

COB-2023-1192

STEREOLITHOGRAPHY PRINTING OF GRAPHENE REINFORCED NANOCOMPOSITES: CHEMICAL AND THERMAL ANALYSIS

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Abstract. *The combination of stiffness, strength and low density makes graphene an attractive material for use as reinforcement material in composites for future applications such as in medical, automotive and aerospace industries. In spite of the growing interest in the Additive Manufacturing technologies and potential benefits of graphene reinforcement to improve the properties of Stereolithography SLA parts; there are few studies focused on SLA processing of nanoreinforced photopolymers. Therefore, this study aims to determine the effect of graphene addition on chemical and thermal characteristics of polymeric matrix composite fabricated by SLA. For that, Graphene was added into a standard photopolymerizable acrylic resin. Samples without and with 0.3 and 0.5% graphene were 3D printed in an SLA printer. The effect of graphene addition was investigated by thermogravimetric analysis (TGA), Differential Scanning Calorimetry (DSC) and Infrared Spectrometry (FTIR). Graphene addition resulted in a minimal modification of polymeric structure however it had a significant impact in thermal properties. By understanding the effect of graphene in the thermal behavior and chemical structure of the polymer we expected to be able to predict the mechanical behavior and tailor composite composition in order to achieve optimum properties for a specific application.*

Keywords: Graphene, Stereolithography, 3D Printing, Nanocomposites

1. INTRODUCTION

Additive manufacturing (AM), more commonly known as 3D Printing, is a revolutionary manufacturing method that opened new ways to create architected metamaterials and composites in the end of the twentieth century with applications in a wide range of fields such as biomedicine, aerospace engineering (Xiao et al., 2021). In this vast field with different techniques of printing, one of the most used is the vat photopolymerization technique which utilizes a vat full of light-curable resin in which the ultraviolet (UV) light makes the resin solid creating the layers of printing. This technology can make complex shape parts with high resolution in a fast time creating a wide range of materials with different properties (Sampson et al., 2021; Pagac et al. 2021). In the LCD technology, an UV light with the shape of a layer of the printing 3D model appears on the screen on the bottom of the vat, then the printing material makes a layer on the platform that moves on Z-axis, after each layer the platform makes a up and down movement to allow the printing compound to fulfill the empty space now created by the created layer. Once this process is finished, the platform is removed from the machine and the piece is carefully extracted from its surface, then the object is washed on isopropyl alcohol to clean all liquid layer of resin and now the final piece is bathed by UV light, this process could be done by natural light (which takes longer, because it depends on the sun) or artificial UV light. When it's done the piece is cured and the printing process is finally completed (Pangac et al., 2021).

The most common type of vat polymerization is Stereolithography (SLA) which has a lot of advantages such as higher resolution for printing, smoother finishes and, in some situations, a short turnaround time (Markandan et al., 2014). Therefore, this technique was the focus of the present study. However, most materials designed by SLA did not achieve suitable mechanical and thermal properties for being used in engineering applications. One solution is to add reinforcement particles in order to improve stiffness, strength and other properties of these materials (Markandan et al., 2014). Graphene due to its high Young's Modulus (1 TPa) and low density (2g/cm³) is a promising reinforcement material (Li et al., 2019). So, in this study, we investigate the effect of graphene addition on SLA resin.

On an epoxy resin, the results of graphene oxide addition show an improvement on Young's modulus, tensile strength and hardness and a decrease on the impact strength, also showing an increased glass transition temperature and an improved thermal stability (Wan et al., 2014; Abdullah and Ansari., 2015). Prolongo et al. (2014) investigated the effect

of addition of graphene nanoplatelets (GNPs) to an epoxy resin and observed that GNPs addition usually results in an increase in the stiffness, but the strength and the elongation are reduced. On the other hand, GNPs greatly increases the thermal diffusivity, electrical conductivity and the hydrophobic behavior of the epoxy resin.

Wan et al. (2014) investigated the effect of the addition of graphene oxide (GO) and diglycidyl ether of bisphenol-A functionalized GO in epoxy resin with different filler loading levels, they evaluated properties like toughness, stiffness and strength. As principal results, they observed an increase in the tensile modulus and strength, glass transition temperature and thermal stability. In another study, Xiao et al. (2021) produced a composite with carbon fiber-graphene oxide to verify how these additions could improve the properties of the resin. The authors observed that graphene addition had increased the compression strength by almost 10 times. These results have shown how effective these graphene nanocomposites are (Xiao et al., 2021).

In this context, this study aims to determine the effect of addition of graphene nanoplatelets (GNPs) on the chemical and thermal properties of photopolymerizable resin used for SLA. For that, samples of standard acrylic based resin with 0, 0.3 and 0.5 wt.% of graphene were produced by SLA printing. To determine the effect of adding GNPs were conducted thermogravimetric analysis (TGA), Differential Scanning Calorimetry (DSC) and Infrared Spectrometry (FTIR).

2. MATERIALS AND METHODS

As starting material were used standard transparent resin for 3D printing (Creality, China) and graphene powder supplied by Alfa Aesar. The standard resin is an acrylic based resin designed for 3D printer vat polymerization at 405 UV. According to the manufacturer it has a density 1.14 g/cm³, a viscosity of 300-400 cps, a hardness of 85-90 D, an elongation of 9-12%, a flexural strength of 90-95 MPa, a tensile strength of 60-68 MPa and a shelf life of 12 months. The graphene powder consists of aggregates of graphene nanoplatelets which are individual sub-microparticles composed of small overlapping graphene sheets.

The graphene was added into the resin in two proportions: 0.3 wt.% and 0.5 wt.%. The resin with graphene addition was mixed in a roller mixer for 180 minutes under 60 rpm. In order to conduct a comparative analysis of chemical and thermal properties of parts with different compositions, test specimens of 10 mm length, 50 mm width and 2 mm thickness were designed and printed using Halot One printer. The printing parameters including layer height, print speed, and exposure time were adjusted to achieve the better parts accuracy. After the printing process, the specimens were carefully removed from the build platform, washed in isopropyl alcohol to clean residual non-polymerized resin and an additional curing step was performed using a 405 nm UV light for 60 minutes.

The effect of graphene addition was investigated by thermogravimetric analysis (TGA), Differential Scanning Calorimetry (DSC), Raman and Infrared Spectrometry (FTIR). DSC analyses were performed in DSC-60 Shimadzu. For DSC analysis the samples were heated up to 300°C with a heating rate of 10 °C·min⁻¹ under a nitrogen atmosphere. The TGA analyses were performed using a TGA-50 Shimadzu. For TGA analyses, first the samples were weighed and placed in a crucible, then they were heated up to 600°C with a heating rate of 10 °C·min⁻¹ under a nitrogen atmosphere. Fourier Transform Infrared (FT-IR) spectra (ATR mode) were recorded on a Bruker Vertex 70 spectrophotometer in the 4000–30 cm⁻¹ range (4 cm⁻¹ of resolution). Confocal FT-Raman spectra were recorded on a Bruker Senterra spectrophotometer using a 785 nm laser line, in the 3500–50 cm⁻¹ region.

3. RESULTS AND DISCUSSION

Figure 1 shows the 3D parts after SLA printing. The addition of graphene changes the color of the resin from transparent to a black, in addition the printed part becomes opaque after curing. Parts without and with 0.3 % GNP addition were successfully printed. However, the parts with 0.5 % GNP addition were not completely printed, only few layers could be printed, it seems that the graphene addition hindered the UV light penetration in the resin, preventing the complete polymerization of the resin.

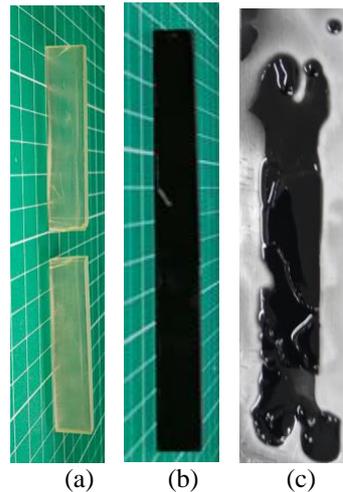


Figure 1. Photographs of 3D parts produced by SLA of pure resin shattered (a) resin with 0.3% of GNPs addition (b) and resin with 0.5% of GNPs addition.

The DSC curves of heating flow versus temperature of the 3D printed parts produced from pure resin and resin with 0.3 and 0.5 wt.% GNP addition are shown in Figure 2. The glass transition temperature of this kind of acrylic resin is below 0 °C, therefore it was not possible with this DSC equipment, to analyze the effect of graphene in the T_g. For that, it would be required to perform DSC analysis in subzero temperatures. In the parts produced from resin with graphene addition, it was observed an exothermic peak at 254 °C, this peak is related to thermal curing. The thermal curing peak intensity was increased in the sample with 0.5 wt.% graphene when compared to the sample with 0.3 wt.% graphene. The presence of thermal curing peak indicated that resin was not fully UV cured, and that amount of non-cured resin increased with higher content of graphene. These results indicated that graphene hindered UV-cure of the resin. An additional study is required to further investigate the role of graphene on UV curing.

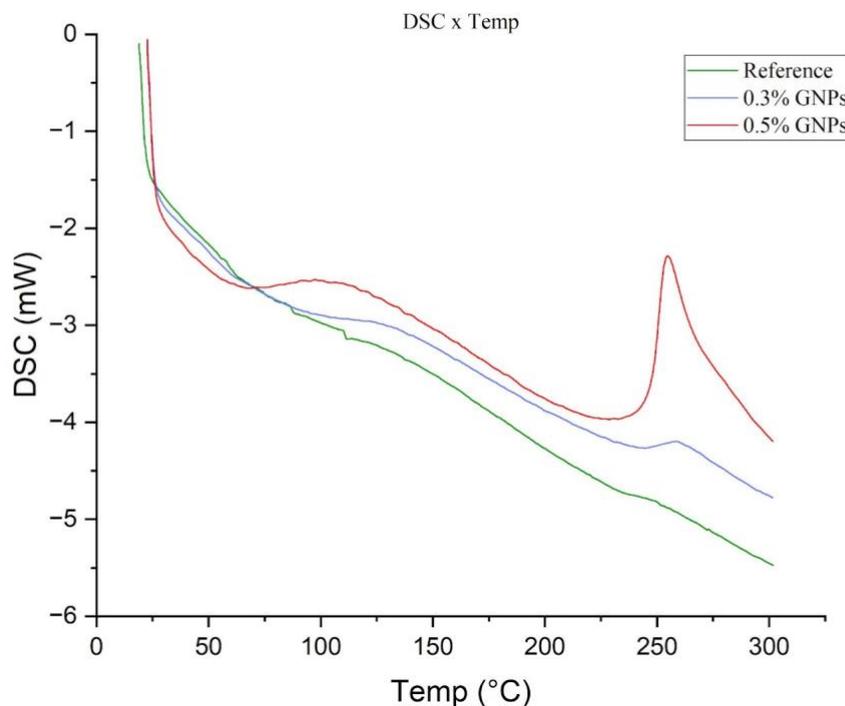


Figure 2. DSC curves of parts produced from pure resin and resin with addition of 0.3 and 0.5 wt.% GNP.

Thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTG) curves are shown in Figure 3 a and b, respectively. The TGA and DTA curves indicate that the samples with GNP addition start to lose mass in lower temperatures compared to samples produced from pure resin. These results indicate the presence of compounds with lower boiling point, which can be related to the high amount of monomers in the resin. These results corroborate with

DSC curves, indicating that UV cure was not completed and because of that high amount of monomers were found in the resin.

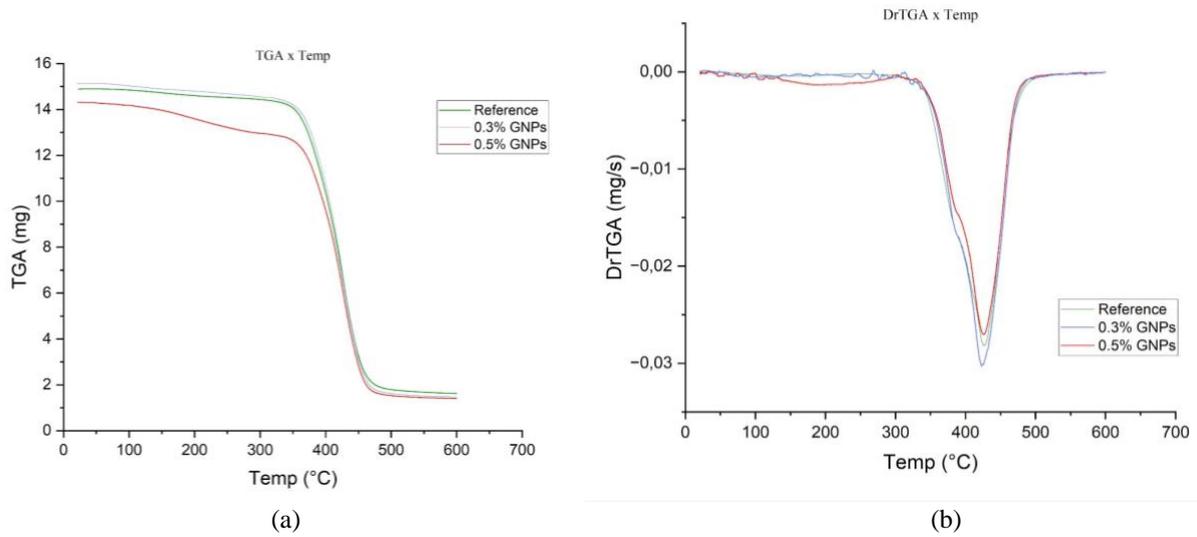


Figure 3. TGA thermograms (a) and DTG thermograms (b) of parts produced from pure resin, resin with addition of 0.3 wt.% GNP and 0.5 wt.% GNP.

The Raman spectra of samples produced from the pure resin and the resin with 0.3 wt.% GNPs did not show any significant change (Figure 4). However, the samples produced from the resin with 0.5 wt.% GNPs showed increased intensity in the peak band at $\sim 1300\text{ cm}^{-1}$. Peak band at $\sim 1300\text{ cm}^{-1}$ is related to sp^2 bond in graphene.

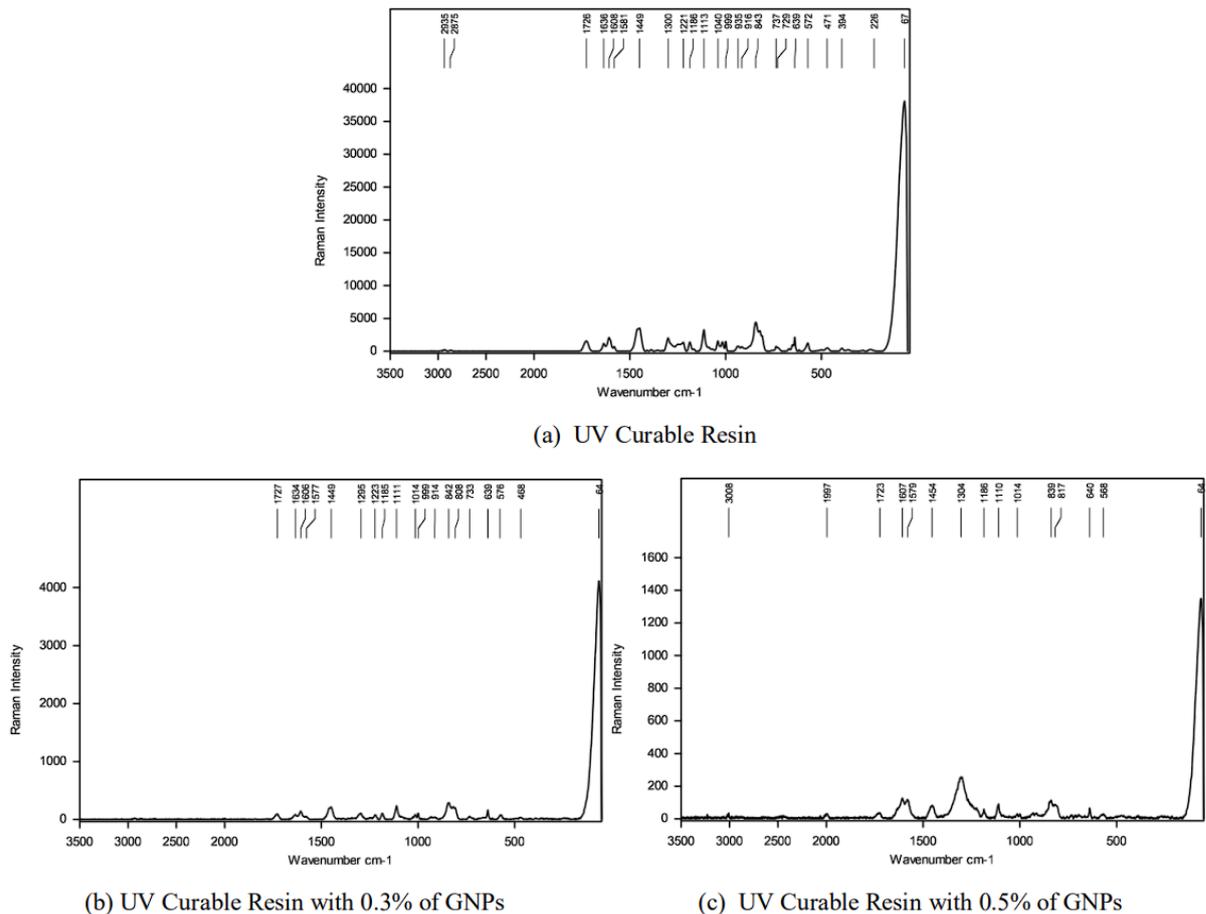


Figure 4. Raman spectra obtained from the parts produced from pure resin (a), resin with 0.3 wt.% graphene (b) and resin with 0.5 wt.% graphene (c).

FTIR spectra of samples produced from pure resin, resin with 0.3 wt.% GNPs and resin with 0.5 wt.% GNPs are shown in Figure 5. All samples had a similar spectrum. However, the intensity of the peaks at 1723, 1636 cm^{-1} increase in the samples with graphene addition. The peaks at 1723 and 1636 cm^{-1} correspond to C=O and C=C vibrations, respectively, C=O and C=C bonds are present in polymer and acrylate monomer as well as in the graohene and graphene oxide. The peak band at 2800-3000 cm^{-1} is related to -CH stretching and therefore shows a higher intensity and spectrum of the samples made from pure resin.

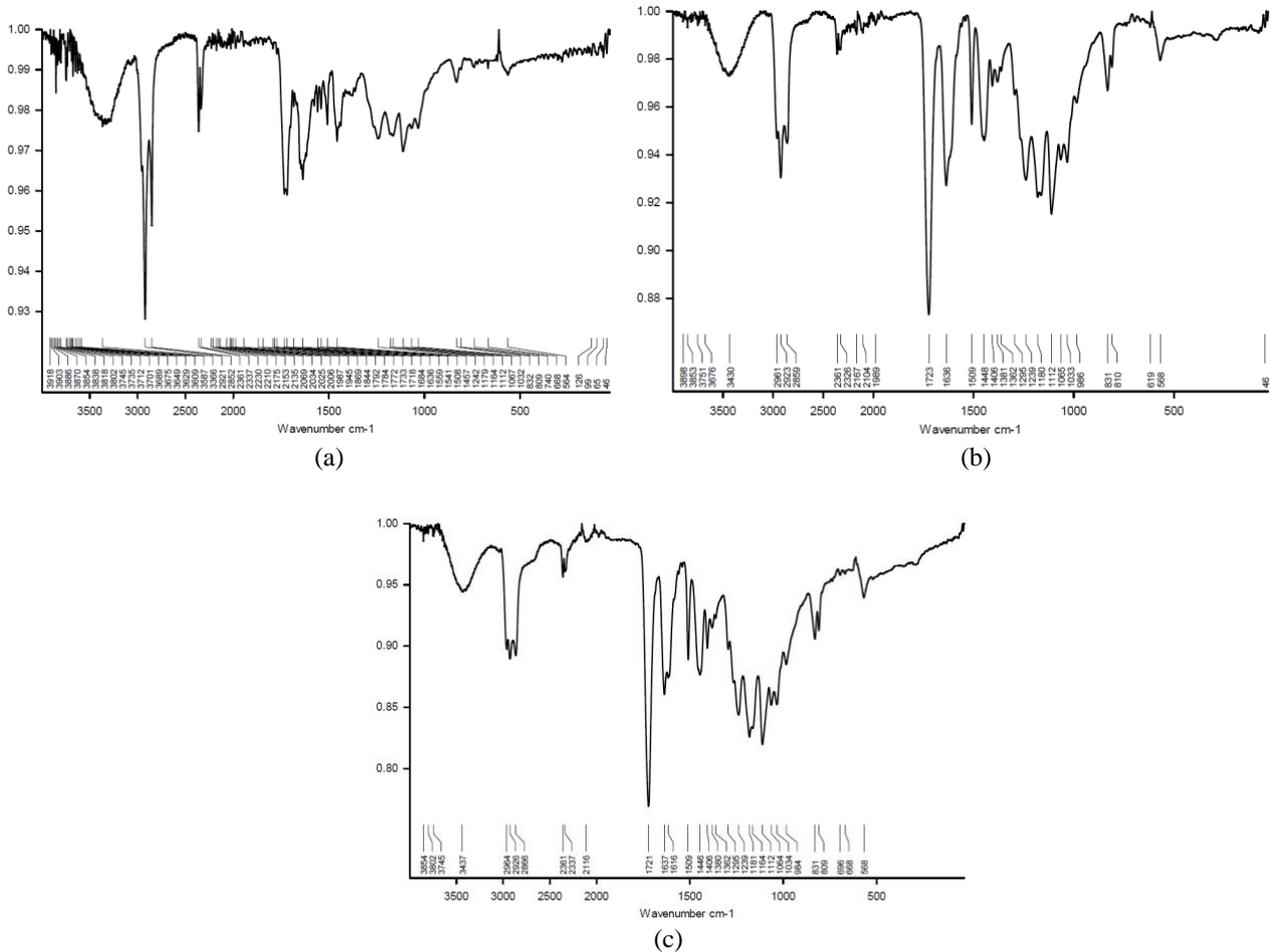


Figure 5. FTIR spectra obtained from parts produced from pure resin (a), resin with 0.3 wt.% graphene (b) and resin with 0.5 wt.% graphene (c).

4. CONCLUSION

This study provides a new outlook on the effect of graphene nanoplatelets in thermal properties of 3D V resin. The addition of graphene nanoplatelets hindered the photopolymerization of standard acrylic resin designed for LCD/SLA printers. Stereolithography of reinforced resins has large potential for many engineering applications. However, a major enhancement in terms of UV cure of graphene reinforced resins is required to improve polymerization of acrylic based resins and to utilize the full potential of the reinforcement. An additional thermal curing step can be an alternative to improve polymerization. In our second study, the effect of graphene in the mechanical properties will be presented.

5. ACKNOWLEDGEMENTS

We thank Prof. Inacio Limberger for the experimental support. This work was funded by CNPq under grant number 403212/2021-9.

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7. RESPONSIBILITY NOTICE

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