Effect of Graphene Oxide Nanofiller Concentration in Photosensitive Resin 3D Printing SLA on Mechanical Properties of Materials

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Abstract. Recently, Additive Manufacturing (AM) technology was undergoing rapid development, incorporating nanotechnology to enhance the final product's quality. Stereolithography (SLA) constitutes a form of AM that fabricates three-dimensional objects by solidifying liquid resin through ultraviolet light exposure, a process known as photopolymerization, layer by layer. Although SLA boasts exceptional print accuracy, its mechanical properties are comparatively weaker than those of other AM technologies. Graphene, a nanomaterial renowned for its exceptional thermal, mechanical, and electrical attributes, presents a promising filler for enhancing material properties. This study focuses on investigating the influence of integrating graphene oxide dispersion filler, at a concentration of 10mg/ml, on the mechanical characteristics of SLA 3D printed products. The research delves into the effects of varying filler additions, specifically at 1, 2, and 5 wt%. To evaluate mechanical property changes, tensile, density, and Shore D hardness tests were executed. The findings revealed that incorporating graphene oxide dispersion enhances the material's tensile strength and hardness values, while causing insignificant changes in density. The optimal addition level was determined to be 2% weight, resulting in a 29% improvement in tensile properties, yielding a tensile strength value of 17.08 MPa, alongside a 7.6% enhancement in hardness value, culminating in a Shore D reading of 70.67.

Keywords: Additive manufacturing, Graphene, Nanofiller, Stereolithography.

1   INTRODUCTION

Additive manufacturing (AM) has undergone rapid evolution in recent years. This technique involves the incremental addition of materials to fabricate three-dimensional objects, layer by layer. Its merits encompass swift adaptability in design, efficient material usage, reduced production waste, the capacity to shape intricate objects, and the production of lightweight materials [1]. Among the various 3D printing technologies, Stereolithography (SLA) employs the Vat Photopolymerization technique for object fabrication. Through this method, photopolymer resin transforms from liquid to solid form in layers, generating structured forms using photopolymerization processes [2]. A notable advantage of SLA lies in its ability to achieve objects with unparalleled resolution, exceptional precision, intricate detailing, and impeccably smooth surfaces. However, SLA is characterized by limited mechanical properties, restraining the potential applications of the produced objects. Present efforts

are concentrated on enhancing the mechanical attributes of printed objects to broaden their practical utility.

Incorporating nanomaterials, such as reinforcing particles or nanofillers, during the composite production process can augment the mechanical attributes of a material [3]. However, challenges persist in the application of nanofillers, such as issues related to material agglomeration and the settling of nanomaterials, which unfavorably impact the final material properties [4]. An additional hurdle emerges when alterations are made to the resin structure, potentially affecting curing performance or the molding procedure by impeding crosslinking during UV exposure. This, in turn, can detrimentally affect the material's mechanical properties [5]. Graphene is renowned for its remarkable thermal, mechanical, and electrical characteristics, positioning it as a prime candidate for diverse applications, including that of a nanofiller [6]. Graphene oxide (GO), an oxidized variant of graphene, boasts high solubility in both water and organic solvents, a vital attribute for its ability to amalgamate with ceramic or polymer matrices [7]. Graphene oxide dispersion is a suspension of graphene in a liquid solvent, where relatively little graphene is used, so this can be an alternative, more economical solution for admixtures as reinforcement.

The incorporation of GO powder at a weight percentage lower than 2 wt% leads to strength enhancement and alteration in strain increments when 3D printing polymers [8]. Additionally, the introduction of 0.5 wt% Graphene nanoplatelets results in improved tribological performance of molded objects, further contributing to enhanced mechanical properties [9]. Moreover, defect-free Graphene processed using the Self-Propagating High-Temperature Synthesis method offers heightened properties of hardness, strength, and thermo-physical attributes in 3D-printed polymer composite materials [10]. Prior research predominantly employed graphene oxide in powder form. This paper seeks to explore the implications by introducing graphene oxide dispersion in the context of printing outcomes

2   MATERIALS AND EXPERIMENTAL METHOD

2.1   Material

The study employs a commercial photosensitive resin, Anycubic Colored UV Sensitive Resin (405nm), in clear color. The selection of clear color enables easy visual detection of changes resulting from the addition of Dispersion Graphene Oxide (DGO) nanomaterial filler from ITNano, with a concentration of 10mg.ml. This liquid is the product of dissolving Graphene oxide powder into distilled water using ultrasonic methods for 10 minutes at room temperature. The resulting material possesses a brownish-yellow color. For further details on the resin and graphene materials utilized in this study, refer to Table 1.

Table 1. Material Specification.

Photosensitive resin		Graphene oxide Dispersion	
Description	**Value**	**Description**	**Value**
Density	1.05 – 1.25 g/cm^3	Purity	99%
Viscosity	150 – 200 mPa.s	Form	Dark Brown Dispersion
Hardness	82 Shore D	Molecular Formula	C140H42O20
Tensile strength	36 – 45 Mpa	Molecular weigt	2043.8
Flexural strength	50 – 65 Mpa	Graphene Oxide Layers	6 – 7 Layers (XRD)
Elongation at break	8 – 12 %	Element Carbon (C)	81.0 wt%
		Element Oxygen (O)	19.0 wt%
		Element Sulfur (S)	0.1 wt%
		Raman (ID/IG ratio)	0.95
		UV-Vis spectrophotometer	230 nm

2.2   Preparation of Resin and Graphene Oxide Dispersion Mixture

The photosensitive resin was first weighed up to 50 grams using a digital balance with an accuracy of 0.01, and then DGO was added up to 0 wt% (standard sample), 1 wt%, 2 wt%, and 5 wt%. The process of mixing the resin and graphene material was performed using a magnetic hot plate stirrer from DLAB (MS-H280-PRO). The stirring speed used was 1500 rpm with a duration of 15 minutes, followed by sonification using (name of sonification device). The sonification process used 70% power with a duration of 15 minutes. The purpose of using sonification is to uniformly distribute the DFO filler without clumping to obtain a homogeneous colloidal mixture. During the sonification process, there will be an increase in heat in the colloidal mixture, therefore, after the sonification process, the resin temperature will be measured with a thermometer stick.

2.3   Preparation of test sample

Photosensitive resin is transformed into a homogeneous colloidal mixture, which is then used to print test specimens that reference ASTM D638 Type IV for tensile testing, ASTM D792-20 for density testing, and ASTM D2240 for Shore D hardness testing. The dimensions of the test specimens are depicted in Figure 1. The 3D Print SLA from Anycubic Photon Mono SE was used to print the test specimens, and the printing parameters can be found in Table 2. Each test sample is printed as five samples, which is the minimum required by the ASTM standard.After the printing process, the specimen is washed with isotropic alcohol to remove any remaining resin using the Anycubic Wash and Cure 2.0 machine. The washing process lasted 5 minutes, followed by a 15-minute post-curing process using the same machine.
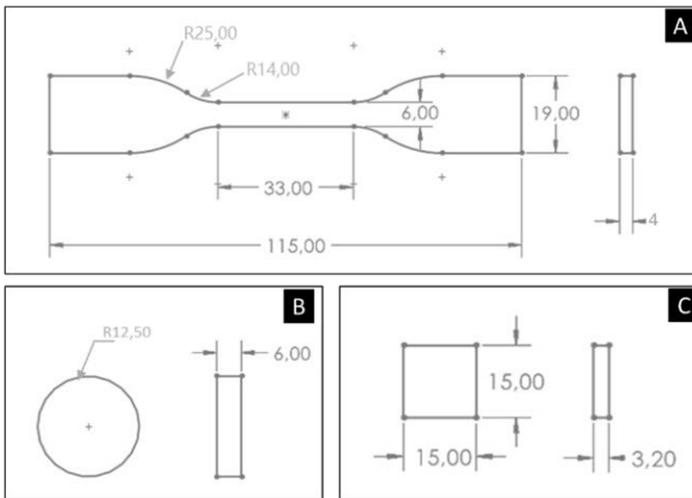
Fig.1 Dimensions of Test Specimens (A) Tensile (B) Hardness and (C) Density.

Table 2. Printing parameters.

Description	Value
Layer Thickness	0.05 mm
Normal Exposure Time	1.5 Second
Off Time	0,5 Second
Bottom Exposure Time	60 Second
Bottom Layers	10
Z lift Distance	5 mm
Z Lift Speed	3 mm/s
Z Retract Speed	5 mm/s

2.4 Tests Method

Mechanical properties were tested using ASTM D638 Type IV tensile test, ASTM D792-20 density test, and ASTM D2240 hardness test. Figure 2 shows the testing scheme, which utilized a universal testing machine (UTM) Carson CRN-50 with a 50 kN capacity and a crosshead speed setting of 5 mm/minute. Test results directly provide the maximum load and maximum strain. Five specimens were used for each variable specified in the tensile test. The average tensile strength is calculated for each specimen using the formula $\sigma = F/A$, where σ represents the tensile strength, F is the pulling force, and A is the cross-sectional area.

Density testing is conducted with an OHAUS analytical balance which applies Archimedes' principle. Density test samples are weighed in air and in a liquid medium, namely distilled water. Five samples are tested and the density value is directly obtained from the test results. Hardness testing is performed with a Shore Durometer D on an operating stand. Five tests are conducted with different pinch locations.
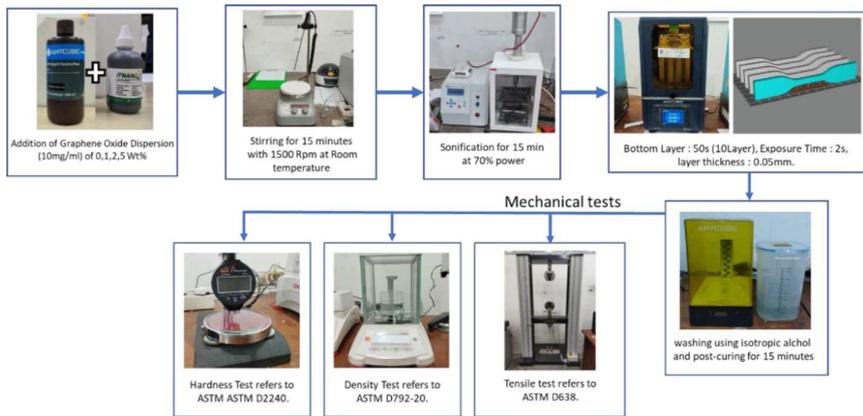
Fig.2 Testing Scheme.

3 RESULTS AND DISCUSSIONS

3.1 The effect of the stirring process on the homogeneity of colloid mixtures

The results that have been observed during the addition of DGO to the photosynthetic resin can be seen in the Figure 3. During the initial mixing stage, agglomeration of DGO occurs upon addition, causing it to mostly float on the surface of the resin, with a small portion settling below. However, after undergoing the stirring process with a magnetic stirrer, the particles in the resin were evenly dispersed. However, it was visually observed that large powders remained in the solution, suggesting agglomeration within each powder speck. To address this issue, a sonication process was conducted, which successfully reduced the size of the powder spots to a level that is not easily discernible to the naked eye. This phenomenon affirmed that the graphene oxide in the colloidal mixture was uniformly dispersed, resulting in a homogeneous colloid. After the sonication process, a temperature increase of 54°F was recorded. However, this temperature value is still within the safe limits recommended by the company for heating photosensitive resins. Therefore, it can be confirmed that the photosensitive resin was not damaged by the process. The addition of weight percentage has an impact on color change. The higher the weight percentage added to the photosensitive resin, the darker the resulting color will be.
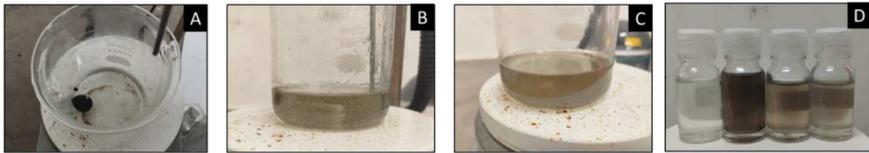
Fig.3 Stages of the mixing process (A) Before stirring (B) after stirring using a magnetic stirrer (C) after sonification process (D) Color change in each increase of the colloidal mixture.

3.2   Effects of DGO contents on tensile strength

In the tensile test graph, there is an increase in mechanical properties with the addition of DGO as seen in Figure 4a. As for the value of the tensile test results can be seen in Figure 4b. An increase in strength is observed when 1% and 2% DGO is added. When 1% DGO is added, a 27.7% increase in tensile strength is achieved, resulting in a tensile strength value of 16.89 MPa. Specimens with the addition of DGO at 2% exhibited a 29% increase in tensile strength, with a value of 17.08 MPa. Conversely, the 5% specimen demonstrated a 10% decrease in tensile strength, with a value of 11.87 MPa, putting it below the tensile strength of the 0% (control) specimen. Based on the conducted tests, adding 2% DGO is the optimal parameter to enhance the material's tensile properties.
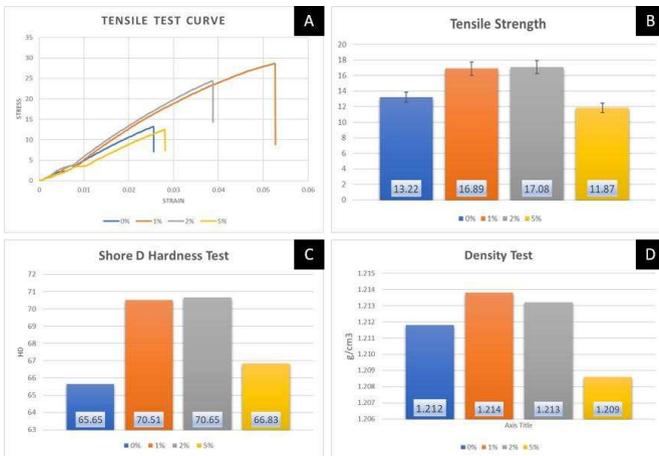

Fig.4 Testing Results (A) Stress-strain curve (B) Tensile strength (C) Shore D hardness (D) Density.

3.3   Effect of adding DGO weight percentage on hardness value

The hardness value is illustrated in Figure 4c. The hardness test results verify that adding DGO enhances the material's hardness. The material's hardness value increased by 7.3% to 70.5 Shore D when 1% DGO was added. Similarly, the addition of 2% DGO resulted in a hardness value of 70.67 Shore D, indicating a 7.6% increase in hardness. However, the addition of 5% DGO produced just a 1.7% increase in hardness.

Therefore, the inclusion of DGO did not significantly affect the hardness value. Based on these findings, it can be inferred that the optimal addition parameter was achieved at a concentration of 2%.

3.4   Effect of adding DGO weight percentage on density value

The results of density measurements with the addition of resin and DGO show that there is a change in the density of the material. It can be seen in Figure 4d, with the addition of DGO at 1%, the density value of 1,234 g/cm3 was obtained, an increase of 0.165%, the addition of 2% obtained a density value of 1,213 g/cm3 increased by 0.083% and the addition of 5% obtained a value of 1,209 decreased by 0.25%. From the results obtained, it can be seen that adding GDO increases the density of the material, but increasing the amount of filler added decreases the density of the material.

4   CONCLUSION

Based on the test results, it is concluded that a magnetic stirrer alone is insufficient for the mixing process :
1. A sonication process is required to ensure that the resulting colloidal mixture has a more uniform filler distribution and to ensure the formation of a homogeneous colloidal mixture. Furthermore, the addition of fillers affects the color of the resin, with a darker color resulting from higher amounts of filler.
2. Tensile strength of the photosensitive material can be augmented by incorporating DGO at a proportion of 2%. Incorporation of DGO resulted in a considerable enhancement of 29% in tensile strength, leading to a strength value of 17.08 MPa. Yet, exceeding this proportion to 5% by weight resulted in a decrease in tensile strength by 10%, producing a strength value of 11.87 MPa. Compared to the control specimen, the tensile strength value at 5% incorporation was lower.
3. There was an increase in hardness value upon addition of DGO to the photosensitive material. The optimal outcome was achieved with the addition of 2% DGO by weight, resulting in a hardness value of 70.67 Shore D.
4. Adding GDO increases the density of the material, but increasing the amount of filler added decreases the density of the material.

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