Techniques and Applications in Dual Material Fused Filament Fabrication with Composite Core-Shell Structures for Enhanced Mechanical Performance and Dimensional Accuracy

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Tuesday, June 4th, 2024 at 1 pm EST in Colburn 366
Zoom: https://udel.zoom.us/j/93152676377

Additive manufacturing, commonly referred to as 3D printing, is an advanced manufacturing technique in which objects are produced in a layer-by-layer mechanism, offering unlimited customization and access to complex geometries that are unattainable through conventional manufacturing techniques. Fused filament fabrication (FFF) is the most widely used additive manufacturing technique due to its well-establishment and low-cost in terms of equipment and raw materials. However, parts produced using this technique have weak mechanical properties due to the insufficient gap filling and limited polymer chain diffusion at the interface between layers. Attempts to mitigate this weakness have been made through engineering new materials and optimizing process parameters, without changes to the actual FFF design. In this work, we present a coextrusion die design, capable of extruding two filamentous polymers simultaneously in a core-shell configuration, with the aim of overcoming the interlayer welding weakness. This unique approach offers a single-step method of creating polymeric composite with core-shell morphology.

First, we investigate the use of a low viscosity thermoplastic as a shell polymer to produce void-free prints with strong interfacial welding, and a high viscosity thermoplastic as a core to provide a stiff skeleton and maintain the printed structure. High-density polyethylene (HDPE) was used as a shell polymer due to its low melt viscosity and satisfactorily short reptation time, aiding the healing process at the interface. However, HDPE exhibits high degree of crystallinity causing severe warpage upon cooling, which leads to delamination of printed parts. As a result, polyethylene terephthalate glycol (PETG), an amorphous polymer with low coefficient of thermal expansion, was chosen as a core polymer to stabilize the printed structure. Composite objects having HDPE shell and PETG core architecture were successfully printed with full interlayer surface contact and an adequate dimensional accuracy. Mechanical testing revealed synergistic enhancements in the impact resistance property caused by core-shell
interfacial debonding which creates new surfaces to deflect the impact. Moreover, increased fiber pullout and extensibility were seen due to the core-shell morphology. In a later chapter, we explore the fabrication of gradient structures of the same polymer system by dynamically controlling the relative flowrate of the core/shell, and subsequently compare their mechanical properties to those of the uniform core-shell composition.

Next, we explore ways to strengthen the core-shell interface. Due to the immiscibility of most polymers, the core-shell interface has weak weld lines. Maleic anhydride (MAH) grafting was utilized to enhance the interfacial adhesion between acrylonitrile-butadiene-styrene (ABS) and HDPE polymer system. ABS-g-MAH filament was fabricated and used as a core feedstock. Mechanical testing of 3D printed samples revealed stronger ABS-HDPE core-shell bonding attributed to MAH grafting. The stronger interface resulted in a 253% and 16% increase in impact resistance compared to pure HDPE and ABS samples, respectively, and a 10% increase compared to the unmodified ABS core-HDPE shell specimens.

Furthermore, the high chemical resistance of HDPE inspired the idea of using a sacrificial core material to create controlled hollow structures, in terms of size and direction, potentially applicable in microfluidic and tissue scaffolding applications. ABS was used as a sacrificial core due to its high solubility in acetone. The pore size can be precisely adjusted by controlling the printer settings, including relative flowrate of the core and shell, nozzle size, layer height, and extrusion width.

Finally, we explore the use of commodity plastics such as polypropylene (PP), polyethylene terephthalate (PET), and HDPE as FFF feedstock. The semicrystalline nature of such polymers hinders their utilization in FFF due to the substantial volumetric shrinkage experienced during crystallization, giving rise to significant warpage and printing defects. However, PET’s lower degree of crystallinity and slower crystallization rate, compared to PP and HDPE, aid in stabilizing the printed structures when used with either polymer (HDPE or PP) in coaxial printing. Objects containing up to 70 vol % polyolefin shell-PET core were printed with adequate dimensional accuracy. In addition to the enhanced dimensional accuracy, higher mechanical properties, in terms of impact and tensile toughness, were afforded due to the core-shell morphology. The highest improvement in mechanical properties was seen in the PET shell-PP core configuration, which exhibited up to 412% and 237% increase in impact and tensile toughness, respectively, compared to pure PP.