Mechanical characterization of FDM filaments with PVDF matrix reinforced with Graphene and Barium Titanate

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Abstract: In past one decade number of studies has been reported on optimization of process parameters of fused deposition modelling (FDM) for in-house developed thermoplastic composite based feed stock filaments. This paper investigates smart polymer-based composites prepared with hybrid feed stock filament (comprising of polyvinylidene fluoride (PVDF) reinforced with graphene (Gr) and barium titanate (BTO) powder). This work started with the Functional prototypes were 3D printed for tensile and flexural characterization using inhouse developed filament (PVDF (78%)+Gr (2%) with BTO (20%)) at optimized settings of FDM. The printed specimens were subjected to destructive testing for mechanical properties (to analyze the process capability indices, Cp and Cpk). For morphological properties, scanning electron microscopy (SEM) images and 3D rendered images of the fractured surfaces of tensile and flexural specimen were used. It has been revealed from the SEM and 3D rendered images that the optimized settings of 3D printing process parameters resulted into uniform morphological features (based upon surface roughness (Ra) and amplitude distribution function (ADF), peak count (PC) and bearing ratio (BR) curve).

1. Introduction
The FDM is an additive manufacturing (AM) process in which 3D physical models are built up by joining the materials in the form of layers as per computerized created 3D solid model and it has ability to produce minimal wastage with acceptable level of accuracy [1]. This creates the possibility to fabricate parts having complex geometry that are difficult to produce via conventional material removal processes [2]. AM does not depend upon the fixtures, coolants, cutting tools, and other conventional resources for the production of parts [3]. In FDM, a hot nozzle-based extruder is used for melting and depositing of semi molten material to build a 3D physical part. FDM generally taking a thermoplastic or polymer matrix composite (PMC) filament as a printing material [4]. The open source FDM printers provide the simple operating conditions and good control over the input variables such as infill speed, infill angle, infill density, raster width, printing temperature, type of fill etc. [5-8]. By varying these printing parameters, it is possible to produce customized parts on demand and allows to optimize the product design [9]. Research studies highlighted that the properties of fabricated parts are function of process variables and can be efficiently improved with appropriate adjustment. For functional prototypes

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the mechanical properties are very important, also it is essential to study the effect of process variables on the mechanical properties of the parts which can be efficiently improved by process optimization [10-13]. Due to wide acceptability of this process and ease of availability of 3D printers, researchers started work to develop new materials for FDM process. So far various polymer matrix composites-based feed stock filaments have been developed by reinforcement of different metal powders or ceramics to improve the inherent properties of the polymer matrices [14-15]. Some of the majorly used polymers as printing material on FDM are acrylonitrile butadiene styrene (ABS), poly lactic acid (PLA), polyamide (PA6), polyvinyl chloride (PVC) or the composites based upon these polymers. In the family of electroactive polymers PVDF is mostly used in piezoelectric sensor applications [16-18]. Similarly, the addition of carbon fibres increased the mechanical properties of nylon-based polymer composite matrix. Some researchers have reported the addition of Gr in various polymer matrices for the development feedstock filament of FDM. It has been observed that the addition of Gr improved the mechanical, electrical and thermal characteristic of base polymeric materials [18]. Some researchers explored the effect of FDM input parameters on the mechanical properties of the 3D printed parts [19].

This study is the extension of previously conducted research work [17,18] in which electroactive polymer composite matrix of PVDF was 3D printed and process parameters of FDM were optimised, but the repeatability/reproducibility and statistical control of process was not addressed. This research work presents the process capability analysis of FDM processing parameters for mechanical properties such as peak strength, break strength and modulus of toughness of electroactive polymer composites-based 3D printed tensile and flexural specimens. As this study reports an extension of previously reported work [18,19] in which a composite of fix proportion of BTO 20% (wt.%) in PVDF (78%) +Gr (2%) was prepared for 3D printing of functional graded prototypes. therefore, no changes have been made in composition of PVDF based composites for 3D printing and similar optimized conditions were used for FDM processing.

2. Experimentation

2.1. Materials and methods

In this study, Gr and BTO were reinforced in PVDF matrix for the fabrication of feed stock filament. A twin screw extruder (TSE) (Model: Mini CTW, HAAKE, Germany) was used for compounding of materials and extrusion of feed stock filament. In the previously conducted research, it has been reported that BT (20%) in PVDF (78%)+Gr (2%) has shown best mechanical properties when extruded at optimized settings of TSE (extrusion temperature 200°C and screw speed 50 rpm) [19]. Therefore in this research work the same proportion of the composition has been taken for the preparation of feed stock filament for 3D printing of the standard specimens. The key point while extruding the feedstock filament is to keep the diameter of the wire within the range of 1.75±0.05 mm (due to the restricted nozzle size available in the existing FDM setup). Finally, the extruded feedstock filament was used to run on an open source FDM printer (Make: Divide by Zero, India) for 3D printing of tensile specimens (as per ASTM D-638) and flexural specimens (as per ASTM D-790) at standard optimized processing conditions (infill speed: 50 mm/s, infill angle: 45° and infill density: 100%).

Ten standard tensile and flexural specimens were 3D printed to report the process capability analysis of 3D printing process parameters. The 3D printed functional prototypes were subjected to universal testing machine (UTM) for destructive testing. The output results of mechanical testing of both type of specimens in the form of peak strength (PS), break strength (BS) and fracture toughness (FT) were noted to perform process capability analysis. Further SEM images were observed for morphological characterization of tensile and flexural specimens tested on UTM. The microscopic images were further used for 3D rendering to generate Ra profile, ADF, PC and BR curve.

3. Results and discussions

3.1. Mechanical testing
After successfully completion of 3D printing of tensile and flexural specimens on the open source FDM setup at standard optimized conditions, destructive testing was performed. The fabricated samples were mechanically tested on UTM (Make: Shanta engineering, Pune, India; Capacity: 5000N).

The output UTM results for tensile and flexural properties in terms of PS, BS and FT are shown in Table 1. The resulted output values of tensile and flexural properties were further used for statistical process capability analysis.

### Table 1. UTM results for tensile (left) and flexural (right) specimens

| S.No. | PS (MPa) | BS (MPa) | FT (MPa) |
|-------|----------|----------|----------|
| 1     | 42.95    | 38.70    | 3.70     |
| 2     | 43.10    | 39.02    | 3.54     |
| 3     | 42.68    | 37.93    | 4.27     |
| 4     | 41.98    | 37.04    | 4.38     |
| 5     | 42.38    | 37.82    | 4.54     |
| 6     | 43.19    | 38.67    | 3.79     |
| 7     | 43.40    | 38.92    | 3.68     |
| 8     | 42.54    | 37.84    | 4.14     |
| 9     | 43.14    | 40.01    | 4.72     |
| 10    | 42.25    | 37.24    | 3.28     |

3.2. Morphological analysis

The fractured surfaces of tensile and flexural specimen were subjected to SEM for morphological properties. Further, the SEM images of fractured surface were 3D rendered using image processing software package tool. Figure 1(a) and 2(a) shows the SEM images of tensile and flexural specimen. Whereas, the figure 1(b) and 2(b) shows the rendered 3D images of tensile and flexural specimen. Based upon 3D rendered images, plots for Ra profile, AFD, PC and BR curve of tensile and flexural specimens were generated (Figure 1 and 2). As plots drawn from 3D rendered images for tensile and flexural specimens represented the similar variations in Ra profile, AFD, PC and BR curve of tensile and flexural specimen, which justifies the selection of optimized settings of parameters and controlled statistical nature of process.

![Figure 1](image1.png)

**Figure 1.** (a) SEM image of fractured surface, (b) 3D rendered image, (c) Ra profile, (d) AFD, (e) BR curve, (f) PC of tensile specimens.
Figure 2. (a) SEM image of fractured surface, (b) 3D rendered image, (c) Ra profile, (d) AFD, (e) BR curve, (f) PC of flexural specimens.

The Ra value for tensile specimen was 27.79 nm at cut-off length of 0.05 whereas Ra value for flexural specimen was observed as 13.63 nm on the same cut-off length. Thus, there is not much variation among the Ra values of both specimens. Similarly, the curves of ADF (Figure 1(d) and 2(d)), BR (figure: 1(e) and 2(e)) (for length of the bearing surface at specified depth in the evaluation area) and PC (figure: 1(f) and 2(f) for both the cases follows the same trend.

4. Conclusions
Following are the conclusions from this study:

- From process capability indices the observed values of Cp and Cpk were greater than 1 for both cases clearly represented that FDM printing of PVDF+Gr+BTO based composite at optimized parametric settings resulted into statistically controlled process.
- It has been ascertained from the SEM images and 3D rendered images that the optimized 3D printing parameters resulted into uniform morphological features (as per Ra, ADF, PC and BR curve) for both tensile and flexural samples.

In future studies, we will investigate the design of novel sustainable composites [20-24] using waste and alternative materials as precursors [25-29] and we will assess their environmental impact [30-31]. Additional future research lines will investigate the use of eco-sustainable materials for the design of next-generation meta-materials and structures, whose properties mainly derive from the geometry of the microstructure [32-35].

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