulus, ultimate tensile strength, and elongation at break, were determined according to ASTM D638 using dogbone specimens. Flexural properties (modulus and maximum stress) were measured via threepoint bending tests following ASTM D790. For each formulation and manufacturing condition, five replicates were examined, and the mean values accompanied by standard deviations are reported.

2.3.4. Microstructural and chemical analysis

Field-emission scanning electron microscopy (FESEM) was utilized to inspect the morphology of cryo-fractured and tensile-fractured surfaces, assessing nanofiller dispersion, interfacial adhesion, and interlayer porosity. Chemical interactions between the PLA matrix and the carbonaceous nanofillers were investigated using Fourier-transform infrared spectroscopy (FTIR), with spectra recorded in attenuated total reflectance (ATR) mode across the 4000–400 cm^{-1} range.

3. Results and discussion

To systematically evaluate the influence of CNTGO hybrid nanofillers and manufacturing method (MEX vs. FGF) on the performance of additively manufactured PLA nanocomposites, thermal stability and crystallization behavior were first characterized using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Subsequently, mechanical properties were assessed via tensile and flexural testing according to ASTM D638 and D790 respectively. For each material formulation and

printing condition, five specimens were tested. All data are reported as mean $\pm$ standard deviation ($n = 5$), and error bars in all figures represent standard deviation. The mechanical results are interpreted alongside FTIR and FESEM to establish structure-property relationships, while TGA and DSC provide insight into thermal performance.

The hybrid CNTGO system employed in this study provides complementary reinforcement mechanisms. The onedimensional CNTs, with their high aspect ratio (~ 67), facilitate effective stress transfer and crack bridging within the polymer matrix. In contrast, the twodimensional GO platelets, with their oxygen-containing functional groups, enhance interfacial adhesion through hydrogenbonding interactions with the PLA matrix (as confirmed by FTIR analysis in Section 3.5). The combination of these mechanisms results in a more balanced property profile than typically observed with singlefiller systems at similar loadings. Specifically, the GOrich formulation (0.10CNT/0.20GO) maximizes stiffness and thermal stability (flexural modulus +41% for MEX; T_{5%} increase of +15 °C), while the CNTrich formulation (0.20CNT/0.10GO) provides higher ductility retention (elongation at break +58% for MEX). The balanced formulation (0.15CNT/0.15GO) achieves the most favorable combination of strength, stiffness, and toughness (tensile strength +19% for MEX; elongation at break +82% for MEX), indicating an optimal synergy between the two nanofillers when used in equal proportions. This complementary behavior is further supported by FESEM observations, which reveal CNT bridging between GO platelets and extensive crack deflection paths, confirming that the hybrid network effectively delays crack propagation and enhances energy dissipation during deformation.

Beyond the standard tensile and flexural specimens examined in this study, the material formulations and processing strategies developed here hold significant promise for fabrication of advanced cellular structures. As highlighted in a recent comprehensive review by Wang *et al.*,⁴³ 3D-printed cellular structures—including honeycomb-like architectures, foam structures, negative Poisson's ratio designs, and tubular configurations—are increasingly explored for impact mitigation and energy dissipation applications due to their superior mechanical properties and design flexibility. The enhanced toughness and deformation capability observed in FGF-processed nanocomposites—particularly the up to 82% increase in elongation at break—suggest that pellet-fed FGF could be a viable route for producing energy-absorbing cellular architectures. Future work should systematically investigate the compressive response and energy absorption behavior of CNT-GO reinforced PLA cellular structures fabricated

via both MEX and FGF, with particular attention to the influence of topological design and the potential advantages of FGF's enhanced ductility in such applications.

3.1. Thermal characterization (TGA and DSC)

The thermal behavior of the neat PLA and CNTGO reinforced nanocomposites, encompassing both degradation stability and crystallization kinetics, was systematically evaluated. A unified summary of the key thermal parameters—including onset degradation temperature ($T_{5\%}$), maximum degradation temperature ($T_{\max}$), char yield, glass transition (T_g), cold crystallization (T_{cc}), melting (T_m), and degree of crystallinity (X_c)—is presented in Table 3 for all formulations and both manufacturing routes (MEX and FGF).

- Thermal stability (TGA): As summarized in Table 3, the incorporation of CNTGO hybrid nanofillers markedly improved the thermal stability of the PLA matrix. Neat PLA exhibited an onset degradation temperature ($T_{5\%}$) of approximately 305 °C, whereas all reinforced formulations displayed elevated $T_{5\%}$ values, with the GOrich composition (0.1 wt.% CNT / 0.2 wt.% GO) reaching the highest value of 319.8 °C (FGF) and 319.5 °C (MEX)—an enhancement of nearly 15 °C. A concomitant increase in the maximum degradation temperature ($T_{\max}$) was also observed, confirming that the hybrid network effectively retards thermal decomposition throughout the primary degradation stage. The improved stability is attributed to the synergistic barrier effect of twodimensional GO nanosheets, which hinder volatile product diffusion, and the thermally resistive CNT network, which obstructs degradation propagation.
- Char yield: The char yield, which was negligible for neat PLA (≤ 0.1 wt.%), rose significantly to 1.13 wt.% for the GOrich formulations. This value exceeds the total nanofiller loading (0.3 wt.%) due to two complementary mechanisms: (i) the physical barrier effect of the CNTGO network, which delays the escape of volatile degradation products and promotes carbonization of the PLA matrix, and (ii) the catalytic charring effect of the oxygen-containing functional groups on GO, which alters the thermal degradation pathway of PLA toward char formation. Similar enhancements in char yield have been reported for PLA-based nanocomposites containing carbonaceous nanofillers, confirming that the hybrid network promotes the formation of a thermally stable carbonaceous residue that protects the underlying polymer matrix.
- Crystallization behavior (DSC): The DSC data in Table 3 reveal that the hybrid nanofillers exert a

pronounced influence on the crystallization kinetics without substantially altering the fundamental phase transitions of PLA. The glass transition temperature (T_g) and melting temperature (T_m) remained largely invariant across all samples, residing within narrow ranges of 60.7–62.5 °C and 169.1–170.6 °C, respectively. In contrast, the cold crystallization temperature (T_{cc}) exhibited a substantial reduction—from 113.4 °C (neat PLA, FGF) down to 103.4 °C for the GOrich FGF formulation. This marked decrease in T_{cc} confirms that CNTGO networks act as highly effective heterogeneous nucleating agents, significantly lowering the energy barrier for crystal formation during heating. Consequently, the degree of crystallinity (X_c) experienced a dramatic increase, rising from approximately 7.5% for neat PLA to a maximum of 21.6% (MEX) and 21.5% (FGF) for the GOrich formulation. This enhancement in crystallinity, alongside the improved thermal stability, contributes positively to the overall mechanical performance, promoting a more balanced and durable material response.

- Effect of manufacturing route: A critical observation drawn from Table 3 is the remarkable consistency in thermal properties between specimens fabricated via MEX and FGF. For every identical material formulation, the $T_{5\%}$, T_{max} , char yield, T_g , T_{cc} , T_m , and X_c values differ only marginally, well within experimental uncertainty. This finding unequivocally demonstrates that the thermal behavior of the nanocomposites is governed primarily by the nanofiller composition rather than by the feedstock preparation or printing

method. Thus, pelletfed FGF—which eliminates the intermediate filament extrusion step—can achieve thermal stability and crystallization performance directly comparable to conventional filamentbased MEX, offering a significant advantage for scalable, industrialscale AM.

3.2 Melt flow index (MFI) results

The melt flow index (MFI) was measured to quantify the influence of nanofiller incorporation and feedstock preparation history on the melt processability of the PLAbased nanocomposites, following the methodology described in Section 2.3.2. The MFI values for all formulations and both processing routes are summarized in Table 4.

Neat PLA exhibited the highest MFI in both routes (8.0–8.4 g/10 min), consistent with commercial AMgrade PLA.²⁰ Incorporation of CNTGO hybrid nanofillers reduced MFI in all formulations, with the CNTrich formulation (0.20CNT/0.10GO) showing the largest reduction (6.5–7.0 g/10 min) due to the higher aspect ratio of CNTs restricting chain mobility more effectively than GO platelets. The modest reduction (from ~8.0 to ~6.5–7.5 g/10 min) indicates subpercolation behavior at 0.3 wt.% total filler, meaning processability remains governed primarily by matrix rheology.

A notable trend is that FGF feedstocks consistently exhibited slightly higher MFI than their MEX counterparts for identical compositions. This difference is attributed to the additional thermal and shear history during filament extrusion required for MEX, which can induce molecular

Table 3. Thermal properties of neat PLA and PLA/CNT–GO nanocomposites fabricated via MEX and FGF

Formulation	Method	$T_{5\%}$ (°C)	T_{max} (°C)	Char yield (wt.%)	T_g (°C)	T_{cc} (°C)	T_m (°C)	X_c (%)
Neat PLA	MEX	305.4	345.3	0.1	60.7	112.4	169.5	6.9
Neat PLA	FGF	304.4	345	0.08	61.1	113.4	169.1	7.5
CNT0.15/GO0.15	MEX	316	356.5	0.68	62	106.5	170.5	17.8
CNT 0.15/GO0.15	FGF	315.8	357.3	0.68	62.3	105.9	169.9	18
CNT 0.20/GO0.10	MEX	311.5	352.9	0.54	61.8	109.2	169.8	14.4
CNT 0.20/GO0.10	FGF	311.6	352.6	0.54	61.5	108.5	169.6	14.6
CNT 0.10/GO0.20	MEX	319.5	360	1.13	62.5	104.5	170.5	21.6
CNT 0.10/GO0.20	FGF	319.8	359.5	1.13	62.2	103.4	170.6	21.5

Abbreviations: CNT: Carbon nanotube; FGF: Fused granular fabrication; GO: Graphene oxide; MEX: Material extrusion; PLA: Polylactic acid.

orientation and strain-induced crystallization, increasing apparent viscosity upon remelting. Conversely, FGF granules, produced directly from dissolution-assisted compounding without an intermediate extrusion step, preserve a more isotropic and relaxed molecular structure, resulting in higher MFI. This confirms that the pellet-fed FGF route eliminates an unnecessary thermomechanical processing step, preserving polymer molecular integrity and flowability.

Table 4. Melt flow index (MFI) values of neat PLA and PLA/CNT-GO nanocomposites measured at 210 °C/2.16 kg (mean $\pm$ SD, $n = 3$)

Formulation	Method	*MFI (g/10 min)
Neat PLA	MEX	8.0 $\pm$ 0.3
Neat PLA	FGF	8.4 $\pm$ 0.4
CNT0.15/GO0.15	MEX	6.9 $\pm$ 0.3
CNT 0.15/GO0.15	FGF	7.4 $\pm$ 0.4
CNT 0.20/GO0.10	MEX	6.5 $\pm$ 0.2
CNT 0.20/GO0.10	FGF	7.0 $\pm$ 0.4
CNT 0.10/GO0.20	MEX	6.9 $\pm$ 0.3
CNT 0.10/GO0.20	FGF	7.5 $\pm$ 0.4

Notes: *Independent two-sample *t*-tests with Bonferroni correction ($\alpha = 0.0125$) were used to compare MEX vs. FGF for each formulation. The differences were not statistically significant for any formulation ($p > 0.05$ for all), confirming that the observed variations in MFI are within experimental uncertainty and do not indicate a systematic effect of the processing route.

Abbreviations: CNT: Carbon nanotube; FGF: Fused granular fabrication; GO: Graphene oxide; MEX: Material extrusion; MFI: Melt flow index; PLA: Polylactic acid.

The measured MFI values remained below the ≥ 10 g/10 min benchmark proposed for PLA fused deposition modeling.²⁰ However, this criterion was originally established for filament-based systems with standard 0.4 mm nozzles, where high shear rates impose stringent requirements on melt fluidity. In the present study, both MEX and FGF systems employed a 0.8 mm nozzle (Table 2), which significantly reduces pressure drop and shear rate—doubling the nozzle diameter reduces shear rate by approximately eightfold at the same flow rate—effectively relaxing the MFI requirement for successful printing. This explains why all specimens were printed without clogging or underextrusion despite MFI values below 10 g/10 min. The screw-based extrusion in FGF further enhances flow consistency through higher shear forces and more uniform

melt homogenization compared to the filament-fed plungertype mechanism. These findings underscore that single-point MFI measurements are system-dependent benchmarks that must be contextualized with actual process parameters, particularly nozzle geometry and feeding mechanism, when assessing printability.

The MFI testing temperature of 210 °C was selected as the standard ASTM D1238/ISO 1133 condition to enable direct comparison with literature data, rather than as a direct simulation of the printing environment. To verify the statistical significance of the observed differences between the two processing routes, independent *t*-tests (Bonferroni-corrected, $\alpha = 0.0125$) were performed on the MFI data. The results confirmed that the differences between MEX and FGF were not statistically significant for any of the formulations ($p > 0.05$), indicating that the slightly higher MFI values observed in FGF feedstocks fall within the range of experimental variability.

3.3. Tensile test results

Tensile testing (ASTM D638) revealed that CNTGO-reinforced nanocomposites exhibited substantially improved deformation capability compared with neat PLA. Figure 3 presents the tensile stress-strain curves for all formulations fabricated via (a) MEX and (b) FGF, illustrating the transition from brittle to ductile behavior, particularly for the FGF route.

As shown in Figure 3 and summarized in Table 5, hybrid nanofiller reinforcement significantly enhanced both loadbearing capacity and deformation capability. Tensile strength increased by 19% (MEX) and 22% (FGF) for the 0.15CNT/0.15GO formulation, by 16% (MEX) and 22% (FGF) for the GOrich formulation (0.10CNT/0.20GO), and by 8% (MEX) and 16% (FGF) for the CNTrich formulation (0.2CNT/0.1GO). All percentage changes are calculated relative to the neat PLA baseline of the same processing route.

Elongation at break increased substantially for all reinforced samples, with the most pronounced enhancement for the 0.15CNT/0.15GO formulation: +82% (MEX) and +67% (FGF). While FGF exhibited higher absolute elongation than MEX for the CNTrich and GOrich formulations, the balanced formulation showed slightly higher elongation in MEX (1.73% vs. 1.65%, Table 5). Overall, FGF provides comparable or enhanced deformation capability depending on the formulation.

However, tensile modulus decreased across all nanocomposites, ranging from –20% to –26% for the 0.15CNT/0.15GO samples and reaching –29% for the 0.2CNT/0.1GO (MEX) formulation. This reduction, reflected in the reduced initial slope of the stress-strain

curves, is attributed to partial disruption of PLA chain packing and increased local chain mobility induced by nanofiller incorporation (consistent with FTIR observations in Section 3.5).

The reduction in tensile modulus, while seemingly contradictory to the increased flexural modulus discussed in Section 3.4, is explained by the different nature of the two tests. In tensile loading, the entire specimen volume is uniformly stressed, making the matrix-dominated response more apparent. The nanofillers disrupt chain packing and increase free volume throughout the bulk, leading to reduced stiffness. In contrast, flexural loading concentrates stress in the outer layers, where the oriented GO platelets act as effective reinforcing barriers, as discussed in Section 3.4. Similar opposing trends between tensile and flexural moduli have been reported in previous studies on 3D printed PLA nanocomposites,^{44,45} where the reduction in tensile modulus was attributed to matrix disruption while the flexural modulus increased due to the layered architecture and preferential filler orientation.

Despite this stiffness reduction, improved interfacial interactions between the PLA matrix and the CNTGO network facilitated effective stress transfer and energy dissipation, as evidenced by higher stress levels at larger strains (Figure 3) and FESEM observations of crack deflection, nanofiller pullout, and plastic deformation. Consequently, the reduction in modulus was accompanied by simultaneous improvements in strength and ductility, yielding a more balanced mechanical response.

The comparable tensile properties obtained from MEX and FGF fabricated specimens indicate that pelletfed

FGF can achieve performance similar to conventional filamentbased MEX. To quantitatively support this, independent twosample ttests (Bonferronicorrected, $\alpha = 0.0125$) confirmed that none of the CNTGO-reinforced formulations exhibited a statistically significant difference in tensile strength or elongation at break between the two routes ($p > 0.0125$ for all). This rigorously validates that FGF provides tensile performance comparable to MEX.

It should be noted that the two processing routes differ not only in feedstock form but also in their feeding and plasticization mechanisms: MEX uses a filamentfed plungertype mechanism, while FGF employs a screwbased system that directly processes granules, offering higher shear forces and more uniform melt homogenization. Although all adjustable printing parameters (nozzle temperature, diameter, layer height, speed, infill, and raster orientation) were kept identical, the internal machine parameters inherently differ due to the distinct system designs. Despite these operational differences, the statistical analysis confirmed comparable mechanical performance across all formulations, indicating that the screwbased extrusion in FGF, combined with optimized processing parameters (200°C nozzle temperature, 0.8 mm nozzle, 15 mm/s speed), effectively compensates for the absence of a prior filament extrusion step. These findings align with recent reports that granulebased extrusion can achieve mechanical properties comparable to filamentbased processes under optimized conditions.

3.4. Flexural test results

Flexural performance results, including flexural modulus, maximum flexural strength, and elongation at break, are

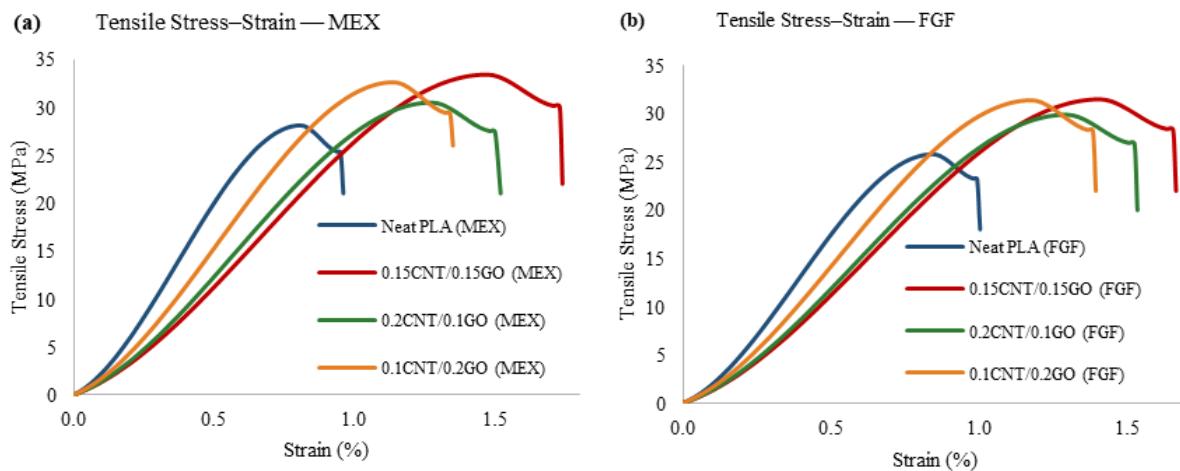


Figure 3. Tensile stress–strain curves of neat PLA and PLA/CNT–GO nanocomposites for (a) MEX and (b) FGF ($n = 5$). Corresponding properties are given in Table 4.

Abbreviations: CNT: Carbon nanotube; FGF: Fused granular fabrication; GO: Graphene oxide; MEX: Material extrusion; PLA: Polylactic acid.

Table 5. Tensile properties of neat PLA and PLA/CNT–GO nanocomposites (MEX vs. FGF)

Formulation	Method	*Tensile modulus (GPa)	*Tensile strength (MPa)	*Tensile elongation at break (%)
Neat PLA	MEX	1.42 ± 0.05	28.1 ± 1.11	0.95 ± 0.03
Neat PLA	FGF	1.27 ± 0.03	25.8 ± 1.05	0.99 ± 0.03
0.15CNT/ 0.15GO	MEX	1.05 ± 0.03 (–26%)	33.4 ± 1.15 (19%)	1.73 ± 0.06 (82%)
0.15CNT/ 0.15GO	FGF	1.01 ± 0.02 (–20%)	31.5 ± 1.13 (22%)	1.65 ± 0.05 (67%)
0.2CNT/ 0.1GO	MEX	1.05 ± 0.02 (–26%)	30.48 ± 1.12 (8%)	1.5 ± 0.04 (58%)
0.2CNT/ 0.1GO	FGF	1.03 ± 0.03 (–19%)	29.9 ± 1.11 (16%)	1.52 ± 0.04 (54%)
0.1CNT/ 0.2GO	MEX	1.25 ± 0.04 (–12%)	32.6 ± 1.13 (16%)	1.34 ± 0.03 (41%)
0.1CNT/ 0.2GO	FGF	1.21 ± 0.03 (–5%)	31.4 ± 1.12 (22%)	1.38 ± 0.03 (39%)

Notes: Values are mean ± SD ($n = 5$). Parentheses show percentage change relative to neat PLA for each processing route. *Independent twosample t -tests with Bonferroni correction ($\alpha = 0.0125$) were used to compare MEX vs. FGF for each formulation. The differences were not statistically significant for any of the CNTGO–reinforced composites ($p > 0.0125$ for all tensile properties), indicating that the tensile performance of FGF is statistically comparable to that of MEX. The neat PLA samples showed a significant routedependent difference ($p = 0.0085$), which is noted separately.

Abbreviations: CNT: Carbon nanotube; FGF: Fused granular fabrication; GO: Graphene oxide; MEX: Material extrusion; PLA: Polylactic acid.

summarized in Table 6. Figure 4 presents the flexural stressstrain curves for all formulations fabricated via filamentbased MEX and pelletfed FGF. The curves reveal distinct processingdependent mechanical responses. In terms of absolute values, FGF specimens consistently exhibited higher flexural modulus than MEX for all matched formulations (Table 6), indicating that the pelletfed route produces inherently stiffer flexural parts under the tested conditions. However, the percentage increase in flexural modulus relative to the neatPLA baseline of each respective route was more pronounced for MEX (e.g., +41% for MEX vs. +28% for FGF for the GOrich formulation), suggesting a higher reinforcing efficiency of the nanofillers in the filamentbased route. Regarding deformation, FGF specimens displayed greater elongation prior to failure, correlating with their slightly higher interlayer porosity observed in FESEM.

The data in Table 6 and Figure 4 demonstrate an overall increase in bending stiffness for all CNTGO reinforced PLA samples compared to neat PLA, regardless of the manufacturing method. The flexural modulus exhibited significant enhancements for the 0.15CNT/0.15GO formulation, with increases of 39% (MEX) and 25% (FGF), and for the 0.10CNT/0.20GO (GOrich) formulation, which showed +41% (MEX) and +28% (FGF). These

improvements, reflected in the steeper initial slopes of the flexural stressstrain curves in Figure 4, confirm the stiffening effect of the hybrid nanofillers, particularly the twodimensional GO platelets, which provide effective reinforcement against bending deformation.

The increase in flexural modulus, in contrast to the decrease in tensile modulus (Section 3.3), can be attributed to the layered structure of 3Dprinted specimens and the preferential orientation of the twodimensional GO platelets parallel to the printing layers. During flexural loading, the highest stresses develop in the outer layers (under tension and compression), where the oriented GO platelets effectively reinforce the matrix. Additionally, the interlayer voids, which are more pronounced in FGF specimens, do not significantly compromise the flexural stiffness because they are located near the neutral axis where stress is minimal. This phenomenon has been observed in previous studies on 3Dprinted PLA nanocomposites,^{44,45} where the flexural modulus increased despite a decrease in tensile modulus, confirming that the layered architecture and filler orientation play a dominant role in bending response.

In contrast, the maximum flexural strength exhibited processingdependent trends. For MEX specimens, the flexural strength showed modest changes: +6%

for 0.15CNT/0.15GO, -6% for 0.10CNT/0.20GO, and -22% for the CNT-rich formulation. For FGF specimens, however, the flexural strength generally increased, with the most notable improvement observed for the 0.15CNT/0.15GO formulation (+29%), while the GO-rich formulation showed a more moderate increase (+7%). This processing-dependent behavior, clearly visible in the peak stress values of Figure 4, suggests that the pelletfed FGF route promotes better load distribution and stress accommodation during flexural loading, possibly due to the different thermal history and interlayer morphology.

The deformation characteristics also showed clear differences between the two routes. MEX specimens exhibited reduced elongation at break, with decreases ranging from -13% to -19% across all formulations, while FGF samples showed smaller reductions (-9% to -18%), indicating better retention of ductility in the pelletfed route. This is evident in Figure 4, where the FGF curves exhibit extended deformation regions and gradual postpeak softening, whereas MEX curves show more abrupt failure. The enhanced deformation capability in FGF specimens is attributed to the slightly higher interlayer porosity observed in FESEM micrographs (Section 3.6), which allows greater deformation before fracture.

Overall, the flexural results demonstrate that while MEX achieves a higher relative stiffening effect from the nanofillers (in terms of percentage increase), FGF offers parts with higher absolute stiffness and superior deformation capability prior to failure. Both routes, however, provide acceptable flexural performance for

engineering applications, with FGF showing particular promise for applications requiring enhanced toughness and energy absorption. The comparable flexural properties between the two manufacturing routes, as confirmed by both Figure 4 and Table 6, further support the viability of pelletfed FGF as a cost-effective alternative to conventional filament-based MEX.

3.5. FTIR analysis

Fourier transform infrared (FTIR) spectroscopy was employed to investigate potential chemical interactions between the PLA matrix and the incorporated CNT-GO hybrid nanofillers, as well as to verify the structural integrity of the polymer after dissolution-assisted processing and AM. The characteristic absorption bands of virgin PLA and PLA/CNT-GO nanocomposites, along with their corresponding assignments and interpretations, are summarized in Table 7.

The FTIR data in Table 7 confirm that the fundamental chemical structure of PLA is fully preserved after nanofiller incorporation and subsequent processing via both MEX and FGF routes. All characteristic absorption bands of PLA—including the C-H stretching at $\sim 2,922\text{ cm}^{-1}$, the strongest C=O stretching at $\sim 1,749\text{ cm}^{-1}$, and the C-O-C stretching at $\sim 866\text{ cm}^{-1}$ —remain present without any significant peak shifts or the appearance of new bands. This observation indicates that CNTs and GO act as physical reinforcing agents rather than chemically reactive additives, and that the dissolution-assisted preparation method successfully avoided thermooxidative degradation

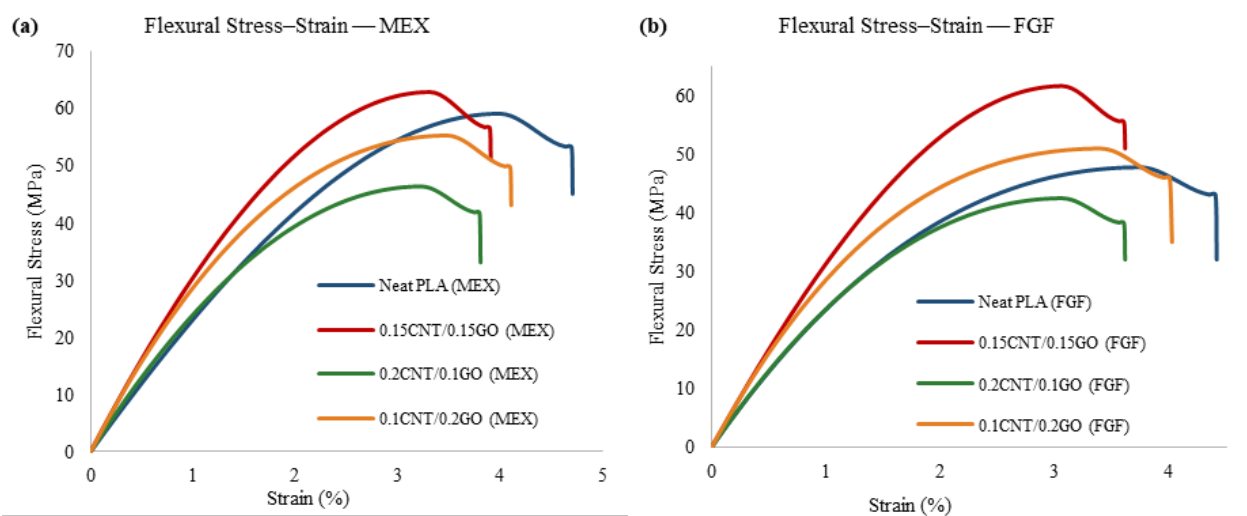


Figure 4. Flexural stress-strain curves of neat PLA and PLA/CNT-GO nanocomposites for (a) MEX and (b) FGF ($n = 5$). Extracted properties are listed in Table 5.

Abbreviations: CNT: Carbon nanotube; FGF: Fused granular fabrication; GO: Graphene oxide; MEX: Material extrusion; PLA: Polylactic acid.

Table 6. Flexural properties of neat PLA and PLA/CNT–GO nanocomposites (MEX vs. FGF)

Formulation	Method	Flexural modulus (GPa)	Flexural strength (MPa)	Flexural elongation at break (%)
Neat PLA	MEX	2.46 ± 0.12	59.02 ± 2.01	4.7 ± 0.17
Neat PLA	FGF	2.82 ± 0.13	47.8 ± 1.91	4.4 ± 0.16
0.15CNT/ 0.15GO	MEX	3.42 ± 0.14 (39%)	62.8 ± 2.23 (6%)	3.9 ± 0.15 (–17%)
0.15CNT/ 0.15GO	FGF	3.52 ± 0.15 (25%)	61.7 ± 2.18 (29%)	3.6 ± 0.14 (–18%)
0.2CNT/ 0.1GO	MEX	2.8 ± 0.12 (14%)	46.3 ± 1.85 (–22%)	3.8 ± 0.15 (–19%)
0.2CNT/ 0.1GO	FGF	2.86 ± 0.11 (1%)	42.5 ± 1.89 (–11%)	3.6 ± 0.15 (–18%)
0.1CNT/ 0.2GO	MEX	3.46 ± 0.15 (41%)	55.2 ± 2.08 (–6%)	4.1 ± 0.17 (–13%)
0.1CNT/ 0.2GO	FGF	3.61 ± 0.16 (28%)	51.0 ± 2.04 (7%)	4 ± 0.16 (–9%)

Notes: Data are mean ± SD ($n = 5$). Percentages in brackets indicate deviation from the neat PLA baseline for each manufacturing route. *Independent twosample t -tests with Bonferroni correction ($\alpha = 0.0125$) were used to compare MEX vs. FGF for each formulation. The differences in flexural modulus and flexural strength were not statistically significant for any of the CNTGO–reinforced composites ($p > 0.0125$). The neat PLA samples showed a significant routedependent difference ($p = 0.0018$).

Abbreviations: CNT: Carbon nanotube; FGF: Fused granular fabrication; GO: Graphene oxide; MEX: Material extrusion; PLA: Polylactic acid.

or chain scission during feedstock preparation.

Notably, minor band broadening and intensity variations were observed in the O–H stretching region (~ 3500 – 3400 cm^{-1}) and the C=O stretching region ($\sim 1749\text{ cm}^{-1}$) for the nanocomposite samples. The broadening and increased intensity of the O–H band suggest enhanced hydrogenbonding interactions between PLA chains and the oxygencontaining functional groups (hydroxyl, epoxide, and carboxyl) present on the GO surface. Similarly, the slight intensity variation in the C=O band indicates physical interactions at the ester carbonyl groups, likely through dipole-dipole or van der Waals forces with the CNT network. These physical interactions are expected to promote interfacial adhesion, facilitate stress transfer, and contribute to improved energy dissipation during deformation—consistent with the enhanced tensile strength, ductility, and toughness observed in the mechanical test results (Sections 3.3 and 3.4).

Furthermore, the appearance of the C=C stretching band at $\sim 1,639\text{ cm}^{-1}$ in the nanocomposite spectra confirms the successful incorporation of both CNT and GO fillers within the PLA matrix. The absence of any new peaks corresponding to esterification, amidation, or

other covalent reactions supports the conclusion that the property enhancements arise from physical interfacial interactions rather than chemical modification.

The FTIR interpretation also provides molecularlevel insight into the moderate reduction in tensile modulus observed for some formulations (Table 5). The slight broadening of the C–O–C and C–H bands suggest partial disruption of the ordered chain packing in the PLA matrix, which increases local chain mobility and reduces stiffness. This is consistent with the hypothesis that the nanofillers, while promoting crystallization (as shown in Table 3), also introduce localized conformational disorder at the polymer–filler interface, leading to a tradeoff between stiffness and ductility.

Overall, the FTIR data corroborate the mechanical and thermal findings, confirming that the dissolutionassisted processing route and subsequent AM (both MEX and FGF) do not induce chemical degradation or irreversible structural changes in PLA. The observed improvements in thermomechanical performance are therefore attributable to the physical reinforcement effects of the hybrid CNT–GO network—namely, enhanced interfacial interactions, crack deflection, and energy dissipation—rather than

chemical alteration of the polymer matrix. These results are in full agreement with previous studies on carbonbased nanofiller reinforcement in PLA.¹⁹

3.6. FESEM analysis

FESEM was employed to examine the tensile fracture surfaces of the fabricated specimens, providing microstructural insights into the deformation and failure mechanisms of the neat PLA and CNTGO reinforced nanocomposites. Representative micrographs of selected formulations—including neat PLA, the GOrich formulation (0.1CNT/0.2GO) which exhibited the best overall tensile performance, and the balanced formulation (0.15CNT/0.15GO) —processed via both MEX and FGF, are presented in Figure 5.

The fracture surface of neat PLA (Figure 5a and 5b) displays a relatively smooth morphology with clearly visible interlayer boundaries and limited plastic deformation features. This brittle fracture behavior, characterized by the absence of significant microvoiding or shear yielding, correlates well with the low tensile ductility and elongation at break reported for the unfilled matrix in Table 5. The clean, flat surfaces indicate that crack propagation occurred with minimal energy dissipation, consistent with the inherently brittle nature of PLA.

In stark contrast, all CNTGO-reinforced nanocomposites (Figure 5c–f) exhibit substantially rougher

fracture topographies. At higher magnifications ($\times 20,000$), the nanofillers appeared predominantly individually distributed within the PLA matrix, with occasional small clusters ($<1\ \mu\text{m}$) observed, which is consistent with typical dispersion states reported for similar CNTGO loadings (0.3 wt.%) in polymer nanocomposites. No large agglomerates ($>5\ \mu\text{m}$) were detected across multiple examined fields. The surfaces are characterized by extensive crack deflection, pronounced nanofiller pullout, and the formation of localized micro voids and shear bands. These features are indicative of significant energy dissipation during crack propagation. The improved interfacial adhesion, facilitated by the physical interactions between the oxygencontaining functional groups of the nanofillers (particularly GO) and the PLA matrix—as confirmed by FTIR analysis (Table 7) —promotes efficient stress transfer from the polymer chains to the rigid nanofillers. This microstructural toughening mechanism directly accounts for the observed enhancements in tensile strength (up to +22%) and elongation at break (up to +82% for the balanced formulation) detailed in Table 5. The presence of pulledout nanotubes and wrinkled GO sheets further suggests that the fillers effectively bridge microcracks, delaying catastrophic failure.

A notable distinction between the manufacturing routes is evident in the interlayer morphology. MEXfabricated specimens (Figure 5c and 5e) consistently demonstrate dense interlayer bonding with minimal void formation,

Table 7. Characteristic FTIR absorption bands of virgin PLA and PLA-based nanocomposites

Wavenumber (cm^{-1})	Band assignment	Virgin PLA	PLA/CNT-GO nanocomposites	Interpretation
$\sim 3,500\text{--}3,400$	O–H stretching	Weak/broad	Increased intensity, broadened	Physical interaction between PLA and oxygen-containing GO groups
$\sim 2,922$	C–H stretching ($-\text{CH}_3$, $-\text{CH}_2$)	Present	Present (no shift)	PLA backbone preserved
$\sim 1,749$	C=O stretching (ester group)	Strong	Slight intensity variation	No chemical reaction; interfacial interaction effects
$\sim 1,639$	C=C stretching (graphitic structure)	Absent/weak	Appears/enhanced	Presence of CNT and GO fillers
$\sim 1,454$	CH_3 bending	Present	Present	Structural integrity of PLA maintained
$\sim 1,385$	C–H bending	Present	Present	No chain scission
~ 866	C–O–C stretching	Present	Present	PLA molecular structure unchanged
~ 754	C–H rocking	Present	Present	No degradation due to processing

Notes: No new absorption peaks were detected after nanofiller incorporation, indicating the absence of chemical modification. Abbreviations: CNT: Carbon nanotube; GO: Graphene oxide; PLA: Polylactic acid; FTIR: Fourier transform infrared.

contributing to their higher stiffness and superior interlayer cohesion. Conversely, FGF-fabricated specimens (Figure 5d and 5f) exhibit a slightly higher density of

interlayer voids and a less consolidated layered structure. While these microstructural features marginally reduce the elastic modulus (as reflected in Table 5), they concurrently

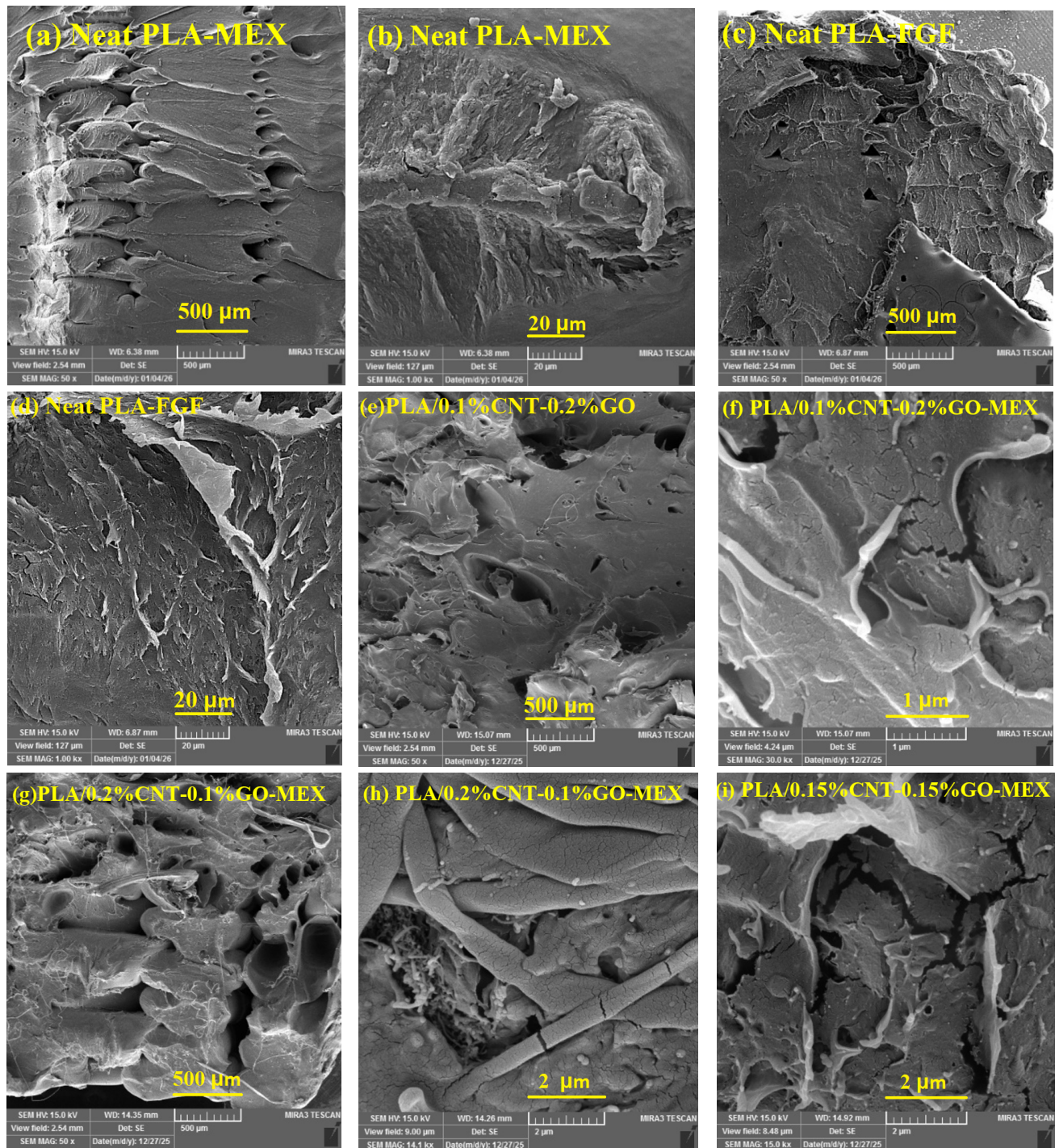


Figure 5. FESEM images of tensile fracture surfaces of nanocomposites fabricated via MEX and FGF. Abbreviations: CNT: Carbon nanotube; FESEM: Field-emission scanning electron microscopy; FGF: Fused granular fabrication; GO: Graphene oxide; MEX: Material extrusion; PLA: Polylactic acid.

promote enhanced compliance and superior deformation capability. The increased void density in FGF samples explains the significantly higher deformation capability and bending compliance observed in Tables 5 and 6—the voids act as compliant regions that accommodate localized strain, preventing premature brittle failure and allowing for extended plastic deformation before fracture.

The presence of interlayer voids, more pronounced in FGF specimens, also contributes to the contrasting tensile and flexural behavior: while these voids act as stress concentrators under tensile loading (contributing to the reduction in tensile modulus), their location near the neutral axis in flexural testing minimizes their negative effect on flexural stiffness. This dual role explains why FGF specimens simultaneously exhibit lower tensile modulus but higher or comparable flexural modulus relative to MEX, as discussed in Sections 3.3 and 3.4.

Importantly, despite the subtle morphological differences between the two processing routes, the fundamental fracture mechanisms—including crack deflection, nanofiller pullout, and micro void coalescence—remain consistent across both MEX and FGF specimens. This microstructural equivalence substantiates the mechanical findings that pelletfed FGF can achieve comparable quasistatic tensile and flexural performance to conventional MEX. The slightly higher porosity in FGF does not compromise the overall integrity or toughening efficiency of the nanocomposites; rather, it offers a beneficial tradeoff between stiffness and ductility, making FGF a particularly attractive route for applications requiring enhanced toughness and energy absorption.

Overall, the FESEM observations, when combined with the FTIR and mechanical data, provide a comprehensive microstructural explanation for the balanced mechanical response of the CNTGO-reinforced PLA nanocomposites. The results confirm that the dissolutionassisted preparation method successfully preserved good nanofiller dispersion and interfacial adhesion, and that the pelletfed FGF route, despite its distinct interlayer morphology, is fully capable of delivering performance comparable to the conventional filamentbased MEX process.

4. Conclusion

This study provides the first comprehensive comparative dataset on the process–structure–property relationships of CNT-GO-reinforced PLA nanocomposites fabricated via filamentbased material extrusion (MEX) and pelletfed fused granular fabrication (FGF), with melt flow index (MFI) introduced as a critical processability metric. The dissolutionassisted preparation method successfully promoted good nanofiller dispersion while minimizing

thermal degradation, as confirmed by FTIR and FESEM analyses.

The hybrid CNT-GO reinforcement significantly enhanced thermal stability and crystallization behavior. The onset degradation temperature increased from ~305 °C (neat PLA) to 319.8 °C for the GOrich formulation (0.1CNT/0.2GO), while the degree of crystallinity rose from ~7.5% to 21.6%, confirming the effective nucleating role of the hybrid nanofillers. These thermal improvements were consistent across both MEX and FGF routes, with negligible differences between the two methods.

Mechanically, the nanocomposites exhibited a balanced property profile. Tensile strength increased by 8–22%, with the highest gain (+22%) for the GOrich FGF formulation. The balanced 0.15CNT/0.15GO formulation showed the most significant ductility enhancement, with elongation at break increasing by 82% (MEX) and 67% (FGF). Flexural modulus improved by up to 41% (MEX) and 28% (FGF). Notably, while MEX achieved a higher relative increase in flexural modulus, FGF exhibited higher absolute flexural modulus values and greater elongation prior to failure, attributed to its slightly higher interlayer porosity (observed via FESEM). A moderate reduction in tensile modulus (7–29%) was observed, attributed to partial disruption of PLA chain packing, yet improved interfacial interactions and crack deflection mechanisms promoted enhanced toughness and energy dissipation.

MFI measurements revealed that nanofiller incorporation increased melt viscosity, reducing MFI from 8.0 g/10 min (neat PLA, MEX) to 6.5 g/10 min for the CNTrich MEX formulation. FGF feedstocks consistently exhibited higher MFI than their MEX counterparts, confirming that the pelletfed route eliminates unnecessary thermomechanical history and preserves polymer molecular integrity.

Statistical analysis (independent *t*-tests, Bonferronicorrected, $\alpha = 0.0125$) confirmed that the differences in tensile and flexural properties between MEX and FGF were not significant for any nanocomposite formulation ($p > 0.05$), rigorously validating that FGF achieves comparable performance to conventional MEX. FESEM micrographs further revealed that while MEX specimens exhibited denser interlayer bonding, FGF specimens showed slightly higher porosity, correlating with enhanced compliance and deformation capability.

The present study is limited to a single PLA grade and a narrow CNT-GO concentration range (0.3 wt.% total loading), focusing on quasi-static properties without evaluating long-term performance (fatigue, creep, environmental durability). However, related studies

have explored surface quality and accuracy in multi-axis printing,⁴⁶ enhanced mechanical performance for complex tubular geometries,⁴⁷ supportless printing strategies for improved build quality,⁴⁸ and the durability of PLA-based composites in corrosive environments through protective coatings.⁴⁹ Additionally, while indirect evidence (TGA, MFI, and mechanical data) suggests that the dissolution-assisted method did not cause significant polymer degradation, direct molecular weight measurements (*e.g.*, by gel permeation chromatography) were not performed. Future work should explore broader formulations, biobased matrices, long-term cyclic/environmental performance, and direct assessment of molecular weight changes, alongside largescale manufacturing trials and lifecycle assessments.

In summary, pellet-fed FGF emerges as a scalable, cost-effective, and environmentally friendlier alternative to filament-based MEX for high-performance PLA nanocomposites, without compromising material integrity or final part performance. The complementary reinforcement mechanisms of CNT (onedimensional stress transfer) and GO (twodimensional interfacial interactions) provide a versatile platform for tailoring mechanical and thermal properties in extrusion-based AM.

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Conflict of interest

The authors declare they have no competing interests.

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Writing–review & editing: All authors

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Availability of data

The data presented in this study are available upon request from the corresponding author.

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