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3D printed highly elastic strain sensors of multiwalled carbon nanotube/thermoplastic polyurethane nanocomposites

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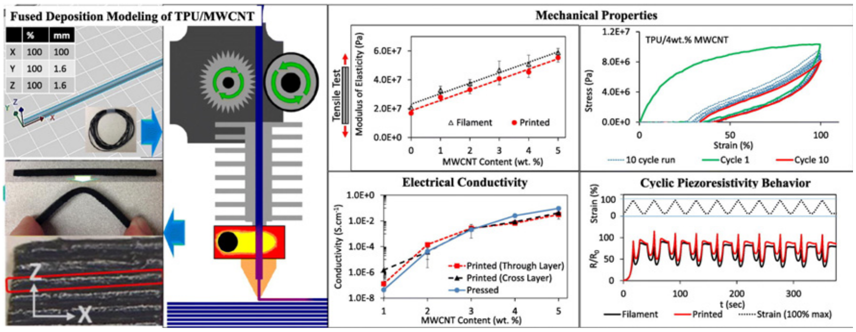
HIGHLIGHTS

- Flexible TPU/MWCNT was successfully 3D-printed as a sensing sensor.
- The presence of MWCNT enhanced the printability of TPU.
- Mechanical and electrical properties were highly preserved after 3D printing.
- Printed sensors showed excellent cyclic piezoresistivity behavior.
- Gauge factors as high as 176 were achieved.

GRAPHICAL ABSTRACT



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ABSTRACT

3D-printable, flexible, and conductive thermoplastic-based material was successfully developed for strain sensing applications. Thermoplastic polyurethane/multiwalled carbon nanotube (TPU/MWCNT) were compounded, their filaments were extruded, and the sensors 3D printed using fused deposition modeling. Mechanical, electrical, and piezoresistivity behaviors were investigated under monotonous and cyclic loadings. MWNCTs enhanced the printing capability of TPU by increasing its stiffness. Very modest decreases were observed in the elasticity modulus of printed nanocomposites (~14%, compared to that of bulk counterparts), indicating excellent interlayer adhesion and superior performance to those reported in literature. Consequently, the conductivity was largely preserved after printing, in both through-layer and cross-layer directions. The piezoresistivity gauge factors of as high as 176 were achieved under applied strains as large as 100%. A highly repeatable resistance-strain response was also obtained under cyclic loadings. The results demonstrate TPU/MWCNT as an excellent piezoresistive feedstock for 3D printing with potential applications in wearable electronics, soft robotics, and prosthetics, where complex design, multi-directionality, and customizability are demanded.

1. Introduction

Recently, significant research endeavors have been made in expanding the additive manufacturing (AM, *aka* 3D printing) technologies to a wide variety of applications [1–7]. AM offers a new and unique method for the fabrication of both mechanical and functional

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components and offers new fabrication capabilities and products that are unobtainable through conventional fabrication techniques [8,9]. Of significant interest within the AM field is the development of metamaterials and mesostructures with the ability to create printable and functional platforms capable of both active and passive sensing functions [9].

AM field employs a variety of manufacturing technologies [8]. These technologies all function similarly in that they produce physical parts from a computer aided design (CAD) program by depositing the feedstock material, layer by layer, onto the build platform until the part is complete. This deposition process can be achieved through multiple methods with the most common being laser sintering, resin-light curing, and fused deposition modeling (FDM) [8]. Of primary interest within this research is FDM. In FDM process, the feedstock, typically a thermoplastic polymer, is fed into a heated nozzle where it is then extruded as a continuous bead of molten plastic. The nozzle is maneuvered by a computer numerical control (CNC) machine which directs the path of the nozzle to pattern out the part as a series of discrete layers, building the part from the bottom, moving upward [8,10–12].

FDM 3D printing has seen significant publicity over the last decade. Due to the relatively simplistic mechanical design, affordability, and the capabilities of FDM machines, it has garnered significant interest in both industry and academia [8,9,13–15]. While the design of FDM printers has seen a rapid growth, the field of printable materials has also experienced a rapid influx of unique and novel thermoplastic materials; conductive, magnetic, flexible, and dissolvable filaments [1,2,5] are just a few to name.

Conductive filler/polymer composites (CPCs) offer many functional uses within the sensing field. CPCs have been used for tactile sensing platforms, thermal sensors, and electrochemical sensors [16,17]. Multiple studies of CPCs have shown strong electromagnetic interference (EMI) shielding potential [18–21], as well as strain sensing applications [22–30] for use in electronics. Recently, few conductive filaments have been introduced by leveraging the properties of graphene and carbon nanotube embedded in polylactide filaments in order to produce CPC filaments [2]. These materials have shown the applications for low-voltage circuitry, strain sensing, and anti-static applications [18,19].

Within the strain sensing field, there has been significant research towards developing highly flexible sensors capable of measuring large strains [31]. This has been usually achieved by combining a highly flexible polymer with some type of highly conductive filler. Boland et al. [24] developed a high-strain motion sensor using a graphene-rubber nanocomposite for use as bodily motion sensing platforms. This was done by soaking rubber bands in a graphene solution. Morteza et al. [26] developed a flexible strain sensor by sandwiching silver nanowires within a polydimethylsiloxane (PDMS) polymeric matrix. They showed an accurate linear correlation between strain and resistance. In another work, Muth et al. [4] was able to fabricate strain sensors by embedding a carbon-based conductive ink within an elastomeric polymer using an inkjet printing process. Yeo et al. [32] fabricated a stretchable strain sensor through the use of silicon molds, pneumatic actuators, and silver ink traces. Leo et al. [33] also developed a flexible paper-based sensor implementing a graphite glue deposited onto a paper substrate using stencil printing.

While all of these sensor designs have shown strong capabilities as strain sensing platforms, a facile fabrication method still remains as a common challenge for the current sensor designs. By developing a highly elastic, electrically conductive thermoplastic nanocomposite for FDM manufacturing, the fabrication of complex and multidirectional sensor patterns should be achievable without the need for complex processing methods. Furthermore, due to the ability to print multiple materials simultaneously through FDM printing, there is significant potential for in-situ integration of sensing platforms within the printed assemblies, according to the design requirements, independent of the design complexity. To the best of the authors' knowledge, electrically conductive and flexible printed materials have not yet been reported for FDM purposes.

This work focuses on developing a TPU/MWCNT based novel FDM feedstock that demonstrates high elasticity and excellent piezoresistive properties. Particular attention is paid towards the mechanical and electrical robustness of the FDM printed materials, compared to their bulk precursors. Moreover, the mechanical, electrical, and piezoresistive characteristics of the FDM printed TPU/MWCNT samples were investigated under both monotonous and cyclic loadings.

2. Experimental procedure

2.1. Materials

TPU and MWCNT were used as the constituents of the nanocomposites. The TPU grade of Elastollan 1185A polyurethane supplied by BASF, with a density of 1.12 g/cm^3 and a shore hardness of 85A was used as the flexible matrix of the nanocomposites. NC7000 multiwalled carbon nanotubes of 90% purity having an average diameter of 9.5 nm, an average length of 1.5 μm, and a volume resistivity of $10^{-4}\ \Omega\cdot$cm were purchased from Nanocyl S.A., Sambreville, Belgium. Both materials were used as received. TPU and TPU/MWCNT were dried at 80 °C for 2 h before any melt processing.

2.2. Fabrication of TPU/MWCNT filaments

First, a twin-screw extrusion process was used to prepare the TPU/5 wt% MWCNT masterbatch. Extrusion was done using a Krauss Maffei Berstorff ZE 25, with a screw length-to-diameter L/D ratio of 36 where the melt temperature, and screw rotational speed were 221–229 °C, and 300 rpm, respectively. TPU was first fed in the main hopper and then carbon nanotubes were dosed into the side feeder at a distance of 14D from the hopper to mix them with the molten TPU. Literature shows that higher shear forces provide a better MWCNT dispersion within the polymer [34]. Therefore, the masterbatch preparation process parameters were chosen to yield a good dispersion.

For the preparation of the TPU/MWCNT nanocomposites with diluted concentrations from the masterbatch, a 16 mm twin-screw extruder type LTE with L/D ratio of 16/40 (LabTech Engineering Company LTD., Thailand) was used. TPU/MWCNT nanocomposites with MWCNT content ranging from 0 to 5 wt% were fabricated. In this step also, the process was optimized to maintain a high level of shear load during dilution to assure that a good dispersion state is maintained. At a given extrusion condition, the diameter of the extrudate varied as the MWCNT content was changed. The extrusion parameters were also optimized such that a constant filament diameter could be obtained at various MWCNT contents. This was done by adjusting the 5 temperature zones and screw rotational speed. Fig. 1 shows the optimized temperature profiles, screw speed, and the resultant torque for each MWCNT content. For the

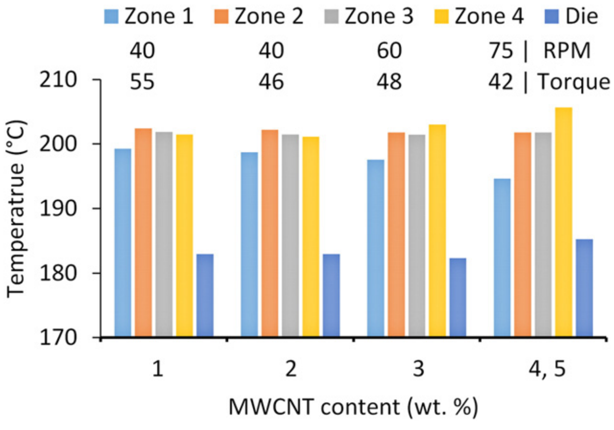

Fig. 1. Twin-screw extruder barrel temperature profile, screw speed, and torque for the filament fabrication of TPU/MWCNT nanocomposites.