FUSED DEPOSITION MODELING USING GRAPHENE/PLA NANO-COMPOSITE FILAMENT

Shilpesh R Rajpurohit, Harshit K Dave

Department of Mechanical Engineering, S V National Institute of Technology, Surat 395 007 Gujarat, India

Corresponding author: Harshit K Dave, harshitkumar@yahoo.com

Abstract: The application area of the fused deposition modeling process can be increased with the development of new composite materials. Hence, in this study, the effort has been made to develop nanoparticle reinforced FDM printable nanocomposite material. Graphene-based PLA nanocomposite filament has been prepared using a single screw extrusion process. Further, the effect of graphene on the mechanical properties of the FDM printed PLA nanocomposite has been also evaluated. It is observed that mechanical strength is decreased with the addition of graphene in the PLA matrix. Further, SEM analysis of a cross section of the fractured surface revealed that due to the presence of the void gap, the mechanical strength is found to be decreased.
Key words: Fused deposition modeling, Polylactic acid, Graphene nanocomposite, Mechanical strength.

1. INTRODUCTION

Over the past decade, Additive Manufacturing (AM) or 3D printing technology is largely adopted in many fields, namely aerospace, medical, electronic, architectural, food and automobile applications, due to its advantages of relatively lower processing cost, ease in operation, and shorter product development time; compared to other traditional processing techniques. FDM is most widely adopted AM technology due to its reliability, repeatability, low processing cost, and simplicity. In FDM printing process, the filament material is extruded through a heated nozzle in a semi-solid state and deposited as a thin layer on to previously deposited layer or on the build platform as defined in slice information. Upon deposition of one layer, the nozzle moves away from the deposited layer along the z-axis by the height of one layer thickness then another layer is deposited and then another layer is deposited and adhered to previous one. After that, whole process is repeated until the completion of a 3D object [1-3].

Printing process variables, such as part orientation, raster orientation, layer thickness, infill density, infill pattern, and printing speed significantly affects the quality of the parts [4, 5]. As the part is formed layer by layer and each layer consists of rasters, because of that property of the layer is decided by the quality of filament, bonding between rasters and amount of voids. Although the FDM process has many significant advantages, the low adhesion between adjacent layer and rasters limits the mechanical properties of FDM produced part relative injection moulded part, and therefore still cannot meet actual need. Besides this, another problem with FDM is the mechanical anisotropy of printed part; mechanical performance of FDM produced component is highly affected by part orientation where out of plane build parts generally have the worst mechanical performance [6-10].

Several studies have been reported that consider tensile properties, flexural properties, and impact properties as an evaluation index to optimize the manufacturing process to fabricate FDM part with optimal mechanical quality [11-14]. Another possible option to enhance mechanical performance is the advancement in the range of filament material by creating new polymer alloys and the addition of fillers such as fibers, metal and ceramic particles into a polymer and so on. Addition of nanofiller or nano reinforcement may improve polymer properties such as mechanical strength, stiffness, toughness, dimensional stability, thermal stability and aging resistant [15-16]. Furthermore, compared to normal filler, nanofillerdo not affect the melt flow and finishing of the produced product the most. Therefore, the development of nanocomposite material is a possible way to enhance the processability of 3D printing and overall performance of parts fabricated by FDM process. Some studies have been reported to use nanofiller for in FDM process printing material such as graphene[17], vapour grown carbon fiber[18], carbon nano tubes[19], clay[20], metal powder [21, 22] and so on. Further, the application of nanocomposite in FDM printing is emerging filed of research.

In this study, graphene was selected as a nano-reinforcing material. Polylactic acid (PLA) has been selected as a polymer matrix because of its outstanding mechanical performance. The mechanical strength and performance of nanocomposite samples of graphene-based PLA printed with FDM were evaluated. The purpose of this research is to develop new materials for the 3D printing process.

2. MATERIALS AND METHODS

2.1 Materials

PLA polymer [Ingeo Biopolymer 3D850, with a density of 1.24g/cc, a glass transition temperature (55-60)°C, and a melt flow index of (7-9)g/10min (210°C/2.16 kg)] were supplied by NatureWorks, India. Graphene nanopowder (purity >99%, average thickness (2-4)nm, average lateral dimension (5-10)µm and surface area 350m^2/g) was supplied by Adnano Technologies Private Limited, India. All the materials were used as received.

2.2 Preparation of Graphene/PLA nanocomposite

The fabrication process of graphene-PLA nanocomposite filament is shown in Figure 1. First, the PLA pellets and graphene nanopowder (the content of graphene nanopowder was mixed at 1wt%, 3wt%, and 5wt%) were physically mixed. Then, the composition was dried at 80°C for 4 hours. After that, the composition system was fed into a single screw extruder machine to manufacture the nanocomposite filament**.**

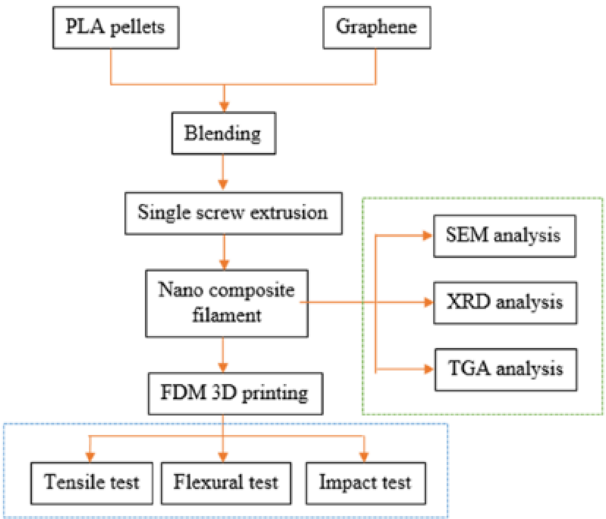


Fig. 1. Filament fabrication and testing procedure

Barrel temperature and die temperature were kept constant on single screw extruder machine for manufacturing of nanocomposite filament as shown in Table 1. Screw RPM and take up speed has been adjusted in such a way that (1.75±0.05)mm filament diameter can be obtained. Figure 2 display the pictorial view of the single screw extruder machine that has been used in the present study to fabricate nanocomposite filament.

Fig. 2. A pictorial view of single screw extruder set up

Table 1. Fixed Single screw extruder process parameters

Parameter	Value
Barrel temperature	
Zone 1	205°C
Zone 2	210°C
Zone 3	215°C
Die temperature	
Zone 1	185°C
Zone 2	180°C

2.3 Sample preparation

After obtaining Graphene-PLA nanocomposite filament with (1.75±0.05)mm diameter, it is used to print the test sample for tensile strength, flexural strength and impact strength using FDM based 3D printer. All the tests specimen were printed on the heated bed without any need of support structure. Table 2 shows the build parameters used to produce the test specimen using fabricated nanocomposite filament.

Table 2. Printing parameter used to print the samples for mechanical testing

Parameter	Value
Layer height	100µm
Raster width	500µm
Raster angle	0°
Liquefier temperature	210°
Bed temperature	70°
No. of perimeters	1
Scan speed	50 mm/sec
% infill	100 %
Infill pattern	Rectilinear

2.4 Filament characterization

A morphological study of the nano reinforcement in the PLA matrix is examined by the scanning electron microscope (Hitachi make TM 3030) analysis. Phase composition of graphene nanocomposite was determined by X-ray diffraction (XRD) recorded on RigakuMiniflex using Cu-Kα radiation (K=1.5418Å). Thermogravatic analysis (TGA) is used to carry out to observe the change in physical properties of composition as a function of temperature. The measurements are mainly used up to 700°C with a scanning rate of 10°C/min to determine the thermal stability of the composition. It is used to examine mass change in composition sample due to change in temperature.

2.5 Mechanical characterization

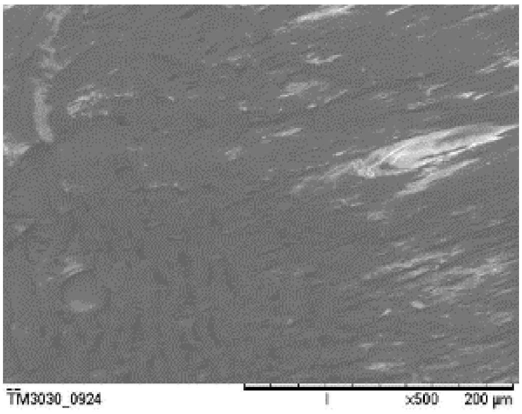
The tensile and flexural strength of specimen at different graphene concentration (0%, 1%, 3%, and 5%) have been investigated by using Tinius Olsen H50KL Universal Testing Machine. Tensile test and flexural test were carrying out as per standard ASTM D638 and ASTM D790, respectively. The impact test has been carried out as per ASTM D256 with Izod Impact Tester (Advance Equipment, Mumbai).

3. RESULTS AND DISCUSSIONS

In the present investigation, the impact of the percentage graphene content on the mechanical properties of the PLA based nanocomposite has been studied.

3.1 Scanning Electron Microscope (SEM) analysis

The quality of nanocomposites does not only depend on the nature of the reinforcement, but also on the final morphology obtained by extrusion. The SEM micrographs are shown in Figure 3 for the nanocomposites systems for PLA and 1%, 3% and 5% loading of Graphene in PLA. The nanocomposite prepared using single screw extrusion process displayed a poor dispersion, as larger aggregates of graphene. In addition, the bonding between the nano reinforcement and the polymer matrix is also quite poor as evidenced by the presence of some voids.



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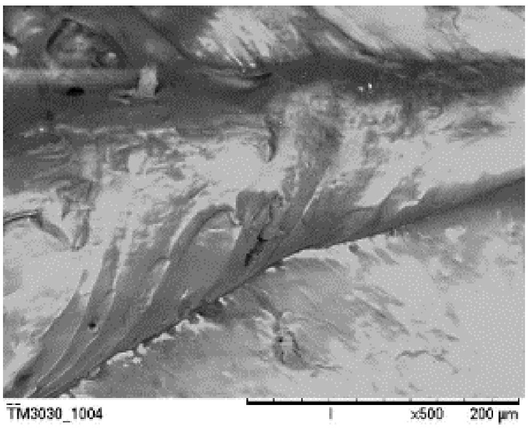

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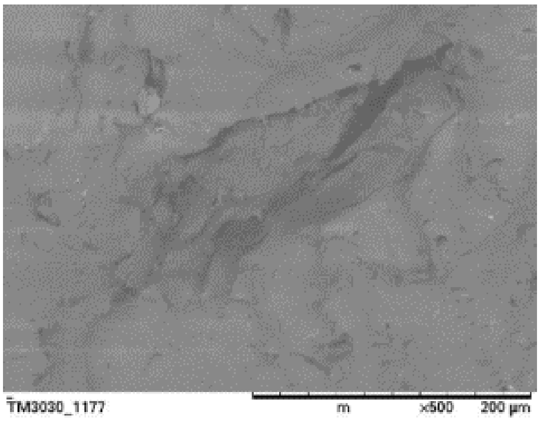

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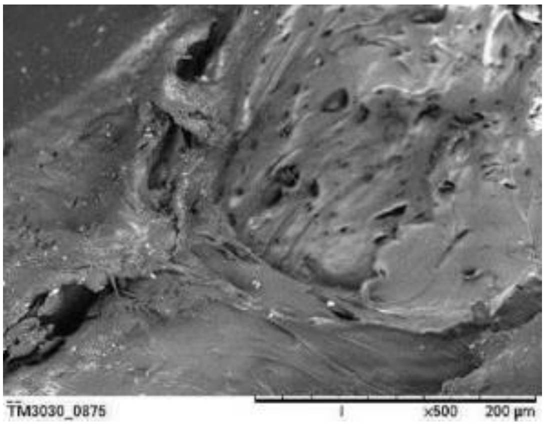

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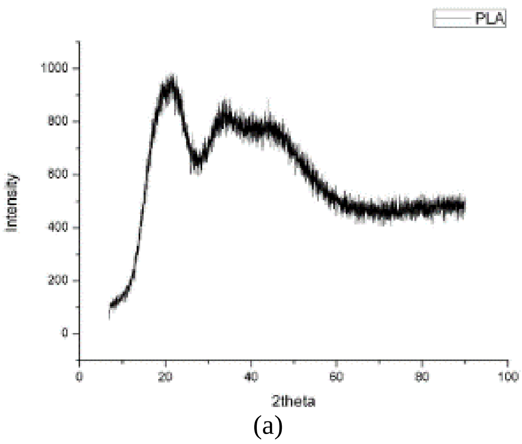
Fig. 3. SEM images: (a) PLA, (b) 1% Graphene/PLA, (c) 3% Graphene/PLA and (d) 5% Graphene/PLA nanocomposite filament

3.2 X-ray Diffraction (XRD) analysis

Further, to examine the structural features of the nanocomposite, the X-ray diffraction pattern of the nanocomposite was obtained and described with the X-ray diffraction pattern of the PLA as shown in Figure 4. A broad amorphous peak was observed in the pure PLA, which shows that pure PLA has essentially amorphous microstructure. A sharp peak around 27.14° that indicates the characteristics peak of graphene appeared in the 1% Graphene/ PLA, 3% Graphene/PLA and 5% Graphene/PLA nanocomposite, indicates that the graphene is not dispersed or completely separate and some sheets are still present in stack form.



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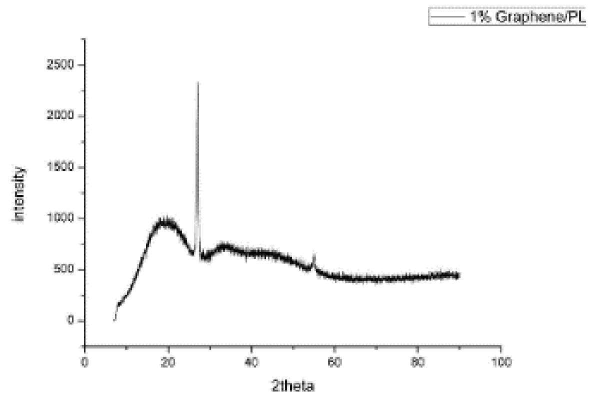

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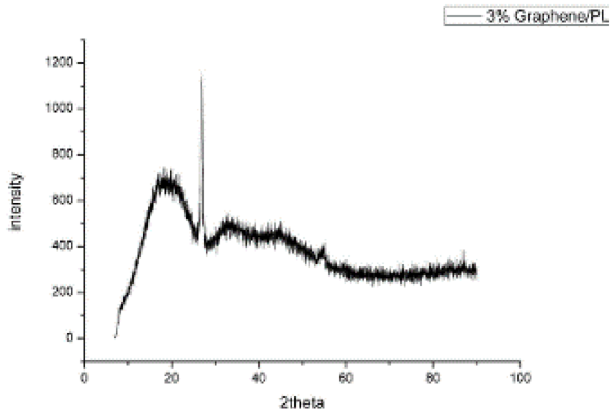

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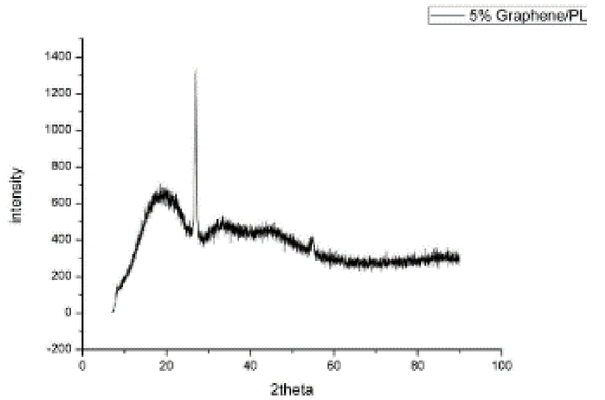

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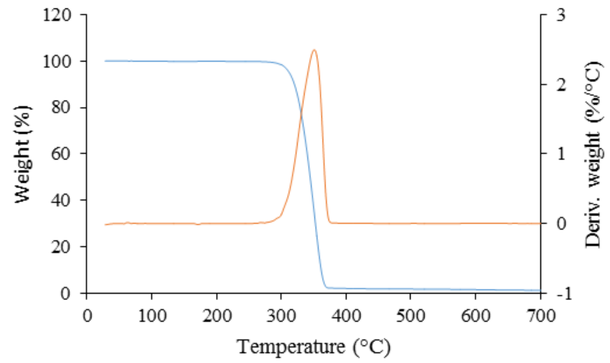
Fig. 4. XRD analysis of: (a) PLA, (b) 1% Graphene/PLA, (c) 3% Graphene/PLA and (d) 5% Graphene/PLA nanocomposite filament

3.3 Thermogravimetric analysis (TGA)

The nozzle temperature must be high enough to soften the nanocomposite filaments. However, too high a temperature may degrade the polymer component. In this case, the TGA studied the thermal stability of the sample (Figure 5) to ensure that the nanocomposite filaments do not disintegrate in 3D printers, but rather stable and simply soften. Under pyrolysis conditions in an N_2 atmosphere, the decomposition of the sample occurs with significant weight loss between 280°C and 380°C, which may involve the formation of organic fragments. The decomposition onset temperature is defined as the temperature at which the test sample loses 5% of its total weight. It can be seen that the minimum onset temperature of these nanocomposite samples is 301°C. Since the temperature of the nozzle is set at 210°C, this is lower by 90°C than onset temperature. Therefore, nanocomposite material simply melts in the viscous fluid instead of decomposing.



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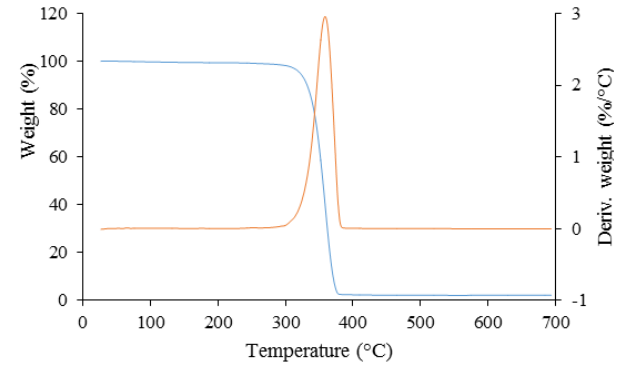

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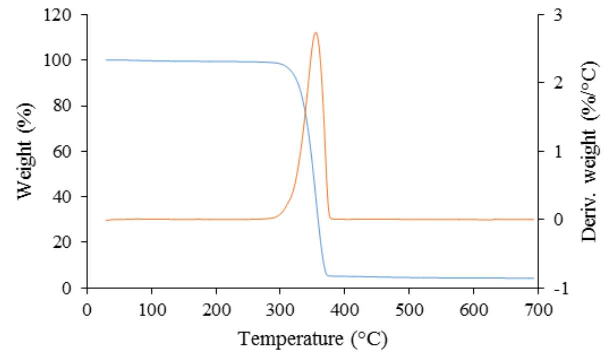

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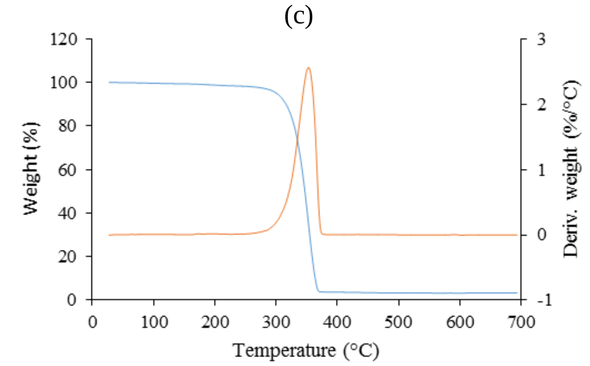

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Fig. 5. TGA curve for: (a) PLA, (b) 1% Graphene/PLA, (c) 3% Graphene/PLA and (d) 5% Graphene/PLA

3.4 Tensile strength

Figure 6depicts the impact of % graphene on the tensile strength of FDM printed PLA. It can be observed that tensile strength is found to be decreased with increase in % graphene.

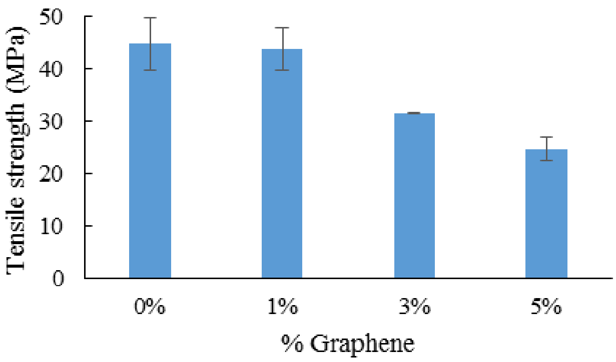


Fig. 6. Effect of % Graphene on tensile strength

The effect of graphene nano reinforcement on the tensile strength, strain at break and elastic modulus on neat PLA and PLA nanocomposite 3D printed parts are depicted in Table 3. In general, it can be observed that the presence of graphene nanofiller, decrease the tensile strength of the PLA matrix. Simentioneouly, a significant amount of drop in the strain at break can be observed when graphene nanofillers are added. The poor joining between nanofiller and PLA matrix could lead to the reduction in tensile strength as shown in Figure 3.

Table 3. Effect of % Graphene on tensile properties

Graphene content	Tensile strength [MPa]	Strain at break [%]	Tensile Modulus [MPa]
0%	44.75 ± 5.02	6 ± 0.68	712 ± 43.84
1%	43.65 ± 4.03	6.54 ± 0.48	817 ± 216.37
3%	31.60 ± 0.14	5.16 ± 0.13	603 ± 42.43
5%	24.65 ± 2.33	4.41 ± 0.71	575 ± 23.33

Figure 7 decipted the SEM images of the fractured surface of the tensile sample with respect as a function of graphene. As it can be seen that tensile strength is found to be decreased with increment in graphene content. At 5% graphene content, the larger positive gap can be seen which may be reduced the tensile strength. While in the case of 3D printed nanocomposite that contains 1% graphene has better diffusion and bonding between adjacent rasters due to that higher strength has been obtained. However, higher modulus of elasticity has been obtained with 1% graphene nano reinforcement then after with further addition of graphene leads to a reduction in modulus of elasticity. In general, it is observed that increasing the graphene content could be the reason behind to have a positive air gap.

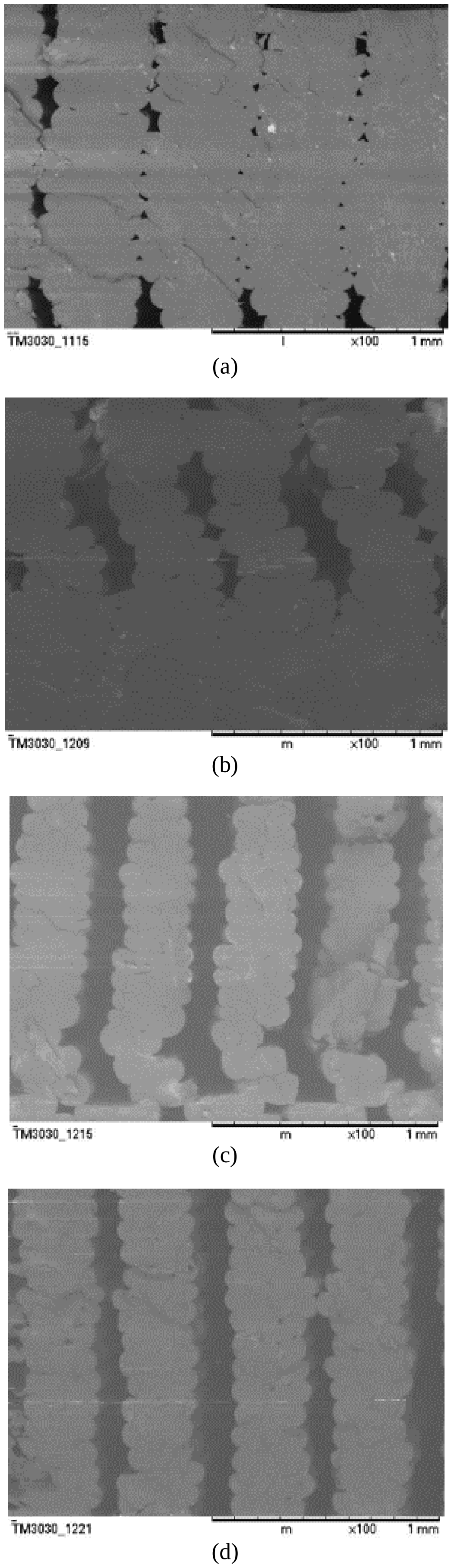


Fig. 7. Fractured surface of tensile specimen at: (a) PLA, (b) 1% Graphene/PLA, (c) 3% Graphene/PLA and (d) 5% Graphene/PLA

3.5 Flexural strength

Figure 8 depicted the impact of incorporation of graphene nanofiller on the flexural strength of the 3D printed PLA matrix. It can be seen that flexural strength is observed to be decreased with increment in the content of graphene nanofiller.

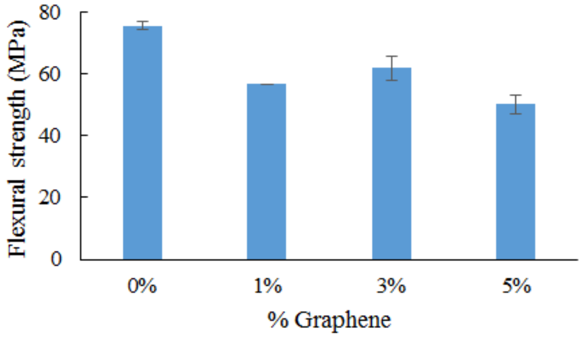
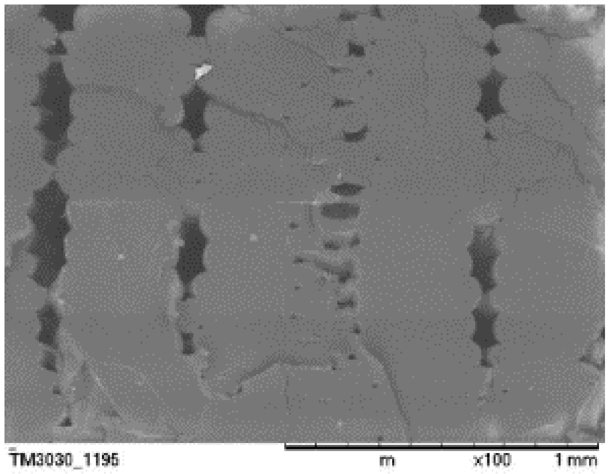


Fig. 8. Effect of % Graphene on flexural properties

The effect of graphene nano reinforcement on the flexural strength, strain at break and elastic modulus on neat PLA and PLA nanocomposite 3D printed parts are shownin Table 4. In general, it can be observed that the presence of graphene nanofiller, decrease the flexural strength of the PLA matrix. The poor bonding between nanofiller and PLA matrix could lead to the reduction in flexural strength as shown in Figure 9.

Table 4. Effect of % Graphene on flexural properties

Graphene content	Flexural strength [MPa]	Strain at break [%]	Flexural Modulus [MPa]
0%	75.50 ± 1.27	3.81 ± 0.01	2525 ± 63.64
1%	56.65 ± 0.07	2.83 ± 0.02	2255 ± 35.36
3%	61.80 ± 4.10	3.16 ± 0.23	2340 ± 84.85
5%	50.55 ± 2.97	2.99 ± 0.11	2110 ± 14.14



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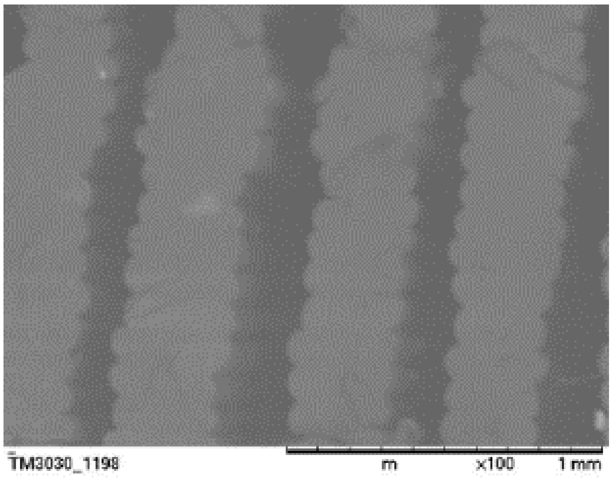

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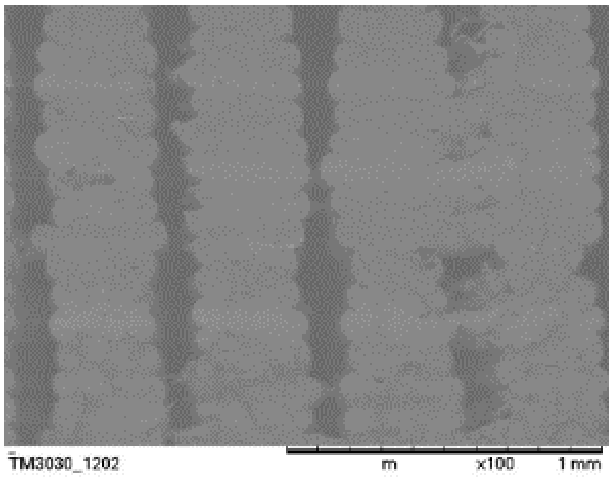

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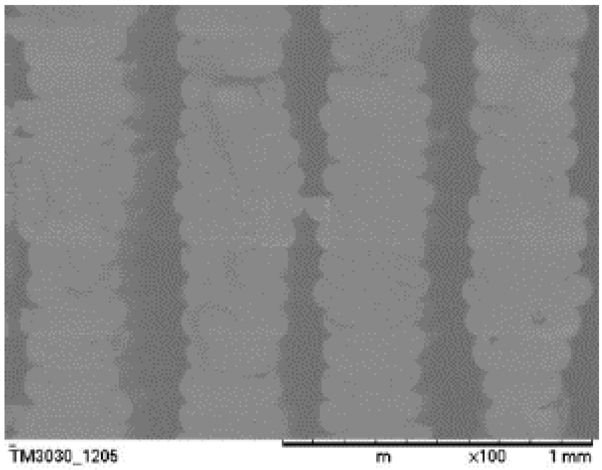

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Fig. 9. Fractured surface of flexural specimen at: (a) PLA, (b) 1% Graphene/PLA, (c) 3% Graphene/PLA and (d) 5% Graphene/PLA

Further, it can also be revealed from Figure 9 that higher positive gap between the adjacent rasters can also be seen with increment in graphene nanofiller. Due to the large positive air gap, it can be noticed that the adhesion between the adjacent raster seems to weaken that may reduce the effective load carrying capacity of the specimen that results in lesser flexural strength.

3.6 Impact strength

Figure 10 depicted the impact of the graphene nanofiller on the impact strength of the PLA matrix. It can be observed that higher impact strength is found to be with 3% graphene nanofiller addition then after further increment in graphene leads to a reduction in the impact strength of the PLA matrix.

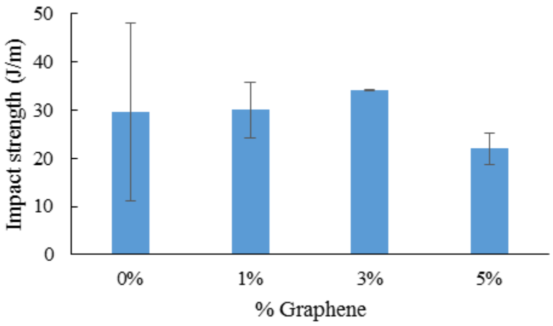
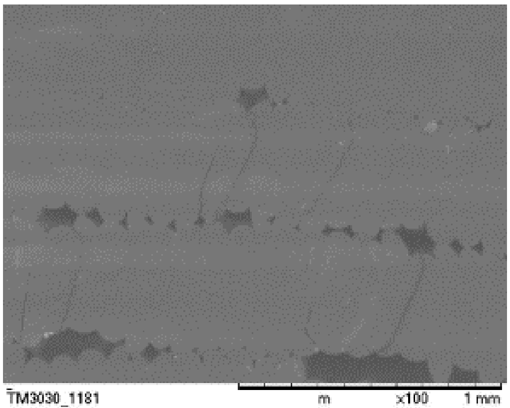


Fig. 10. Effect of % Graphene on impact strength

Figure 11 shows SEM images of a fractured surface of the test specimen after impact testing. It can be observed that crack has been initiated from the notch side and it is propagated through the thickness of the specimen towards other side but at the other side, the specimen has been held together by the some of the layers that have not been fractured due to impact. Further, it can also be observed that higher positive air gap between the layers for 5% graphene/PLA lead to a lesser impact strength.



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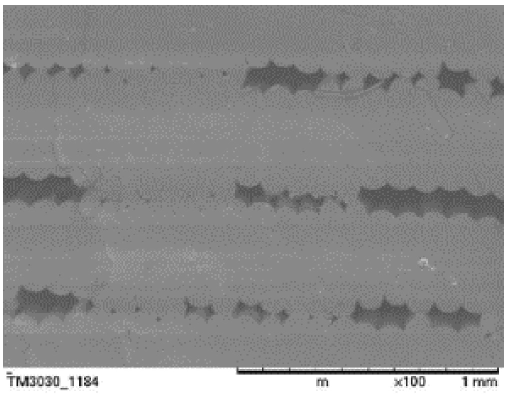

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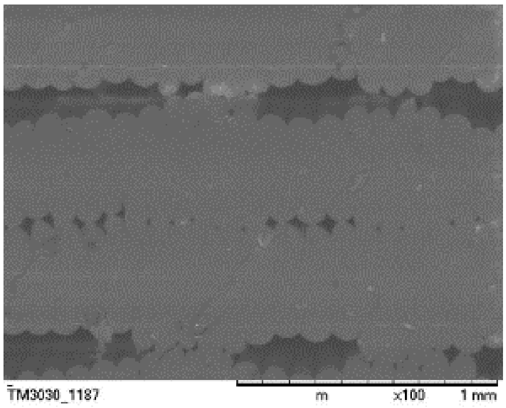

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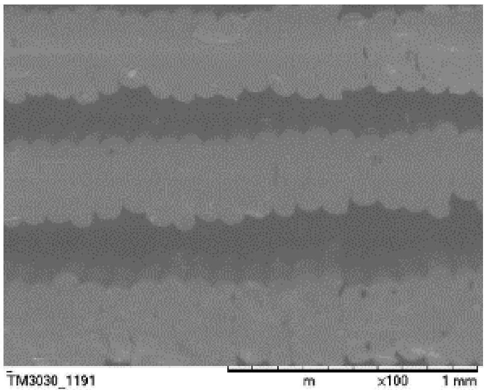

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Fig. 11. Fractured surface of impact specimen at: (a) PLA, (b) 1% Graphene/PLA, (c) 3% Graphene/PLA and (d) 5% Graphene/PLA

As the higher impact strength has been obtained with 3% graphene nanofiller, the hinged and complete failure has been observed. The impact of graphene nanofiller on the impact strength and type of fracture has been summarized inTable 5.As discussed earlier at 5% graphene nanofiller, poor adhesion between the nanofiller and PLA matrix may be lead to reducing the capacity to absorb impact energy and that reduces the impact strength of the PLA matrix.

Table 5. Effect of % Graphene on impact strength

Graphene content	Impact strength [J/m]	Type of Failure
0%	29.623 ± 18.4	Hinged
1%	29.951 ± 5.8	Hinged
3%	34.051 ± 0.14	Hinged and complete
5%	21.932 ± 3.3	Hinged and complete

4. CONCLUSIONS

In the present study, an attempt has been made to fabricate the nanocomposite filament using graphene as nano reinforcement in PLA matrix. Nanocomposite filament with different weight proportion of graphene in PLA has been prepared using a single screw extrusion process. The quality of the prepared nanocomposite filament has been evaluated using SEM, XRD and TGA analysis and it is revealed that the prepared composite can be used for 3D printing application. Furthermore, mechanical testing of the specimen printed using developed nano composite filament was carried out. Tensile strength is found to be decreased with increment in graphene nanofiller in the PLA matrix. However, higher modulus of elasticity is observed with 1% graphene incorporation. Flexural strength is also found to be decreased with the addition of graphene nanofiller in the PLA matrix. Higher impact strength has been observed with 3% graphene nanofiller then after its start in decreasing the impact strength of the PLA matrix. Addition of graphene nanofiller in PLA matrix leads to brittle failure that reduces the stain at the failure. Raster to raster gap seems to be increasing with increment in graphene nanofiller that reduces the mechanical performance of the nanocomposite filament in spite of the addition of nanofiller that needs further detailed investigations.

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