

Electronic Supplementary Information (ESI)

Preparation and 3D-Printing of Highly Conductive Polylactic Acid/Carbon Nanotube Nanocomposites via Local Enrichment Strategy

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Materials

Polylactic Acid (trade name: 4032D, PLA) with a density of 1.24 g/cm³ and a melting point of 160 °C, was provided by NatureWorks, USA;

Polycaprolactone (trade name: 6800, PCL) with a melting temperature of 60 °C, was supplied by Shenzhen Brightchina Industrial Co. China;

Carbon Nanotube (trade name: NC7000, CNT) with an average length of 1.5 μm, an average diameter of 9.5 nm and a specific surface area of 250-300 m²/g, was provided by Nanocyl, Belgium.

Sample Preparation

The CNTs coated filaments preparation

The pure PLA filaments (Φ 1.75mm) were prepared for 3D-printing at 190°C in a single screw extruder (RM-200C, Harbin HAPRO electric Technology Co. LTD, China) with a screw speed of 10 rpm. Then, the CNTs were dispersed in a polycaprolactone solution using dichloromethane as the solvent (the mass ratio of CNTs : polycaprolactone : dichloromethane = 1:10:90), after that the pure PLA filaments were went through above prepared CNTs contained polycaprolactone solution for depositing CNTs on the surface of filament. Subsequently, the CNTs coated filaments were dried in vacuum oven (50 °C, 6 h), and the weight difference of filament between

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before and after depositing was used to evaluate the content of CNTs loaded in filaments. After calculation, the coated filaments with a concentration of 1wt% CNTs were prepared by local enrichment strategy. As a comparison, the reference PLA/CNTs materials with the same composition were prepared at 190°C in a twin screw extruder with length to diameter (L/D) ratio of 32 and screw speed of 30 rpm. Then, the reference PLA/CNTs materials were used to prepare filaments in a single screw extruder following the same procedure.

Computer Simulation

In order to further investigate the viscoelastic flow in printing die, the finite element simulation (FES) was carried out by software ANSYS POLYFLOWs 17.0 (ANSYS, Inc., USA) with an ICEM module for meshing the structured grid. The typical geometry of the printing die and the mesh of the whole liquefier channel, which was consisted of 44473 elements and 14680 nodes, were illustrated in Fig. S1. The governing equations including continuity equation, momentum equation and constitutive equation under the Cartesian coordinate system for simulation were given as following:

$$\nabla \cdot v = 0 \quad (1)$$

$$-\nabla p + \nabla \cdot \tau = 0 \quad (2)$$

$$\tau = 2\eta(\dot{\gamma})D \quad (3)$$

Where, v is the velocity vector, p is the pressure, τ is the stress tensor of the viscous fluid, η is the apparent viscosity, $\dot{\gamma}$ is the shear rate and D is the deformation tensor.

The boundary conditions of the printing die were assumed for the simulation, as follows: a) from the inlet to the outlet boundaries, the volume flow rate was constant; b) at the planes, zero traction condition was assumed; c) at the walls, the slip velocity was zero. Besides, the volume flow rate of 3.7 mm³/s and the printing temperature of 190 °C were fixed in simulation. Finally, the comprehensive FES analyses of melting flow in the whole die were conducted.

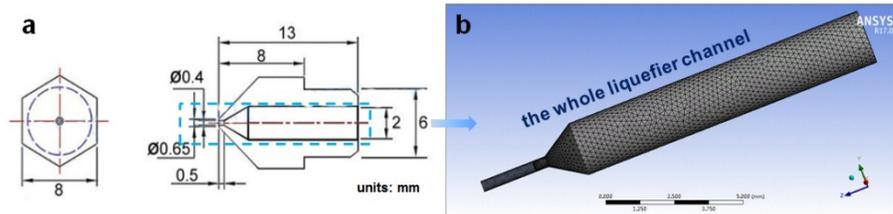


Figure S1 the geometry of die (a) and the finite element mesh of the whole liquefier channel with 44473 number of elements and 14680 number of nodes (b). The flow (extrusion) direction is in positive Z-axis.

FDM 3D-printed part preparation

The FDM 3D-printed part was prepared by the German RepRap X350pro standard open-air desktop printer (Feldkirchen, Germany), and the printing model was generated by using Pro/Engineer 5.0. The printing parameters were listed in Table S1.

Table S1 The FDM printing parameters

Printing temperature	Platform temperature	Layer thickness	Printing speed	Infill density	Nozzle diameter	Nozzle length
190 °C	50 °C	0.3 mm	200 mm/min	100%	0.4mm	13mm

Characterization

Rheological measurements

The rheological behaviors of pure PLA were measured on a parallel-plate rotational rheometer (TA Instruments, USA). The diameter was 25 mm and the gap was 1 mm. The frequency sweep was conducted at different temperature ranging from 180 °C to 220 °C. The scanning frequencies were changed from 0.01 to 100 rad/s and the 5% strain was used. The complex viscosity data was fitted by using the Carreau–Yasuda model, as indicated by the following equation (4)¹:

$$\eta(\dot{\gamma}) = \eta_{\infty} + (\eta_{\infty} - \eta_0) \left(1 + (\lambda \dot{\gamma})^a\right)^{\frac{n-1}{a}} \quad (4)$$

Where, η_{∞} is the infinite shear viscosity, η_0 is the zero shear viscosity, λ is the relaxation time, a is the shift factor and n is the Power law index. The corresponding parameters of PLA used for Carreau–Yasuda model were listed in Table S2. All these viscosity parameters were adopted in the computer simulation.

Table S2 the viscosity parameters of PLA

Zero-shear viscosity	Relaxation time	Shift factor	Power law index
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692.273 Pa·s	0.074s	2.840	0.948
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Polarized optical microscope (POM) observation

Polarized microscope photo of the fractured surface of filament marked with dye tracers after printing was observed by polarized optical microscope (Linkam THMS600, Linkam Scientific Instruments Ltd., UK).

Scanning electron microscope (SEM) observation

The morphologies of the surface and the fractured cross-section of filament before and after printing were investigated by using a FEI Inspect F-SEM instrument with an acceleration voltage of 20 kV. Before the observation, the samples were gold-sputtered.

Electrical conductivity measurements

The electrical resistance of FDM 3D-printed circular part with a diameter of 12mm and a thickness of 2mm were measured on a four-point probe instrument (RK-FA, Ningbo Ruikeweiye instrument Co., Ltd, China). It should be noted that the electrical resistance of the reference sample was tested on a Keithley 4200 SourceMeter® (Keithley Instruments, USA). Before measurement, the conductive silver glue was spread on the both sides of the circular part to ensure good contact between the sample and the electrodes. For each sample, five measurements were repeated and the averaged value was calculated. In addition, for more intuitive comparison of the difference of two parts in electrical conductivity, the 3D-printed wave-like parts were directly connected in a simple direct-current circuit.

Fourier transform infrared spectroscopy (FT-IR) analysis and results

The FTIR spectra of pure PLA and PLA/CNTs samples over the wavenumber range of 4000-400 cm^{-1} were used a Nicolet 6700 spectrometer (Thermal Scientific, USA) to study the interaction between CNTs and PLA. The result was shown in Fig. S2. As can be seen, there was no chemical interaction occurring between CNTs and PLA, e.g. graft reaction, since the characteristic peaks of PLA (-CH₃ & -CH groups: stretching vibrations $\nu=2998\text{cm}^{-1}$, 2943cm^{-1} , bending vibrations $\delta=1457\text{cm}^{-1}$, 1391cm^{-1} ; -C=O: $\nu=1756\text{cm}^{-1}$; -C-O-C: $\nu=1185\text{cm}^{-1}$, 1091cm^{-1}) do not shift and change after incorporating CNTs.

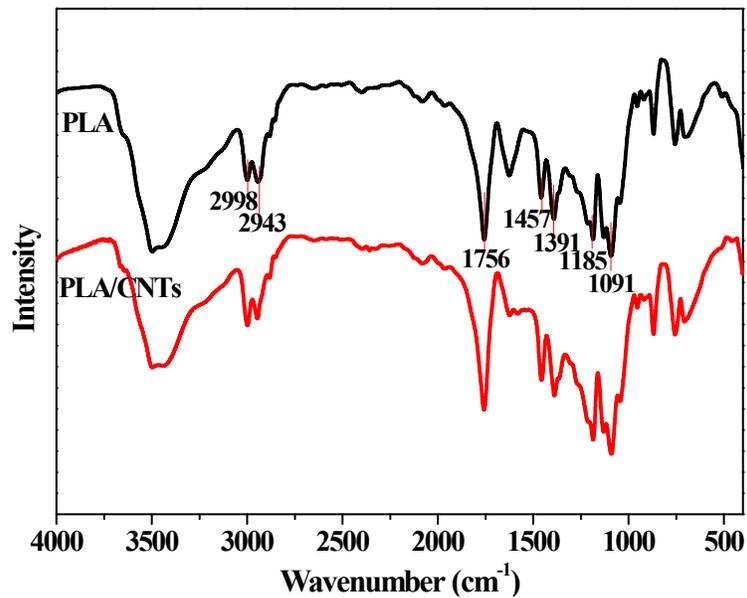


Figure S2 FT-IR spectra of pure PLA and PLA/CNTs samples.

References

1. M. Ebrahimi, V. K. Konaganti, S. Moradi, A. K. Doufas and S. G. Hatzikiriakos, *Soft Matter*, 2016, **12**, 9759-9768.