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Structure-property relationships of 3D-printed carbon nanotube/polymer composites

Huseini S. Patanwala and Anson W. K. Ma

A dimensionless volumetric flow rate is found to be a critical parameter for understanding the microstructure and subsequent mechanical properties of 3D-printed composites.

Fused deposition modeling (FDM) is one of the most common methods of 3D printing. The technique is based on micro-extruding thermoplastic polymers in a raster pattern through a nozzle. To achieve better processibility, most FDM methods use thermoplastics, such as poly(lactic acid) (PLA) and acrylonitrile butadiene styrene.

However, although FDM parts are extremely useful for rapid-prototyping purposes, they lack the physical properties—e.g., mechanical strength and thermal stability (due to weak inter-road bonding and low heat-deflection temperature, respectively)—required for practical applications. There are two general approaches to enhancing the properties of FDM parts: by choosing polymers with better properties (e.g., polyaryletherketone[1] or liquid crystalline polymers[2]); or by incorporating fillers in the neat polymers.[3,4] Indeed, identifying appropriate polymer grades and developing new formulations for 3D printing constitute an active area of research. Compared to conventional processing methods (e.g., injection molding), structure–processing–property relationships in 3D printing are not well established. Many studies have attempted to optimize mechanical properties by varying the process parameters used (e.g., deposition speed, nozzle temperature, the gap between the print nozzle and build plate, the infill pattern, infill density, and part-slicing layer thickness).[5,6] However, because there are many parameters to choose from, and due to the absence of a standardized methodology, optimizing the properties of FDM parts is challenging.

To improve the thermal and mechanical properties of PLA-based FDM parts, we have explored the use of carbon nanotubes (CNTs) as short-fiber fillers. Furthermore, we have investigated the effects of CNT concentration on the structure and subsequent properties of the 3D-printed parts. Finally, in order to lay down the foundation for property optimization, we have proposed an approach that uses a non-geometric process parameter. This parameter, the volumetric flow rate, is capable

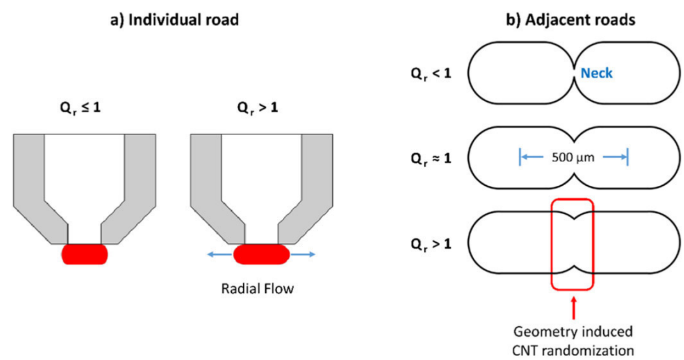

Figure 1. *Schematic diagrams of hypothesized factors leading to carbon nanotube (CNT) misalignment during 3D printing: (a) radial flow occurring as the material overfills the gap, and (b) geometry-based fusion between adjacent roads. Q_r: Dimensionless volumetric flow rate.*

of influencing the microstructure of the printed composite at a given layer thickness and print speed.

We chose to use CNTs as reinforcement material because of their excellent intrinsic mechanical, thermal, and electrical properties.[7–9] Furthermore, CNTs are available in powder form and can therefore be directly blended into PLA and extruded into feedstock filaments for the FDM printer. This process is different from printing continuous-fiber composites, for which a specialized printer and carefully chosen polymers (e.g., Markforged) are required.[10,11]

In 3D-printed parts, the width of a printed road (see Figure 1) depends on the interplay between the printing flow rate, the velocity of the print nozzle (relative to the build plate), and the gap between the nozzle and the build plate during printing. We therefore evaluated the use of a dimensionless volumetric flow rate (Q_r) to predict the microstructure of the 3D-printed part. This parameter is defined as the ratio of the actual volumetric flow rate to the ideal volumetric flow rate (i.e., the rate required to completely fill a given gap between the nozzle and the

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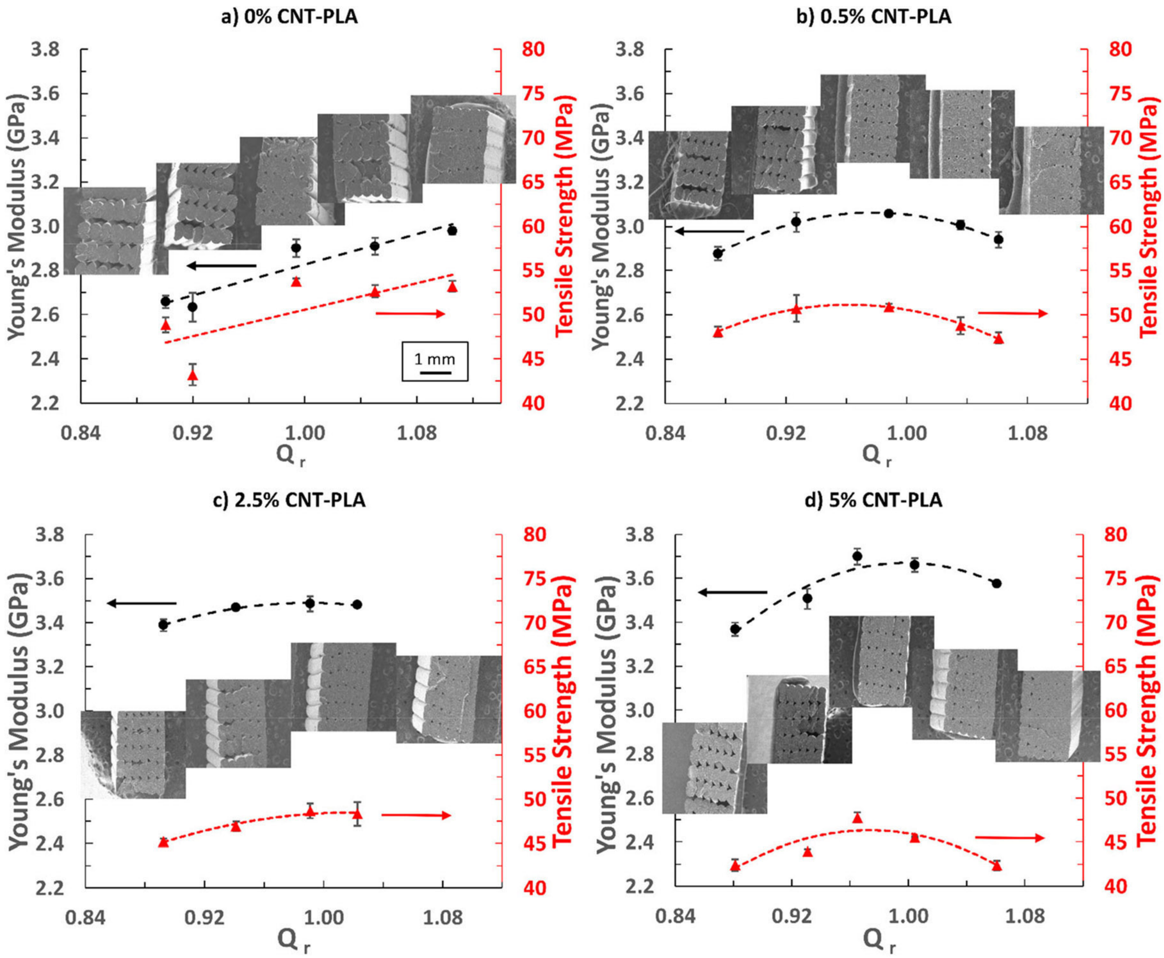

Figure 2. *Young's modulus (black), tensile strength (red), and scanning electron microscope (SEM) images of the fractured surface as a function of dimensionless volumetric flow rate (Q_r) for CNT/poly(lactic acid) (CNT-PLA) composites with varying CNT content (0–5%). (a) 0% CNT-PLA, (b) 0.5% CNT-PLA, (c) 2.5% CNT-PLA, and (d) 5% CNT-PLA, respectively. The scale shown in (a) applies to all SEM images.*

build plate at a given relative velocity of the print head). Q_r is particularly important because it helps to map out regions of 'under-flow' and 'over-flow,' indicated by values of $Q_r < 1$ and $Q_r > 1$, respectively. These values enable prediction of the microstructure, and therefore the mechanical properties, of the 3D-printed PLA-CNT composites. For a fixed road-to-road distance, $Q_r > 1$ leads to a wider neck, whereas $Q_r < 1$ results in a narrower neck, or a lack of bonding between the roads: see Figure 1(a) and (b).

In the absence of CNTs, we found that the Young's modulus and tensile strength of the PLA samples increased as a function of increasing Q_r. We attribute this result to the reduction of the void fraction and better bonding between individual PLA roads. However, in the case of the CNT-PLA samples, we observed the highest Young's modulus and tensile strength at a Q_r close to 1 ($Q_r \approx 1$). The trends for the control (i.e., 0% CNT-PLA) and CNT-PLA samples are shown in Figure 2. As in the neat PLA case, we found that increasing the volumetric flow rate for underfilled samples ($Q_r < 1$) reduces the void fraction between roads and thus increases the stress transfer between individual roads under tension. Theoretically, as the volumetric flow rate is increased, the shear rate within the liquefier should also increase, thus leading to a higher degree of CNT alignment and consequently a higher modulus. However, we observed the opposite trend in terms of CNT alignment because overfilling ($Q_r > 1$) leads to randomization of CNT orientation.

To quantify the degree of CNT alignment, we carried out x-ray diffraction analysis on the fabricated samples, both within printed roads

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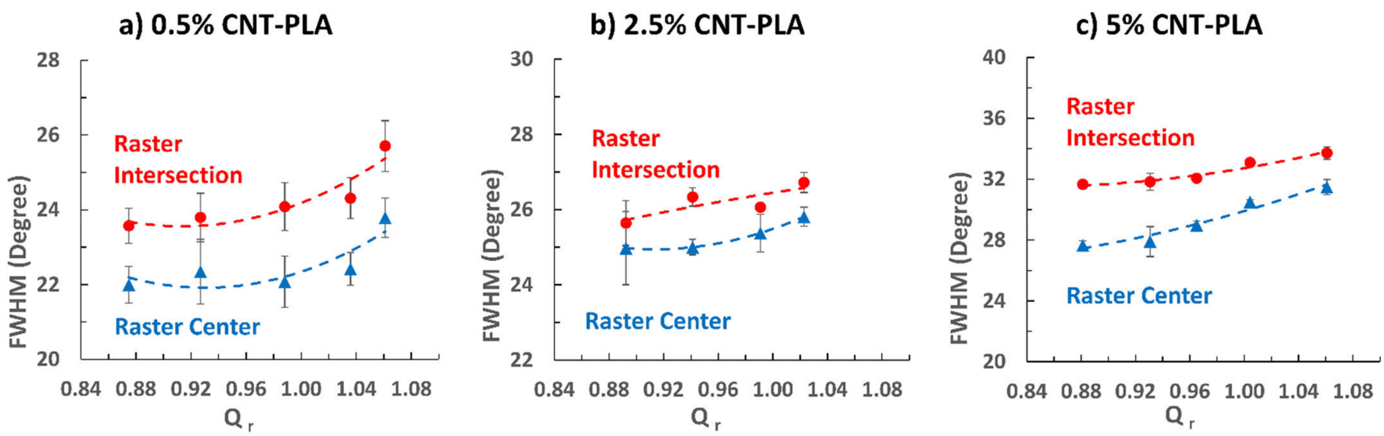

Figure 3. *Full width at half-maximum (FWHM) of: (a) 0.5% CNT-PLA, (b) 2.5% CNT-PLA, and (c) 5% CNT-PLA as a function of Q_r. The error bar represents the standard deviation of at least three samples.*

and at the intersections between the roads. To this end, we used full width at half-maximum (FWHM) measurements of the azimuthal ring integral of the 2D diffraction pattern of single-layer FDM samples. As shown in Figure 3, the degree of CNT alignment decreased as a function of increasing Q_r. This result is counterintuitive, since a higher Q_r would lead to a higher wall shear rate and therefore a higher degree of alignment. These experimental observations can be explained, however, by a combination of flow and geometry-induced effects, as illustrated in Figure 1(a) and (b).

Further, Figure 3 shows that the CNTs were less aligned at the intersection of adjacent roads compared to those at the center of the road. A higher degree of CNT alignment is expected at the intersections due to the higher shear rates close to the wall within the liquefier. However, we did not observe this in our experimental results. We attribute the reduced alignment of CNTs at the intersection to the convergence zone in the nozzle. For a given volumetric flow rate, the flow velocity increases as the cross-sectional area decreases. This increase in the flow velocity leads to extensional deformations, which further align CNTs at the core,[12] thus helping to explain the observed trend.

In summary, we have explored the 3D printing of CNT-PLA composites using an extrusion-based FDM method. By investigating the effects of volumetric flow rate and CNT concentration, we found that the dimensionless volumetric flow rate (Q_r) was a useful parameter for understanding the microstructure and subsequent mechanical properties of FDM parts.[13] In our future work, we intend to use a similar approach for other functional fillers (e.g., boron nitride nanotubes and cellulose nanofibers) to understand the structure–processing–property relationships for such systems.

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