THERMO-MECHANICAL PROPERTIES OF ABS MATRIX COMPOSITE FILAMENT REINFORCED WITH MULTI-LAYER GRAPHITE OXIDE COMPOSITE FIBERS FOR FDM 3D PRINTING

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The properties of plastic filaments have an essential role in the printability and properties of printed products made by 3D printing FDM. Therefore, graphite oxides reinforced ABS plastic filament were fabricated to investigate the properties change for the purpose of improving the properties of products printed from ABS plastic. Graphite oxides reinforced ABS plastic filament with 1 %, 3 % and 5 % content, respectively, was fabricated and tested for mechanical properties, printability, and printing temperature, which showed some changes in properties compared to original ABS plastic filaments.

KEYWORDS

3D printing, FDM, ABS, Multi-layer graphite oxide

1 INTRODUCTION

Fused Deposition Modeling (FDM) is a gradual additive manufacturing process that belongs to the material extrusion process. This method mainly applies to printing polymer materials such as acrylonitrile butadiene styrene (ABS), polylactic acid (PLA)... When the nozzle has reached the print temperature, the molten plastic filament is fed to the nozzle to melt material. The melting materials is extruded into thin filaments and deposited layer by layer at predetermined positions to shape the product. [Mwema et al. 2020]. The strength of printed products often depends on the infill density and printing pattern [Do et al. 2022]. However, the strength and properties of the printed product also depend on the properties of the original printed filament, and this is attractive research objective to improve the properties of the printed product. To enhance the properties of ABS printed plastic filament, some studies have tried to mix with other additives such as Cu & Fe particles [Nikzad et al. 2011, Hwang et al. 2014] and with graphene nanocomposites [Dul et al. 2016, Guerra et al. 2020], and both additives can improve mechanical properties and thermal conductivity, reduce the coefficient of thermal expansion of composite ; mixed with zinc ferrite [Aqzna et al. 2019] lead to the strength increase ; mixed with short glass fiber [Love et al. 2016] increases strength and stiffness; mixed with Multi-Walled Carbon Nanotubes [Le et al.2021] show that melt flow index decrease when increase the reinforcement ratio while the strength of composite is increased, similar to the previous study of [Sezer et al. 2019] and [Jyoti et al. 2015] confirmed the strength increased proportionally with the content of fiber reinforcement. Adding Graphene oxides to the polymer matrix enhance thermal, electrical conductivity and even antibacterial properties [Nandhini et al. 2017]. With the goal of improving the printability and properties of 3D printed products from ABS plastic by improving the properties of the printed filament, the research focuses on creating multi-layer graphite oxide (MLGO) reinforced ABS plastic filaments and evaluated the printability, print temperature and strength with the reinforcement ratio of 1 %, 3 % and 5 %, respectively.

2 MATERIALS AND METHODS

2.1 Materials

The ABS plastic used in the study is a common ABS plastic in the form of granules having 2 mm diameter and 3 mm length (Fig. 1). This plastic has a density of 1.05 g/cm^3 and melt flow index (MFI) = 6.5 g/10 min. Multi-layer graphite oxide powder was fabricated by the thermal shock method from the research group of ITIMS Institute - Hanoi University of Science and Technology, see Fig. 2. Mixing ratio of MLGO and ABS plastic is shown in Table 1.

Figure 1. ABS plastic pellets

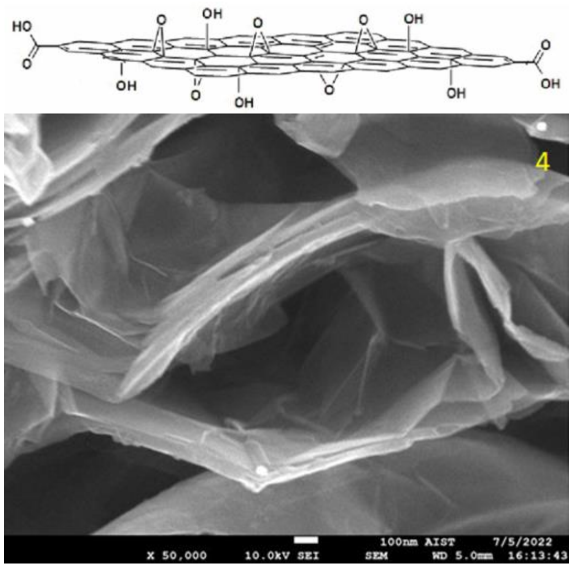


Figure 2. Multilayer graphite oxide

Graphite oxide (g)	ABS plastic (g)	Graphene oxide percentage by mass (%)
0.5	49.5	1
1.5	48.5	3
2.5	47.5	5

Table 1. Mixing ratios of ABS pellet and MLGO powder

2.2 Methods

The MLGO reinforced ABS filament (MLGO/ABS) fabrication process and testing are shown in Fig. 3. The mechanical mixing was carried out by a single screw mixer at ambient temperature which can help graphene oxide powders will temporarily adhere to the surface of the ABS pellets, then the mixture was brought to the hot melt extrusion (Fig. 4). The extrusion temperature during the process was 200 °C and the extruded fibers were cut into small pieces then put them again into extruder to create filaments having 1.75 mm diameter. The above procedure was repeated three times to uniformly disperse the MLGO reinforcement in final filament at 1 %, 3 % and 5 %, respectively.

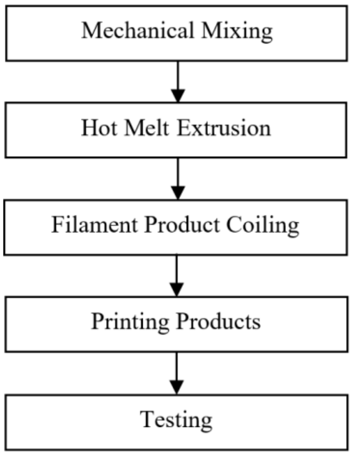


Figure 3. Filament fabrication and testing process

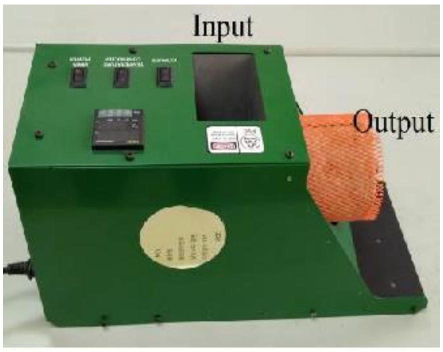


Figure 4. Single filament extruder

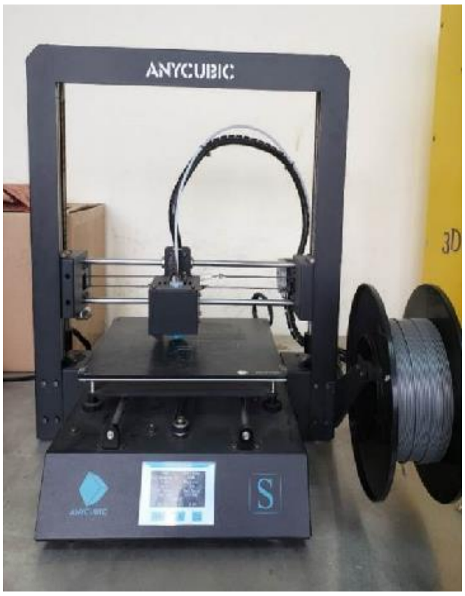


Figure 5. ANYCUBIC Model S 3D Printer

The fabricated The MLGO reinforced ABS filaments were anlyzed by Differential Scanning Calorimetry (DSC) method on the JINHAIHU DSC - 1150B machine to examine the influence of the MLGO reinforcement on the glass transition temperature (T_g) and the melting temperature (T_m) of the fibers. The range of testing temperature was set from 25 °C to 300 °C with heating rate of 10 °C/min.

The MLGO/ABS filament product was used for printing on the ANYCUBIC Model S 3D printer (Fig. 5) with nozzle having 0.4 mm diameter to evaluate the printability of fabricated fiber. The print parameters were set the same for all prints as shown in table 2. The fabricated filaments were used to print into a tensile specimen according to ASTM D638 standard type IVb with a length of 115 mm, a width of 6 mm, a thickness of 4 mm and gauge length of 25 mm. The tensile tests were performed on the MTS Exceed Model E45 mechanical testing machine having the maximum load of 50 KN with the velocity of 0.5 mm/s at ambient temperature. After tensile test, the broken samples were put on the scanning electron microscope (SEM) JSM – 7600F to observe the damage surface.

Print temperature (°C)	230
Temperature of print bed (°C)	100
Print speed (mm/s)	30
Print layer thickness (mm)	0.2
Print orientation (°C)	[0-90]
Printer nozzle diameter (mm)	0.4

Table 2. Printing parameters of MLGO/ABS

3 RESULTS AND DISCUSSION

3.1 *Glass transition and melting temperature of* MLGO reinforced ABS filament

The analysis results of glass transition and melting temperatures of MLGO/ABS filaments are shown in the DSC thermogram in Fig. 6. The glass transition temperatures of the samples are in the range of 90 °C to 110 °C, the melting temperature is in the range of 220 °C to 250 °C. The melting point of the samples tend to decrease slightly when the amount of graphite oxide in the ABS polymer increase. It is apparent that the increase of content of Graphite oxide in the ABS plastic will improve the heat transfer capacity in the MLGO/ABS composite fiber, so the polymer composite fiber being easier to melt. However, the small reduction at the peak values of the T_g and T_m is still relatively close to each other, indicating that the structure of the ABS substrate is not degraded or changed too much during the hot melt extrusion and reinforcing graphite oxide particles. The increase of MLGO reinforcement also rises the energy required to melt or transform the printed material.

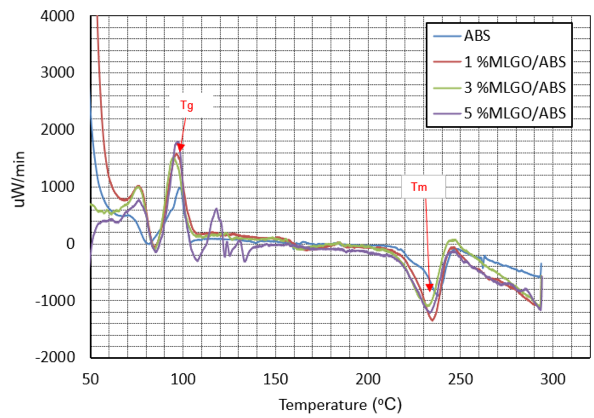


Figure 6. DSC thermogram for MLGO/ABS filament and print sample

3.2 *Printability of MLGO/ABS filament*

MLGO reinforced ABS filaments were capable FDM printed fluently with a 0.4 mm diameter nozzle. There wasn't any nozzle clogging during printing for all specimens with different MLGO reinforcement content. The filaments were easy to roll, and they didn't break inside the printer's teflon tube. The printed products from ABS reinforced MLGO filaments weren't different from the other printed from orginal ABS fiber (fig. 7).

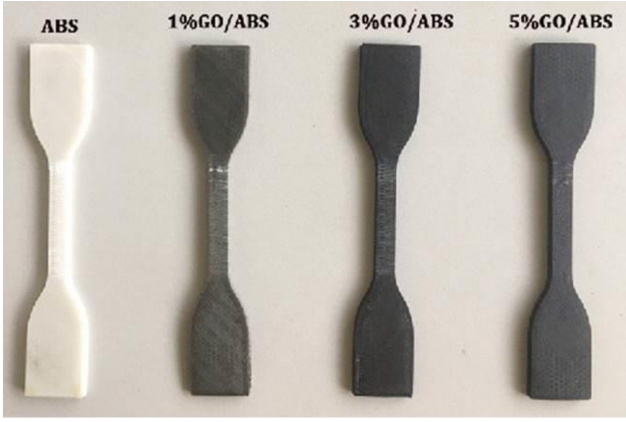


Figure 7. Tensile samples printed from MLGO reinforced ABS filament

3.3 Mechanical properties of printed samples from MLGO/ABS filament

Tensile tests were carried out with printed samples from original ABS pellets and composite filaments with graphite oxide reinforcement by weight 1 %, 3 % and 5 %, respectively. The results of measuring the tensile strength and elongation of the printed samples are shown in Figure 8. In general, the tensile strength of specimens printed from MLGO/ABS fibers are reduced and worse than the sample printed from original ABS. The 1 % MLGO reinforcement printed sample achieve a tensile strength of 32.12 MPa compared to value 36.88 MPa of the ABS plastic printed sample used in this study (12.91% reduction). With the 3 % MLGO reinforcement specimen, the strength decreased to 30.75 MPa and the reduction reached 30.51 MPa with the 5 % MLGO reinforcement sample. The decrease in strength of MLGO/ABS samples may be due to the poor adhesion between the graphite oxide surface and the base matrix, instead of providing the ability to improve stress transmission in the composite structure, the graphite oxide reinforcement now is a hindrance that interferes the continuous bonding between polymer layers in the printed structure of MLGO/ABS composites. The elastic modulus of polymer composite also decreases with increasing proportion of MLGO reinforcement. Besides, the elongation of the printed samples also decreases when the proportion of MLGO reinforcement are increased, and they are lower than that printed from the original ABS plastic base.

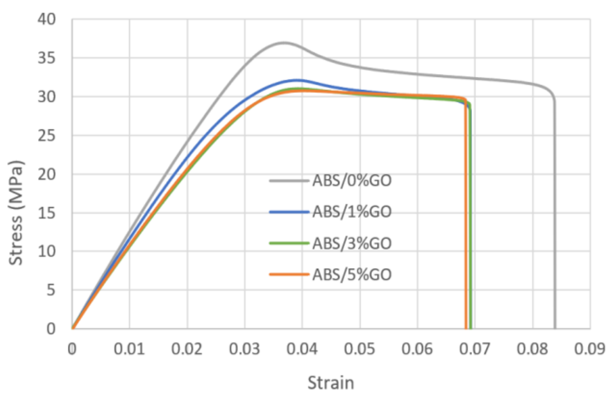
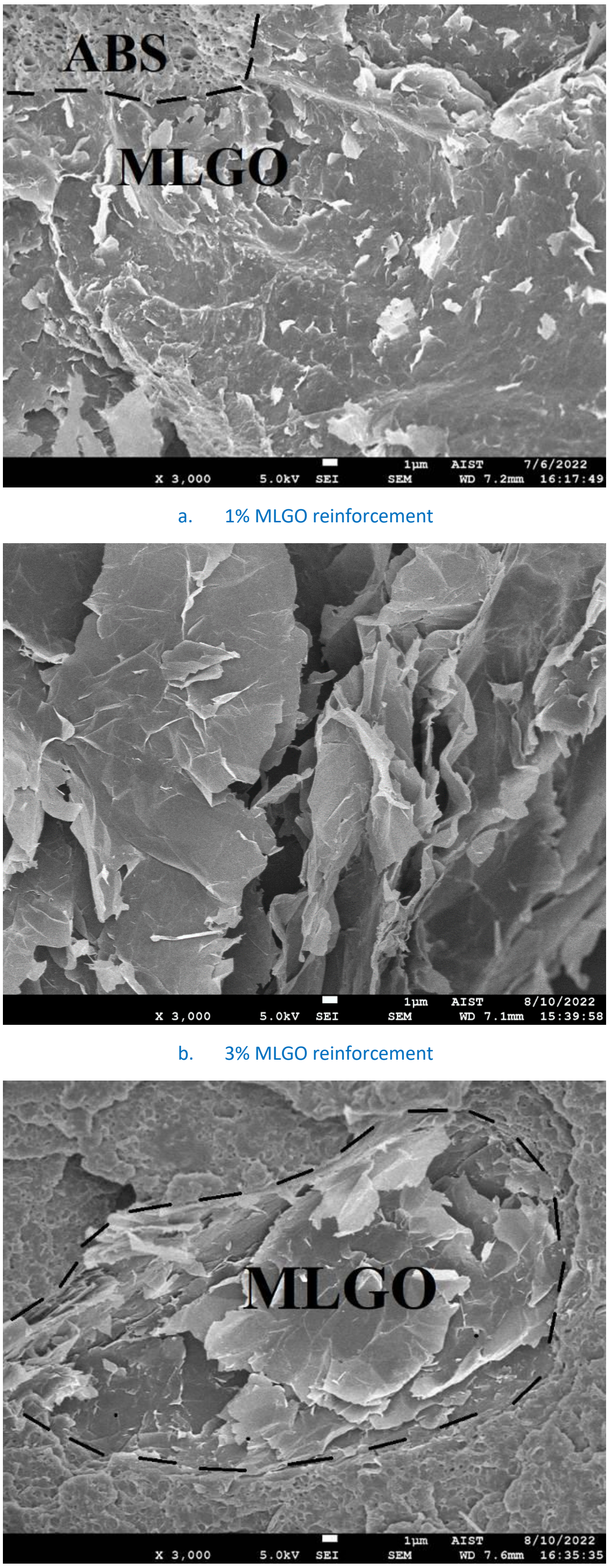


Figure 8. Stress and strain curves of printed samples printed from MLGO reinforced ABS plastic composite.

The microstructure of the fracture surfaces of 1 %, 3 %, and 5 % MLGO reinforcement samples observed on scanning electron microscopy reveal the cause of the strength decrease of the printed specime from MLGO/ABS filaments.



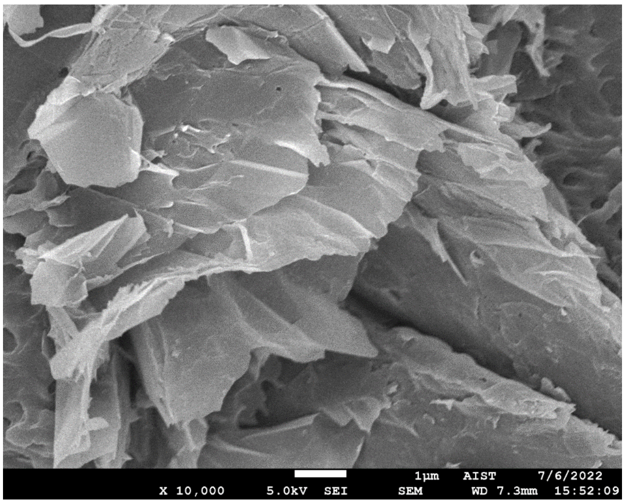
a. 1% MLGO reinforcement

b. 3% MLGO reinforcement

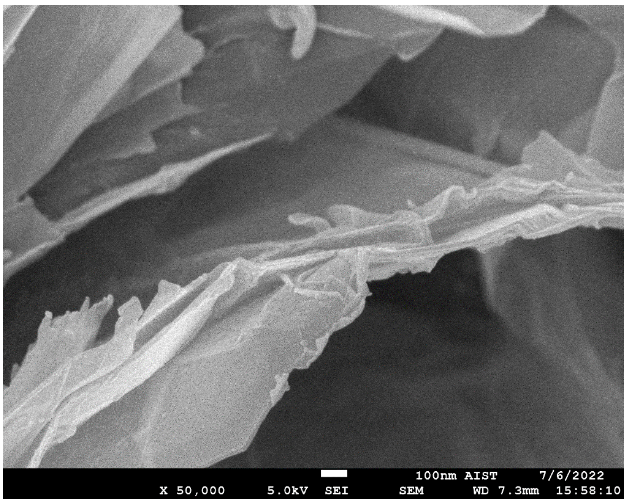
c. 5% MLGO reinforcement

Figure 9. Fracture surface of tensile specimen printed from MLGO/ABS filament.

The fracture surface image of 1 % graphite oxide reinforcement sample at 3000x magnification shows the locally dispersed of graphite oxide on the ABS plastic substrate. Besides the pitting on the plastic surface is the appearance of the split layers of graphite oxide. This phenomenon may be the main cause of the reduction of MLGO/ABS composite strength. Multi-layers graphite oxide has a small size with layers having a thickness approximately 100 nm, so the plastic cannot fill the inside these oxide layers. When MLGO is locally concentrated in a certain area, leading to that area there is no continuous connection between the surface of the ABS plastic base and the MLGO reinforcement in the middle of the graphite oxide layers, causing the material's durability reduction after print. The fracture surface in Fig. 9b and Fig. 9c at 3000x magnification of 3 % and 5 % MLGO mixed samples also have clumping areas similarly to 1 % MLGO sample, which further clarifies the dispersion and bad bonding between the MLGO and ABS plastic.



a. 10,000X magnification



b. 50,000X magnification

Figure 10. Fracture surface of tensile specimen printed from 1% MLGO reinforced ABS filament

The 10000x and 50000x magnification images show more clearly the destruction and delamination of graphite oxide (figure 10). Graphite oxide reinforcement can clump inside the ABS base during extrusion and both don't create a new bond inside the GO layers. Thus, graphite oxide layers which have a lack of bond between them are easily separated when deformed, which explains why the properties of the composite material are reduced compared to the original material.

4 CONCLUSIONS

Multi-layers graphite oxide reinforced ABS polymer filament has been successfully fabricated up to 5 % MLGO content. The filament product can print well on FDM 3D printers with a small print nozzle of 0.4 mm.

Multi-layers graphite oxide reinforced ABS polymer filament has a lower melting point than original ABS filament, so it can reduce print nozzle and print bed temperatures, leading to print easier.

The Multi-layers graphite oxide reinforcement is not only unimproved the mechanical properties but also reduces the strength of the printed product compared to original ABS.

The electrical and magnetic properties of MLGO/ABS composite will be studied further.

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