

Evaluation of graphene addition on 3D resin for MSLA vat polymerization

Matheus Klement Sebben¹, Rafael de Lima Perottoni¹, Cândida Alíssia Brandl²,
Moisés Xavier Guimarães Valentim^{1,3}, Juliana Rosemara Felisberto da Silva¹,
Bárbara Tirloni², Natália de Freitas Daudt^{1,3} 

¹Universidade Federal de Santa Maria, Departamento de Engenharia Mecânica, Grupo de Tecnologia e Mecânica dos Materiais. 97105–900, RS, Brasil.

²Universidade Federal de Santa Maria, Departamento de Química, Programa de Pós Graduação em Química. 97105–900, RS, Brasil.

³Universidade Federal de Santa Maria, Departamento de Engenharia Mecânica, Programa de Pós Graduação em Engenharia Mecânica. 97105–900, RS, Brasil.

e-mail: natalia.daudt@ufsm.br, skmatheus2002@gmail.com, rafael.perottoni@acad.ufsm.br, candida.brandl@acad.ufsm.br, moisesxavier@live.com, juliana.silva@ufsm.br, barbara.tirloni@ufsm.br

ABSTRACT

Additive manufacturing opens new possibilities for new designs and manufacture of architected metamaterials and nanocomposites. Among the 3D printing technology, vat polymerization is highlighted due its higher resolution, smother surface and printing speed. In spite of the growing interest in the Additive Manufacturing technologies and the potential benefits of graphene reinforcement to improve the properties of parts produced by vat polymerization-based 3D Printing; there is a lack in understanding of the effects of adding graphene to photosensitive vat resin. Therefore, in this study the effect of adding graphene (0.3 and 0.5%) on the chemical, thermal and mechanical properties of parts fabricated by vat polymerization of a standard photosensitive acrylic resin was determined. Graphene addition resulted in a minimal modification of polymeric structure; however, it had a significant impact in the UV curing. The addition of graphene nanoplatelets hindered the photopolymerization of standard acrylic resin as consequence a higher amount of unpolymerized monomers are found after printing. Regarding the mechanical properties, graphene addition promoted a slight improvement in the Elastic Modulus while decreased tensile and flexural strength and it had no significative impact in toughness. An additional thermal curing step can be an alternative to improve polymerization and mechanical strength. These findings contribute to a deeper understanding of the effects of adding graphene to vat polymerization and its potential and limitations.

Keywords: Vat polymerization; Graphene; Nanocomposite; 3D printing.

1. INTRODUCTION

Additive manufacturing has attracted a growing attention in a wide range of fields such as biomedical, automotive and aerospace sectors due its ability to produce complex parts in shorter production times with a low material waste [1, 2]. Furthermore, it opens new possibilities for new designs and manufacture of architected metamaterials and nanocomposites [2–4]. Among the 3D printing technology, vat polymerization is the oldest and most established technology. It is highlighted due its higher resolution, smother surface and printing speed [5, 6]. Vat polymerization is dived in three main technologies: Stereolithography (SLA), Digital Light processing (DLP) and Mask Stereolithography (MSLA). Among these technologies, MSLA is the most affordable, usually the resin is placed in a resin tank with transparent vat at the bottom, than the build platform is moved down to the resin tank an a UV light is projected from LCD screen in the vat with the image of each layer, the UV light cure the layer than the build platform moves up, the process is repeated until the part is finished [5–7].

Nanoparticles have been reported to enhance mechanical properties [8–10], conductivity/electrical [11, 12], thermal properties [13] and magnetic properties [14, 15] of polymeric parts produced by vat polymerization. Graphene nanoparticles have been highlighted due its unique combination of exceptional stiffness (1 TPa), strength (130 GPa), low density, electrical and thermal conductive ($\sim 5000 \text{ W m}^{-1} \text{ K}^{-1}$) [3, 16–18]. Incorporating graphene presents an opportunity to enhance the performance of components produced by vat polymerization based additive manufacturing processes [3].

Recently many studies focused on developing graphene and graphene oxide reinforced polymers have been reported. For demonstration, ABDULLAH and ANSARI [19] investigated the effects of graphene oxide (GO) on epoxy composites prepared by casting method, their results showed a clear improvement of mechanical properties such as elastic modulus, strength and microhardness, however a decrease in the impact strength was observed. EDWARDS *et al.* [20] investigate the addition of graphene oxide as reinforcement in epoxy composites and demonstrate that by adding graphene oxide (up to 1%) the mechanical properties were increased. WAN *et al.* [21] obtained epoxy composites filled with GO and diglycidyl ether of bisphenol-A (DGEBA) with 61–75% improved strength, and 26–41% increased fracture toughness when compared to neat epoxy, furthermore the addition of GO and DGEBA increased the glass transition temperature and improved thermal stability. HOEPFNER *et al.* [22] analyze the effect of graphene oxide and graphene nanoplatelets on polyvinylbutyral (PVB) using dynamic mechanical analyses, they results indicate that increase in the degree of oxidation of the nanoreinforcements contributed to a better dispersion and adhesion of these to the polymer matrix. PROLONGO *et al.* [23] investigated the effect of adding graphene nanoplatelets (GNPs) to an epoxy resin and observed that GNPs addition usually increases stiffness, while reduces strength and the elongation due to weak interfaced formed between GNP and polymeric matrix. However, the use nanocomposites to improve performance of parts produced by vat polymerization are still limited [2].

MARKANDAN and LAI [24] were the firsts to report graphene polymer composite fabrication by vat polymerization, they introduced graphene varying from 0.01 to 0.1 wt.% in a commercial resin and use a stereolithography (SLA) printer to produce the samples. Graphene addition improved elastic modulus and strength, according to the authors the amount of graphene necessary to improve mechanical properties was much lower compared to order process. UYSAL *et al.* [25] produced graphene oxide/epoxy acrylate nanocomposite by SLA using a surface modified and unmodified GO and analyzed. The unmodified GO decreased tensile strength while the modified GO increased, the author attributes the poor performance of unmodified GO to its disordered structure which prevent a smooth chemical bond with the polymeric resin leading to weak linkage regions.

The results reported in the literature regarding the properties specially the mechanical properties of graphene polymeric nanocomposites produced by vat polymerization show a large variation. Graphene layer size, dispersion, oxidation state as well as interaction with the polymeric matrix play an important role in the composite properties. Graphene may result in different properties depending on which vat process (SLA, DLP, MSLA) is applied. Currently most studies have been focused on the SLA process. Furthermore, there are a number of resins available for vat polymerization such as acrylic, polyurethane, epoxy, PLA and ABS based resins. Graphene-polymer matrix interactions will change for each resin composition, so that graphene may be suitable reinforcement for some vat resins, but not for all. Therefore, more studies are still required to better understand the effects of adding graphene in vat polymerization.

As in innovation, in this study, graphene was added (0.3 and 0.5%) in a standard photosensitive acrylic based resin designed for vat polymerization; both graphene and vat resin are commercially available. A MSLA printer was used to produce samples. The graphene-polymer interactions were evaluated by infrared and Raman spectroscopy. Thermal properties were analyzed by DSC and TGA, and mechanical properties by tensile, compressive and impact tests.

2. MATERIALS AND METHODS

As starting materials were used a standard 3D Printer UV curable resin (Creality, China) and a graphene powder (Alpha Aeser, USA). The standard Creality resin is an acrylic based resin designed for 3D printer, 405 UV curable according to the manufacturer it has a density of 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.

Graphene was added to the resin at a concentration of 0.3 wt.% and 0.5 wt.% prior to printing. In this study, the addition of higher amounts of graphene in comparison with previous reports in the literature [24, 25] were investigated. The maximum amount of graphene was selected from our preliminary study [26]. The resin with graphene addition was mixed in a roller mixer for 180 minutes under 60 rpm to ensure the homogeneity of the mixture. Tensile specimens of 50 mm gauge length, 13 mm parallel section width and 2 mm thickness following the ASTM D-638, flexural specimens of 125 mm length, 20 mm width and 4 mm thickness (ASTM D-790) and impact specimens of 80 mm length, 10 mm width, 4 mm thickness (ISO 179) were printed using MSLA resin printer (Halot One, Creality, China). The printing parameters including layer height (50 μm) and exposure time (2.5 – 10 s) were adjusted to achieve better part accuracy. After the printing process, the specimens were carefully removed from the build platform, washed on isopropyl alcohol to remove unpolymerized resin from

the surface and an additional curing step was performed using a 405 nm UV light for 60 minutes, following the resin manufacturer instructions. The 3D printed samples were labeled as reference (neat resin), 0.5% GNP (resin with 0.3 wt.% graphene) and 0.5% GNP (resin with 0.3 wt.% graphene).

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. Differential Scanning Calorimetry (DSC) analyses were conducted by a DSC-60 Shimadzu, with a heating rate of 10°C·min⁻¹ up to 600°C under a nitrogen atmosphere. Thermogravimetric Analysis (TGA) analyses were performed using a TGA-50 Shimadzu, with a heating rate of 10°C·min⁻¹ up to 600°C under a nitrogen atmosphere. Mechanical behavior at room temperature (ca. 24°C) with humidity of ca. 60% was investigated by means of tensile, flexural and impact tests. A universal-testing machine (EMIC-2000, EMIC, Instron, Brazil) was used to perform tensile and flexural tests. Tensile tests were performed in 6 samples of each composition with a speed of 10 mm/min. Flexural tests were performed in 6 samples of each composition following ASTM D-790. The Charpy impact tests were performed in 10 samples of each composition in CEAST Resil 25 following ISO 179-1.

3. RESULTS AND DISCUSSION

The addition of graphene changes the color of the resin from transparent to black, in addition the printed part becomes opaque after curing. Parts without and with 0.3 wt.% GNP were successfully printed. However, the parts with 0.5 wt.% GNP were not completely printed, only few layers could be printed, as it can be seen in Figure 1.

FTIR spectra of samples produced from neat resin, resin with 0.3 wt.% GNPs and 0.5 wt.% GNPs are shown in Figure 2. The peaks at 2800-2900 cm^{-1} are related to $\nu(\text{C-H})$ stretching which is present in the polymeric chain [27, 28], therefore they have a higher intensity in the samples produce from neat resin. The peaks at 1723, 1636, 1509, 1400, 1090-1300 cm^{-1} correspond to (C=O), (C=C), amide II vibration CH_3 and C-O-C respectively [28]. The C=C peak can be an indicative of the presence of unpolymerized compounds. The relative intensity of peaks at 1723 and 1636 cm^{-1} corresponding to (C=O) and (C=C) bonds have been used in the literature to evaluate the degree of polymerization of acrylic based resins, since the (C=C) bonds presented in the methyl methacrylate monomer open to form (C-C) bonds in the large polymeric chain during polymerization, while (C=O) bonds is presented in both monomer and polymeric chains [29, 30]. In the samples containing graphene the peaks at 1723 and 1636 cm^{-1} are also related to (C=C) and (C=O) bonds of graphene and graphene oxide. Therefore, in this study the ratio between (C=O) and (C=C) bonds could not be used to measure the degree of polymerization.

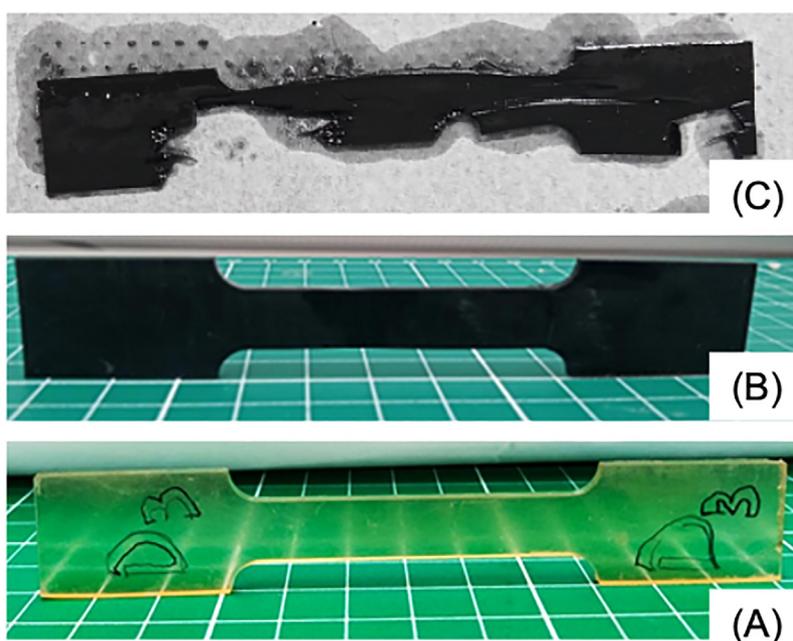


Figure 1: Photographs of 3D parts produced by vat polymerization: (A) reference, (B) 0.3% GNP (C) 0.5% GNP.

The Raman spectra of samples with 0.3 wt.% GNPs did not show any significant change in comparison with the neat resin samples (Figure 3). However, the samples produced from the resin with 0.5 wt.% GNPs showed prominent peak at $\sim 1304\text{ cm}^{-1}$ bands, which is related to the D-band of graphene [21, 24].

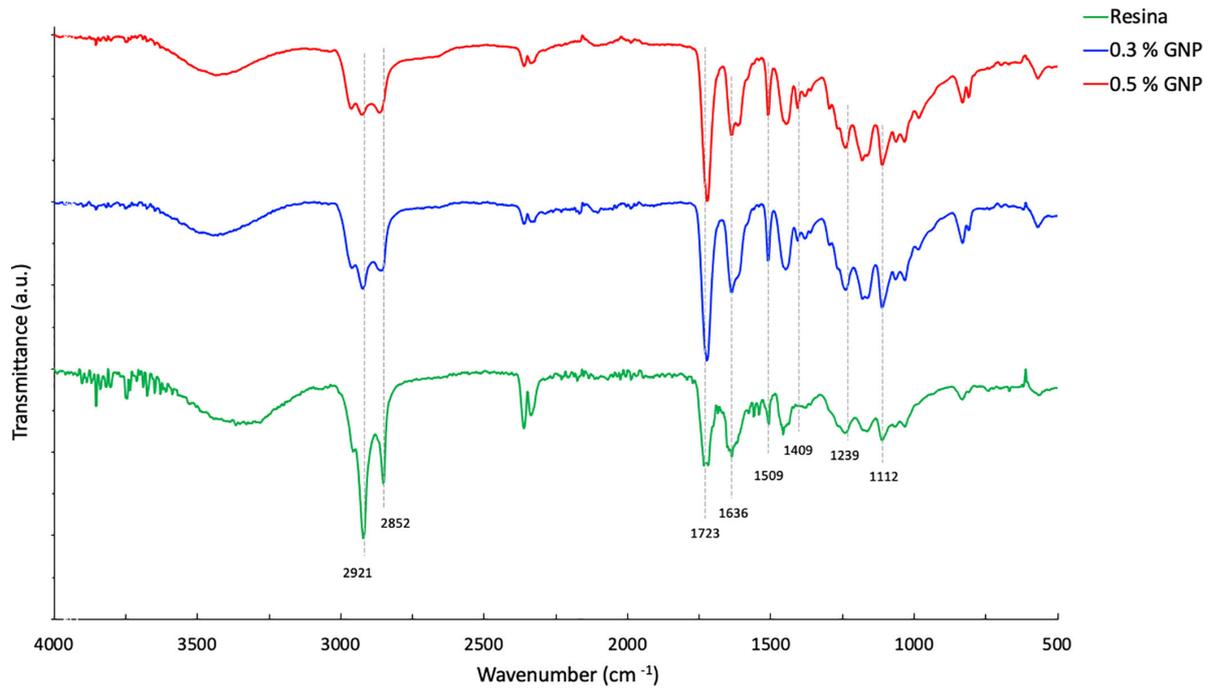


Figure 2: FTIR spectra of the parts produced from vat polymerization.

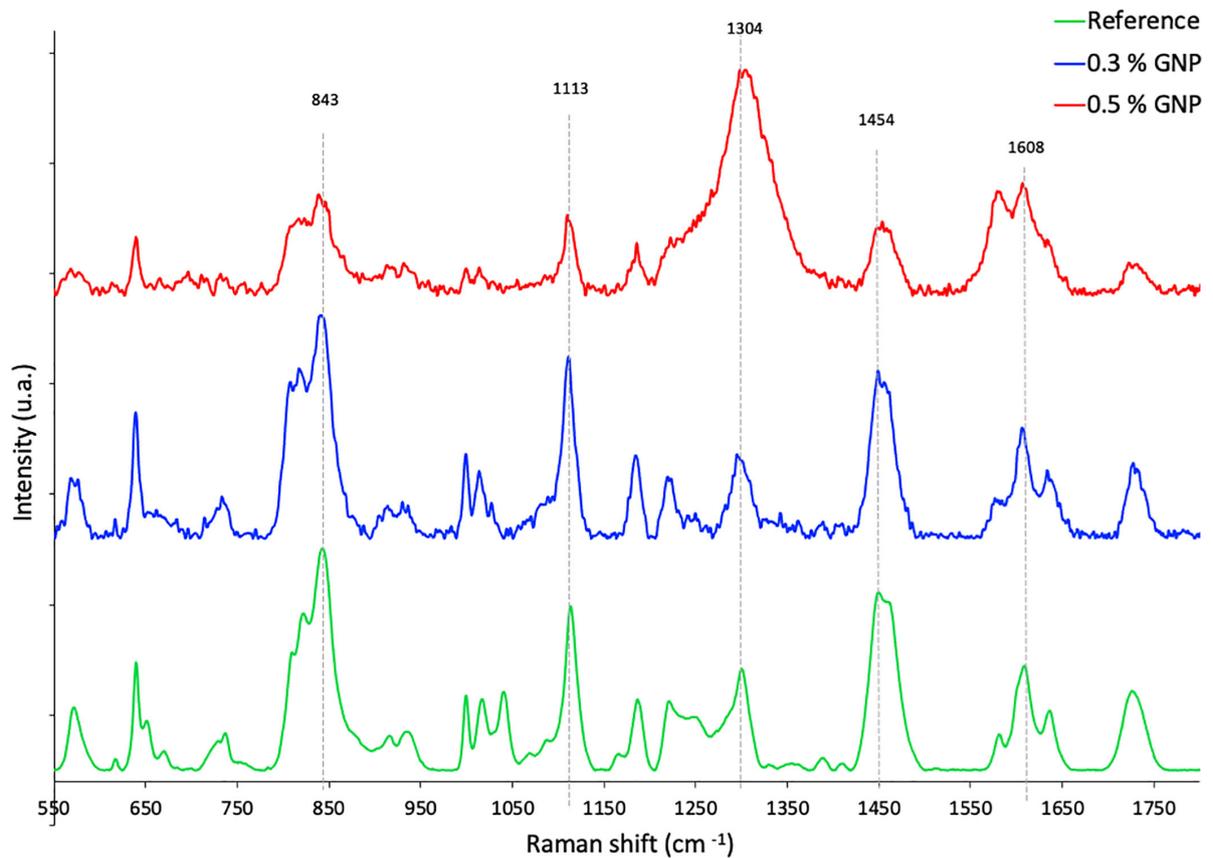


Figure 3: Raman spectra of the parts produced from vat polymerization.

The DSC curves of heating flow versus temperature of reference, 0.3% GNP and 0.5% GNP 3D parts are shown in Figure 4. 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.% GNP when compared to the sample with 0.3 wt.% GNP. The presence of thermal curing peak indicated that resin was not fully cured by UV light, and that amount of non-cured resin increased with higher content of graphene. These results indicated that graphene hindered UV-cure of the resin. LOPEZ DE ARMENTIA *et al.* [31] also observed that graphene addition can decrease the degree of photopolymerization in acrylic based resins. More studies are required to broaden understand the role of graphene on UV curing of 3D printing resins.

Thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTGA) curves are shown in Figure 5 a and 5b, respectively. The TGA and DTGA curves indicate that the samples with GNP

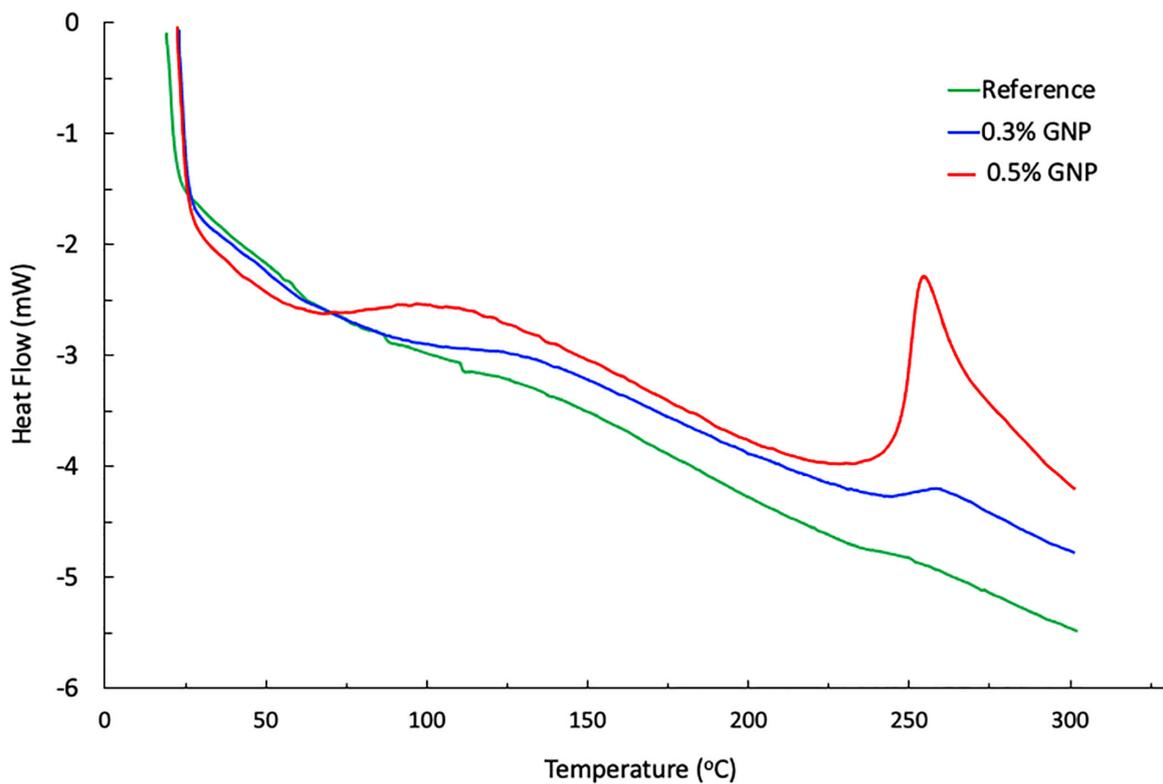


Figure 4: DSC curves of the parts produced from vat polymerization: reference, 0.3% GNP. and 0.5% GNP.

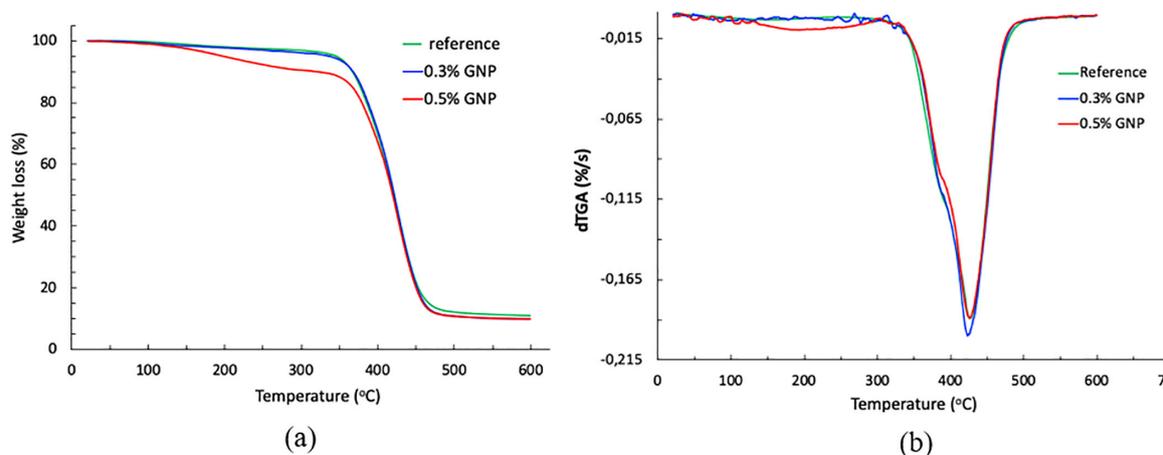


Figure 5: TGA thermograms (a) and dTGA thermograms (b) of the parts produced from vat polymerization.

Table 1: Mechanical properties of 3D printed parts.

SAMPLE	REFERENCE	0.3% GNP
Elastic Modulus (GPa)	1.2 ± 0.2	1.4 ± 0.1
Yield Strength (MPa)	21.0 ± 8	24.0 ± 2.7
Tensile Strength (MPa)	52.4 ± 7.4	37.5 ± 6.3
Flexural Strength (MPa)	82.3 ± 11	35.6 ± 4
Charpy Impact Energy (J)	0.39 ± 0.19	3.39 ± 0.11

addition started to lose mass in lower temperatures compared to samples produced from neat resin. These results indicate the presence of compounds with lower boiling point, which can be related to the high content of monomers in the printed part. These results corroborate with DSC curves, indicating that UV cure was not completed and result in a higher content of monomers in the 3D parts with graphene addition. The main degradation temperature was not modified by graphene addition. The literature report by MANAPAT *et al.* [32] suggested that an annealing treatment can increase thermal stability of graphene-resin based nanocomposites.

The mechanical properties of reference and 0.3% GNP 3D printed parts are shown in Table 1. Mechanical tests were not performed in the parts with 0.5% GNP due to their low printability. Incorporating graphene as expected increased the elastic modulus, once graphene has a high stiffness. The increment on elastic modulus was, however, low compared to 3D parts produced by SLA reported in the literature [21, 24, 32], this result may be related to the higher content of monomers in graphene reinforced 3D parts. In SLA process the UV intensity is higher, and therefore may contribute to decrease the amount of unpolymerized compounds. Tensile and flexural strength were decreased by graphene addition, similar result was also observed by PROLONGO *et al.* [23] and may also be related to low polymerization degree. Nevertheless, DSC analysis indicated that adding thermal curing step in the graphene reinforced 3D parts can improve polymerization and as consequence increase strength and stiffness. The impact tests showed that the addition of graphene did not result in change the impact toughness of the samples.

4. CONCLUSIONS

This study provides a new outlook on understanding the effect of adding graphene nanoplatelets onto standard resin designed for vat polymerization. The addition of graphene nanoplatelets hindered the photopolymerization of standard acrylic resin as consequence a higher amount of unpolymerized monomers are found after printing. A higher amount of monomer contributes to decrease mechanical strength, nevertheless due to graphene high stiffness an improvement in the elastic modulus was observed. Vat polymerization 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 in MSLA. An additional thermal curing step can be an alternative to improve polymerization and mechanical strength.

5. ACKNOWLEDGMENTS

We thank Prof. Inácio da Fontoura Limberger for the experimental support. This work was funded by the Conselho Nacional de Desenvolvimento Científico e Tecnológico - CNPq under grant number 403212/2021-9. Matheus Klement Sebben and Rafael de Lima Perottoni thank the Universidade Federal de Santa Maria for the scholarships.

6. BIBLIOGRAPHY

- [1] DE LEON, A.C., CHEN, Q., PALAGANAS, N.B., *et al.*, “High performance polymer nanocomposites for additive manufacturing applications”, *Reactive & Functional Polymers*, v. 103, pp. 141–155, 2016. doi: <http://doi.org/10.1016/j.reactfunctpolym.2016.04.010>.
- [2] WU, H., FAHY, W.P., KIM, S., *et al.*, “Recent developments in polymers/polymer nanocomposites for additive manufacturing”, *Progress in Materials Science*, v. 111, pp. 100638, 2020. doi: <http://doi.org/10.1016/j.pmatsci.2020.100638>.
- [3] LI, Y., FENG, Z., HUANG, L., *et al.*, “Additive manufacturing high performance graphene-based composites: a review”, *Composites. Part A, Applied Science and Manufacturing*, v. 124, pp. 105483, 2019. doi: <http://doi.org/10.1016/j.compositesa.2019.105483>.

- [4] JIANG, Y., WANG, Q., “Highly-stretchable 3D-architected mechanical metamaterials”, *Scientific Reports*, v. 6, n. 1, pp. 34147, 2016. doi: <http://doi.org/10.1038/srep34147>. PubMed PMID: 27667638.
- [5] LI, Y., WANG, W., WU, F., *et al.*, “Vat polymerization-based 3D printing of nanocomposites: a mini review”, *Frontiers in Materials*, v. 9, pp. 1118943, 2023. doi: <http://doi.org/10.3389/fmats.2022.1118943>.
- [6] SHAH, M., ULLAH, M.K., AZHER, K., *et al.*, “Vat photopolymerization-based 3D printing of polymer nanocomposites: current trends and applications”, *RSC Advances*, v. 13, n. 2, pp. 1456–1496, 2023. doi: <http://doi.org/10.1039/D2RA06522C>. PubMed PMID: 36686959.
- [7] ZHANG, F., ZHU, L., LI, Z., *et al.*, “The recent development of vat photopolymerization: a review”, *Additive Manufacturing*, v. 48, pp. 102423, 2021. doi: <http://doi.org/10.1016/j.addma.2021.102423>.
- [8] WENG, Z., ZHOU, Y., LIN, W., *et al.*, “Structure-property relationship of nano enhanced stereolithography resin for desktop SLA 3D printer”, *Composites. Part A, Applied Science and Manufacturing*, v. 88, pp. 234–242, 2016. doi: <http://doi.org/10.1016/j.compositesa.2016.05.035>.
- [9] SONG, S.Y., PARK, M.S., LEE, J.W., *et al.*, “Study on the rheological and mechanical properties of photo-curable ceramic/polymer composites with different silane coupling agents for SLA 3D printing technology”, *Nanomaterials*, v. 8, n. 2, pp. 93, 2018. doi: <http://doi.org/10.3390/nano8020093>. PubMed PMID: 29414912.
- [10] RAJ, R., DIXIT, A.R., SINGH, S.S., *et al.*, “Print parameter optimization and mechanical deformation analysis of alumina-nanoparticle doped photocurable nanocomposites fabricated using vat-photopolymerization based additive technology”, *Additive Manufacturing*, v. 60, pp. 103201, 2022. doi: <http://doi.org/10.1016/j.addma.2022.103201>.
- [11] ZHANG, G., SONG, D., JIANG, J., *et al.*, “Electrically assisted continuous vat photopolymerization 3D printing for fabricating high-performance ordered graphene/polymer composites”, *Composites. Part B, Engineering*, v. 250, pp. 110449, 2023. doi: <http://doi.org/10.1016/j.compositesb.2022.110449>.
- [12] GONZALEZ, G., CHIAPPONE, A., ROPPOLO, I., *et al.*, “Development of 3D printable formulations containing CNT with enhanced electrical properties”, *Polymer*, v. 109, pp. 246–253, 2017. doi: <http://doi.org/10.1016/j.polymer.2016.12.051>.
- [13] PEZZANA, L., RICCUCCI, G., SPRIANO, S., *et al.*, “3D printing of PDMS-like polymer nanocomposites with enhanced thermal conductivity: boron nitride based photocuring system”, *Nanomaterials*, v. 11, n. 2, pp. 373, 2021. doi: <http://doi.org/10.3390/nano11020373>. PubMed PMID: 33540598.
- [14] OKORUWA, L., SAMENI, F., BORISOV, P., *et al.*, “3D printing soft magnet: binder study for vat photopolymerization of ferrosilicon magnetic composites”, *Polymers*, v. 15, n. 16, pp. 3482, 2023. doi: <http://doi.org/10.3390/polym15163482>. PubMed PMID: 37631539.
- [15] ZHAO, W., WANG, Z., ZHANG, J., *et al.*, “Vat photopolymerization 3D printing of advanced soft sensors and actuators: from architecture to function”, *Advanced Materials Technologies*, v. 6, n. 8, pp. 2001218, 2021. doi: <http://doi.org/10.1002/admt.202001218>.
- [16] GEIM, A.K., NOVOSELOV, K.S., “The rise of graphene”, *Nature Materials*, v. 6, n. 3, pp. 183–191, 2007. doi: <http://doi.org/10.1038/nmat1849>. PubMed PMID: 17330084.
- [17] SHIN, S.R., LI, Y.C., JANG, H.L., *et al.*, “Graphene-based materials for tissue engineering”, *Advanced Drug Delivery Reviews*, v. 105, n. Pt B, pp. 255–274, 2016. doi: <http://doi.org/10.1016/j.addr.2016.03.007>. PubMed PMID: 27037064.
- [18] LEE, C., WEI, X., KYSAR, J.W., *et al.*, “Measurement of the elastic properties and intrinsic strength of monolayer graphene”, *Science*, v. 321, n. 5887, pp. 385–388, 2008. doi: <http://doi.org/10.1126/science.1157996>. PubMed PMID: 18635798.
- [19] ABDULLAH, S.I., ANSARI, M.N.M., “Mechanical properties of graphene oxide (GO)/epoxy composites”, *HBRC Journals*, v. 11, n. 2, pp. 151–156, 2015. doi: <http://doi.org/10.1016/j.hbrj.2014.06.001>.
- [20] EDWARDS, E.R., ALMEIDA, R.C., SANTOS, M.B., *et al.*, “Application of graphene oxide as (nano) reinforcement in epoxy composites”, *Matéria*, v. 27, n. 2, e13177, 2022. doi: <http://doi.org/10.1590/s1517-707620220002.1377>.
- [21] WAN, Y.J., TANG, L.C., GONG, L.X., *et al.*, “Grafting of epoxy chains onto graphene oxide for epoxy composites with improved mechanical and thermal properties”, *Carbon*, v. 69, pp. 467–480, 2014. doi: <http://doi.org/10.1016/j.carbon.2013.12.050>.
- [22] HOEPFNER, J.C., PORTO, R.C.T., UCHÔA, P.Z., *et al.*, “Dynamical mechanical properties of polyvinylbutyral nanocomposites: a comparison between different nano-carbon reinforcements”, *Matéria*, v. 27, n. 2, e13223, 2022. doi: <http://doi.org/10.1590/s1517-707620220002.1323>.

- [23] PROLONGO, S.G., MORICHE, R., JIMÉNEZ-SUÁREZ, A., *et al.*, “Advantages and disadvantages of the addition of graphene nanoplatelets to epoxy resin”, *European Polymer Journal*, v. 61, pp. 206–214, 2014. doi: <http://doi.org/10.1016/j.eurpolymj.2014.09.022>.
- [24] MARKANDAN, K., LAI, C.Q., “Enhanced mechanical properties of 3D printed graphene-polymer composite lattices at very low graphene concentrations”, *Composites. Part A, Applied Science and Manufacturing*, v. 129, pp. 105726, 2020. doi: <http://doi.org/10.1016/j.compositesa.2019.105726>.
- [25] UYSAL, E., ÇAKIR, M., EKICI, B., “Graphene oxide/epoxy acrylate nanocomposite production via SLA and importance of graphene oxide surface modification for mechanical properties”, *Rapid Prototyping Journal*, v. 27, n. 4, pp. 682–691, 2021. doi: <http://doi.org/10.1108/RPJ-06-2020-0114>.
- [26] LIMA, R.P., SEEBEN, M.K., BRANDL, C.A., *et al.*, “3D stereolithography printing of graphene reinforced nanocomposites: chemical and thermal analysis”, In: *Proceedings of the 27th International Congress of Mechanical Engineering (COBEM)*, Florianópolis, 2023.
- [27] VIRATYAPORN, W., LEHMAN, R.L., “Spectroscopic analysis of poly(methyl methacrylate)/alumina polymer nanocomposites prepared by in situ (bulk) polymerization”, *Journal of Materials Science*, v. 45, n. 21, pp. 5967–5972, 2010. doi: <http://doi.org/10.1007/s10853-010-4682-2>.
- [28] MARIN, E., BOSCHETTO, F., ZANOCCO, M., *et al.*, “UV-curing and thermal ageing of methacrylated stereo-lithographic resin”, *Polymer Degradation & Stability*, v. 185, pp. 109503, 2021. doi: <http://doi.org/10.1016/j.polymdegradstab.2021.109503>.
- [29] ZHANG, X., XU, Y., LI, L., *et al.*, “Acrylate-based photosensitive resin for stereolithographic three-dimensional printing”, *Journal of Applied Polymer Science*, v. 136, n. 21, pp. 47487, 2019. doi: <http://doi.org/10.1002/app.47487>.
- [30] DENG, Y., LI, J., HE, Z., *et al.*, “Urethane acrylate-based photosensitive resin for three-dimensional printing of stereolithographic elastomer”, *Journal of Applied Polymer Science*, v. 137, n. 42, pp. 1, 2020. doi: <http://doi.org/10.1002/app.49294>.
- [31] LOPEZ DE ARMENTIA, S., FERNÁNDEZ-VILLAMARÍN, S., BALLESTEROS, Y., *et al.*, “3D printing of a graphene-modified photopolymer using stereolithography for biomedical applications: a study of the polymerization reaction”, *International Journal of Bioprinting*, v. 8, n. 1, pp. 503, 2022. doi: <http://doi.org/10.18063/ijb.v8i1.503>. PubMed PMID: 35187285.
- [32] MANAPAT, J.Z., MANGADLAO, J.D., BUADA TIU, B.D., *et al.*, “High-strength stereolithographic 3D printed nanocomposites: graphene oxide metastability”, *ACS Applied Materials & Interfaces*, v. 9, n. 11, pp. 10085–10093, 2017. doi: <http://doi.org/10.1021/acsami.6b16174>. PubMed PMID: 28230346.