Graphene-enhanced ABS for FDM 3D printing: effects of masterbatch preparation techniques

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Abstract. 3D printing technologies have received a lot of attentions because of the high flexibility of the process as well as the capability of producing complex shaped and high detailed artifacts with ease. This study focuses on the development of acrylonitrile butadiene styrene (ABS)/graphene composite materials, which can be used as a filament for the melt extrusion 3D printing or FDM 3D printing technique. Since the dispersity of graphene in the polymer matrix is the key parameter of controlling the properties of the composites, the ABS/graphene masterbatches with high concentration of graphene were produced via three techniques: dry mixing; solvent mixing and coagulation techniques. The obtained high concentration ABS/graphene masterbatches were then mixed with pure ABS and melt extruded to produce ABS/graphene composites filament with 1 wt% of graphene. The ABS/graphene composites preparing via solvent mixing and coagulation were found successfully 3D printed. The dry mixing method brought about the aggregation of graphene particle and failed the print.

Keywords: Acrylonitrile butadiene styrene; Graphene; 3D Printing; Nanocomposite; Fused Deposition Modeling

1. Introduction

3D printing technologies have gained a huge popularity due to the capability of making a customized part easily without a requirement of large-scale production. Among various 3D printing techniques, the fused deposition molding (FDM) technology is currently the most widely available 3D printing platforms. This technique uses a tiny die with a heater to melt thermoplastic materials in the form of a continuous filament. The melted materials were then extruded and building up the 3D object on the platform. However, the mechanical properties of FDM 3D printed parts are different from those fabricated by the conventional processes, especially the injection molding process [1]. ABS is one of the most common thermoplastics used to produce filament for 3D printing. Graphene is allotropy of carbon crystal similar to graphite diamonds or carbon nanotubes. Graphene is very strong, lightweight, almost transparent and has a good conductivity both heat and electricity. Fabricating ABS/graphene composites will potentially enlarge the applications and functionalities of the 3D printed products [2].
However, the effects of the preparation method used to prepare the ABS/graphene composites are rarely demonstrated. This study aims to investigate the optimal method for mixing ABS and graphene for fabricating good-quality and functional filaments for the FDM 3D printing process.

2. Materials and method

2.1. Materials
The graphene used in this study was prepared from graphite using the improved Hummer’s method [3]. The polymer matrix used in this work was ABS (AP102, IRPC Public Company).

2.2. ABS/graphene composite filaments preparation
The ABS/graphene composite filaments were prepared by the melt extrusion technique. The masterbatches were prepared via three methods. First is the coagulation method in which the obtained graphene was first dispersed in DMF and mixed with the ABS solution in DMF. The concentration of graphene in the ABS solution was set to 10wt%. The ABS/graphene composite solution was then precipitated in methanol. The obtained precipitated ABS/graphene was dries and mixed with virgin ABS to further produce the 1.75 mm diameter ABS/graphene filament by the melt extrusion technique. The obtained filament was called ABS/G1A. The second method is the solvent mixing method. Here, the ABS/graphene solution was prepared using the same method used for the coagulation sample. Instead of precipitation in methanol, DMF was evaporated. The obtained ABS/graphene composite after solvent evaporated was then mixed with virgin ABS and melt extruded to produce the ABS/graphene filament, which further called as ABS/G1B. The last method is the dry mixing method, which the dry graphene powder was mixed with virgin ABS and melts extruded to produce the filament. The filament prepared via the dry mixing method was further called ABS/G1C.

2.3. Fabrication of 3D printed samples
The tensile testing specimens (Type V, according to the ASTM D638-14) [4] were 3D printed using the WANHAO Duplicator 6 FDM 3D printer. Each sample was printed individually at the center of the printing bed by using the parameters given in Table 1.

| Parameters                  |       |
|-----------------------------|-------|
| Nozzle diameter [mm]        | 0.4   |
| Layer Height [mm]           | 0.1   |
| Infill [%]                  | 30    |
| Printing Temperature [°C]   | 230   |
| Build Plate Temperature [°C]| 80    |
| Printing Speed [mm/s]       | 25    |

2.4. Characterization
The graphite oxide and the obtained graphene were characterized using an X-ray diffractometer (Bruker AXS Model D8 Discover). The graphene sample was scanned over the range of 2θ = 2 - 50° and measurements were recorded at every 0.02° interval.

The decomposition of pure ABS, ABS/G1A, ABS/G1B, and ABS/G1C were analyzed using the TGA model TG 209 F3 Tarsus®. The samples were heated from 50-700 degrees Celsius with 10K/min ramping step under the nitrogen atmosphere.

The melt flow rate (MFR) of ABS/graphene composites; ABS/G1A, ABS/G1B and ABS/G1C were measured according to ASTM D1238 standard, at a temperature of 240 °C with 2.16 kg load applied [5].
The tensile properties of all 3D printed specimens were measured according to ASTM-D638 standard using a Universal Testing Machine equipped with a 5 KN load cell at a crosshead speed of 5 mm/min.

3. Results and discussion
The crystal structures of graphite, graphite oxide and the synthesized graphene were analyzed by XRD technique and presented in Fig.1. The characteristic peaks of graphite was observed at $2\theta = 26.46^\circ$. The peak of graphite oxide was shifted to $2\theta = 11.26^\circ$. The distance between the carbon atom planes of graphite increases from the oxidation reaction to graphite oxide as can be seen from the broader peak, representing the increase in the interlayer spacing. After the reduction step, the sharp peak of graphite oxide disappeared and the broad peak showed up at $2\theta = 25.42^\circ$. The broad and low intensity of the peak indicated the disorder of the graphene particle structure.

![Figure 1. X-ray diffraction graph of graphite, graphite oxide and synthesized graphene.](image)

Fig.2 shows the TGA thermogram of pure ABS, ABS/G1A, ABS/G1B, and ABS/G1C composite filaments. The ABS/graphene composite materials showed slightly higher initial decomposition temperatures; compared to the pure ABS. However, the decomposition of the ABS/graphene composites prepared from the different three methods appeared at almost the same temperature. Thus, it could be concluded that the different methods used to prepare the ABS/graphene composite in this work had no significant effect on the thermal stability of the obtained composites.

![Figure 2. TGA thermogram of ABS, ABS/G1A, ABS/G1B and ABS/G1C.](image)
Fig. 3 shows the MFR values of the three ABS/graphene composites as well as the pure ABS. The MFR values of pure ABS, ABS/G1A, ABS/G1B and ABS/G1C are $6.7 \pm 0.8$, $6.8 \pm 1.4$, $6.5 \pm 1.0$ and $7.0 \pm 0.1$ g/10 min, respectively. It was found that the MFR values slightly increased after the graphene was incorporated. However, the ABS/G1A showed the largest extent of deviation, which may be attributed to the inhomogeneous of the material.

Fig. 4 shows the tensile properties of ABS, ABS/G1A, ABS/G1B and ABS/A1C composites. Incorporating 1wt% of graphene significantly enhanced the tensile properties of the pure ABS. The coagulation (ABS/G1A) and dry mixing methods (ABS/G1C) gave a comparable Young’s modulus values, however, the composite prepared by the coagulation method delivered the better improvement in the tensile strength and elongation at break. The solvent mixing method (ABS/G1B) offered the best improvement in the tensile strength, Young’s modulus as well as the Elongation at break.

![Melt flow rate (MFR) of ABS and ABS/graphene composites; ABS/G1A, ABS/G1B and ABS/G1C.](image1)

**Figure 3.** Melt flow rate (MFR) of ABS and ABS/graphene composites; ABS/G1A, ABS/G1B and ABS/G1C.

![Tensile properties of 3D printed specimens from ABS, ABS/G1A, ABS/G1B and ABS/G1C.](image2)

**Figure 4.** Tensile properties of 3D printed specimens from ABS, ABS/G1A, ABS/G1B and ABS/G1C.

**4. Conclusion**

Graphene was successfully used to enhance the mechanical performance of ABS as evidenced from the improvement in tensile properties. Among three methods used to prepare the ABS/graphene masterbatch in this study, no significant different in the flowability and thermal stability were observed. The ABS/graphene composite preparing by the solvent mixing method (ABS/G1B) exhibited the best improvement in the tensile strength, elongation at break and Young’s modulus. Therefore, the solvent mixing method seems to be the most promising method and will be used to prepare the ABS/graphene composites for further study.

**References**

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