

Thermal Characterization of Graphene Oxide-Epoxy Nanocomposites Produced by Aqueous Emulsion

H. A. Brandão Cordeiro, M. G. Bocardo, N. C. Penteado, V. T. de Moraes, S. M. Giampietri Lebrão, G. W. Lebrão

Abstract—The present study desired to obtain a nanocomposite of epoxy resin reinforced with graphene oxide (OG), for aerospace application, produced by aqueous emulsion. It was obtained proof bodies with 0.00 wt%, 0.10 wt%, 0.25 wt% and 0.50 wt% in weight of nanoparticles, to check the influence of it in the final quality of the obtained product. The validation of the results was done by the application thermal characterization by differential scanning calorimetry (DSC). It was seen that the nanocomposite reinforced with 0.10 wt% of OG showed the best results, the average glass transition temperature, at 2 °C, compared to the pure resin.

Keywords—Aqueous emulsion, graphene, nanocomposites, thermal characterization.

I. INTRODUCTION

COMPOSITE is a kind of material formed by two different phases; the first one is called matrix and the second one, reinforcement. These materials have unique characteristics and are widely used in industry due to its economic and structural advantages. Polymeric nanocomposites have attracted a lot of attention from scientists because of its amazing performance [1]. These materials are a polymeric resin in which are added nanoparticles with dimensions at about 10^{-9} meters. The addition of these nanoparticles, even in small amounts, has really increased the properties of the final material without changing its essential characteristics. Among the various types of nanoparticles studied, graphene (GNP) has excelled, because of its outstanding chemical and physics properties. There are no other nanoparticles with these combinations of properties, which is why graphene is the best reinforcement that can be used in a nanocomposite. A number of studies have been developed to explain its incredible properties, such as its electrical and thermal conductivity, lightness, flexibility and resistance [2]-[5].

Polymeric nanocomposites are materials which have at least one dimension around 100 nm, and they can be in a thermoplastic, thermoset and elastomers matrix, offering the resulting composite material the multifunctional property [6], [7].

The graphene can be defined as one atomic layer of graphite composed by hexagonal carbon structures. It was discovered in 2004 by Geim and Novoselov [8], using an adhesive tape to

exfoliate the graphite; however, this method was impossible to be applied at an industrial scale. Since it was discovered, a lot of methods have been developed, but, until now, all of them seems to be inefficient and very complex.

The main challenge of nanocomposite productions is to obtain a good dispersion, avoiding agglomerations, which can concentrate tensions and decrease the resistance of the material. Because of that, some techniques and procedures were developed trying to minimize these effects, using solvents or dispersants [9]. However, those procedures required an additional step after the production to separate it, what makes the process more expensive. Therefore, studies have turned to other cleaner production routes, such as by aqueous emulsion process.

Only 1% of researchers studied about the thermal properties of graphene, the most properties available are electrical properties, around 34%, followed by 14% about synthesis and 13% about electrical application [1].

Some studies of microemulsion with expandable graphite (EG) in concentrations 0%, 3%, 5% 10%, 15% and 20%; sodium dodecyl sulfate (SDS), Azobisisobutyronitrile (AIBN); PS; 1-pentanol; THF; methyl alcohol presented melting temperature increase 16 °C with incorporation of 20% of graphene in PS (polystyrene) and around 17% in glass transition temperature (T_g) [10]. Others evaluated graphene nanosheets-polystyrene nanocomposites prepared by in situ emulsion polymerization and reduction of graphene oxide using hydrazine hydrate. PS microspheres covalently linked to the edges of graphene nanosheets [11], results in an increase of glass transition temperature; however, the studies also used toxic solvent such as toluene, chloroform and pentanol, to guarantee the emulsion.

In this paper, the main objective of the study will be to determine a procedure for nanocomposites production by aqueous emulsion, looking for the optimization of dispersion and the sustainability of the process. It is desired to obtain a composite that can be used in the aerospace industry, as a structural component.

II. MATERIALS AND METHODS

The polymeric matrix will be a high performance epoxy/phenolic resin. The nanocomposites will be produced using graphene oxide, changing the mass proportion of it in 0.10 wt%; 0.25 wt% and 0.50 wt%. As well, the thermal properties of nanocomposites and pure resin will be compared, doing some laboratorial tests.

Materials used in the procedure were: epoxy resin Araldite LY 5052, catalyzer Aradur 5052, both of HUNTSMAN, and

Helio Augusto Brandão Cordeiro, Marília Gomes Bocardo, Nathalia Cabral Penteado, Viviane Tavares de Moraes and Susana Marraccini Giampietri Lebrão are with the Institute Maua of Technology, São Caetano do Sul, CO 09580-900 Brazil.

Guilherme Wolf Lebrão is with the Institute Maua of Technology, São Caetano do Sul, CO 09580-900 Brazil (phone: 055-11-4239-3000; e-mail: guinet@maua.br).

commercial graphene oxide, of Sigma-Aldrich (4-10% oxidized, with at about 15 layers).

The methods were based in an aqueous emulsion, using ultrasound (UNIQUE MODEL USC-750A), from the Maua Institute of Technology. It is important that all materials used (beaker, stirrer, mold) are plastics/PTFE.

The development of nanocomposites epoxy-graphene oxide has been done by emulsion preparation and the analysis, by application of test, in the same way for all proof bodies.

A. Development of Nanocomposites by Aqueous Emulsion

It was used, 25 g of epoxy resin and graphene oxide in proportion of 0.00 wt%; 0.10 wt%; 0.25 wt% and 0.50 wt% relative to resin mass.

The procedure for preparation of nanocomposite by aqueous emulsion was presented in Fig. 1.

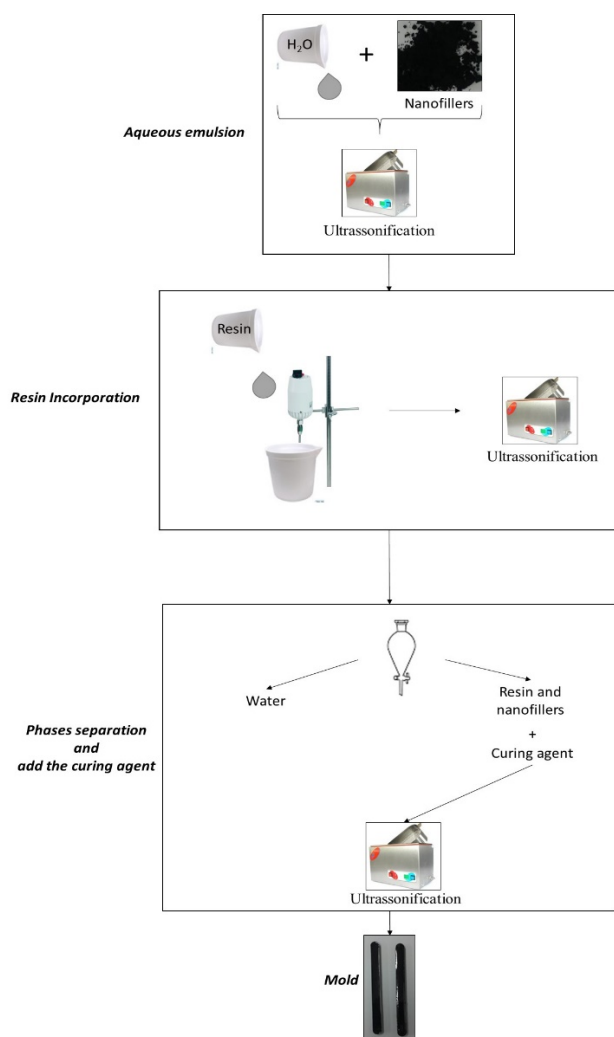


Fig. 1 Process to development of nanocomposites by aqueous emulsion

The nanocomposites have been produced by the procedure described above as:

Step 1. Aqueous emulsion:

- i. Add 25 mL of distilled water to nanofillers.
- ii. Ultrasonification of the water and nanofillers for about 30 minutes.

Step 2. Resin incorporation:

- iii. Drip resin solution under high mechanical agitation.
- iv. Keep mechanical stirring for about 1 hour.
- v. Put the system in an ultrasonic bath for 20 minutes.

Step 3. Phases separation and add curing agent:

- vi. Removing the water by phase separation.
- vii. Add the curing agent (38% of resin weight) and mix well.
- viii. Put the system in an ultrasonic bath for 5 minutes.

Step 4. Mold:

- ix. Transfer the material to the PTFE's mold (casting).
- x. Remove it from the mold after complete cure of resin (7 days at ambient temperature, as indicated by the manufacturer).

B. Applied Tests: DSC

DSC by heat flow was used to verify the thermal behavior of the nanocomposites and how graphene oxide influence the glass transition temperature (T_g) of them, using DSC Q20 V24.4 equipment (TA Instruments).

III. RESULTS AND DISCUSSION

The aqueous emulsion process used for the production of the nanocomposite epoxy reinforced with graphene proved to be quite satisfactory, and especially highly sustainable. The addition of the nanoparticle using water as the solvent makes it an environmentally friendly process; being considered, therefore, advantageous when compared with processes which utilize organic solvents. Moreover, the procedure is quite simple and easy to reproduce. However, it is appropriate to further study, the verification of the influence of certain variables that were not considered in the analysis, such as temperature and the presence of emulsifiers and dispersants in the procedure. These variations may be suitable for improving the dispersion of the nanofiller process, returning to a lesser clumping, and consequently, greater resistance presented by the proof bodies. Furthermore, it may be possible to make viable the addition of a larger amount of nanocomposites improving the performance of the material.

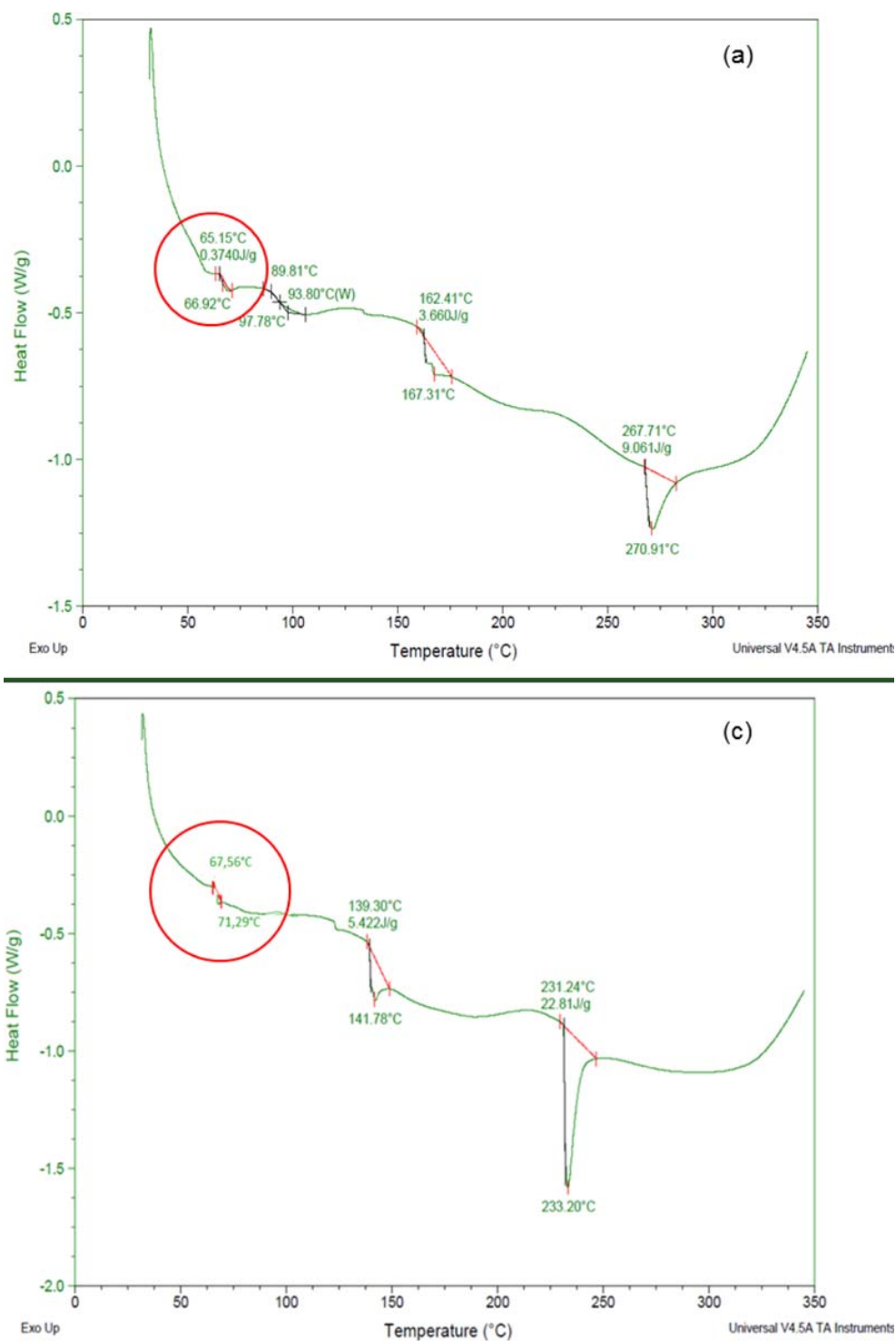
Another factor of great importance for determining the quality of the process used refers to the percentage of nanoparticle dispersed in the polymer matrix. As previously mentioned, it is considered that nanocomposites with 0.10 wt% and 0.25 wt% OG showed adequate dispersion, unlike that observed in specimens containing 0.50 wt% by weight. This composition indicated adequate dispersion achieved by inserting 0.10 wt% OG in an epoxy matrix, but showed the presence of agglomerates by adding 0.50 wt% of nanoparticle.

Regarding the producing of nanocomposites with 0.75 wt%, 1.00 wt% and 2.00 wt% by weight of nanoparticle, it was not possible to obtain specimens with adequate dispersion as evidenced by performing electron microscopy, being suggested, including, the use of smaller percentage mass flow [6].

The DSC test was done to verify if there was a difference in

the glass transition temperature (T_g) of the epoxy resin reinforced with graphene oxide and if this difference was

significant or not. The curves relating the heat flow with temperature are shown in Fig. 2.



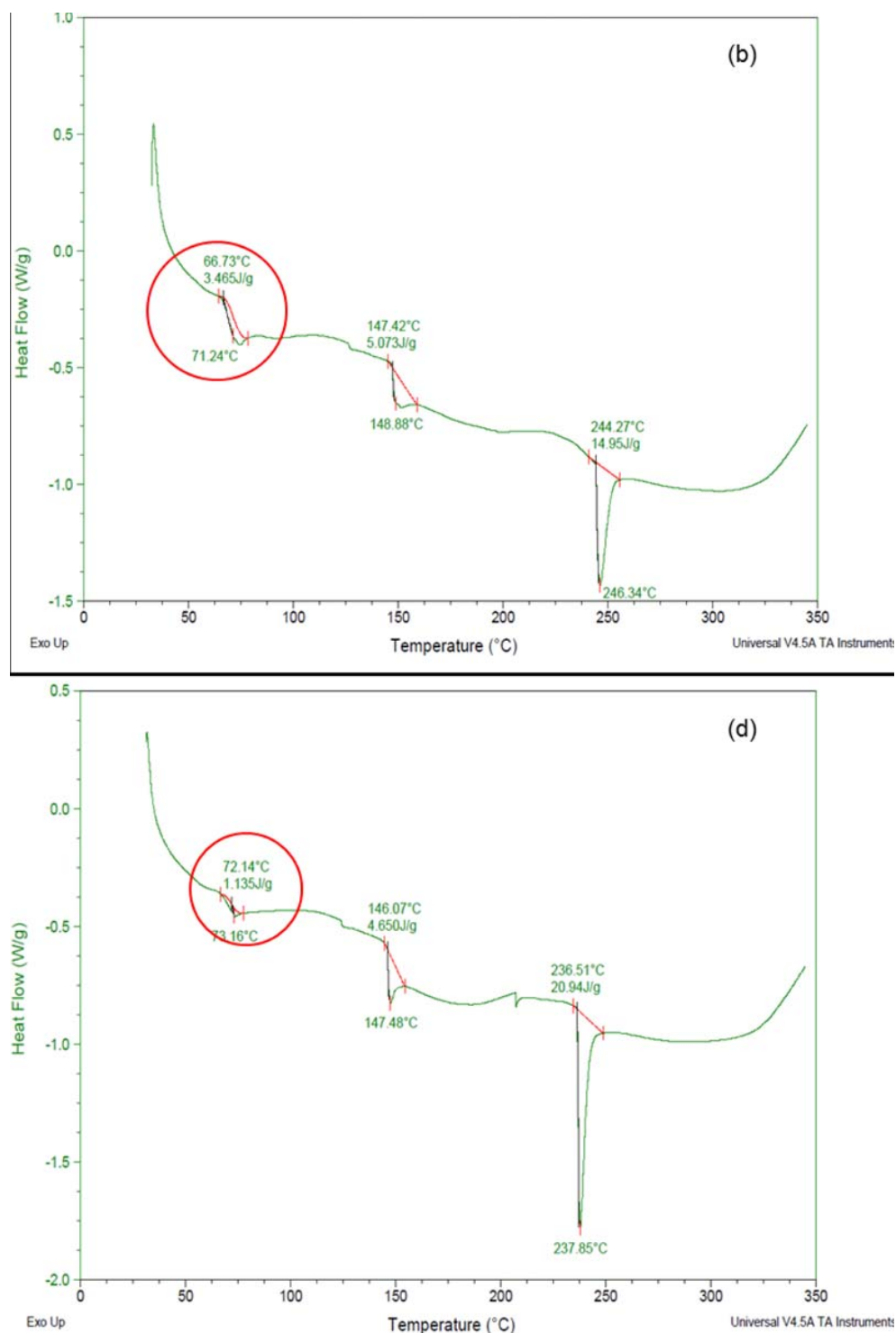


Fig. 2 DSC curves for the samples: (a) pure epoxy resin 0.0 wt% of OG; (b) 0.10 wt% of OG; (c) 0.25 wt% of OG; (d) 0.50 wt% of OG

According to the technical specifications of the resin and data found in the work, the glass transition temperature of the cured epoxy resin Araldite LY 5052 at room temperature is in the range 62 °C to 66 °C. This information was very important to be possible to set the peaks of the curves representing the

T_g of the material. Based on those values was defined that the first peak of the curves is T_g. These temperature ranges can be seen more clearly in Table I.

TABLE I
GLASS TRANSITION TEMPERATURE OF NANOCOMPOSITES

Sample	T _g	T _g average
0.00 wt%	65.95 – 66.92°C	66.43°C
0.10 wt%	66.73 – 71.24°C	68.98°C
0.25 wt%	67.56 – 71.29°C	69.42°C
0.50 wt%	72.14 – 73.16°C	72.65°C

According Ganguli et al. [12], increases in the T_g of the epoxy resin nanocomposites with carbon loads are related to both the decrease in free volume as the increase in crosslink density and restriction of movement at the molecular level. Hu et al. [11] observed an increase in T_g from 101 °C to 109 °C in polystyrene nanocomposite/OG and associated the result of the difficulty of movement of polymer chains due to the polymer's interaction with OG, increasing its density and thus the T_g. Since Silva [13] did not achieve significant improvement in the nanocomposite epoxy/phenolic/OG in most part of concentrations study, only a slight improvement was observed when adding 0.05 wt% OG. He attributed this to the presence of microvoids in the material structure, bubbles originating from the polymerization step inadequate curing cycles and the possible presence of residual solvents. Thus, the increase in T_g observed may be explained by the restriction of movement of polymer chains caused by the addition of graphene oxide. But, it is also important to note that the adhesion of the OG was an effective matrix generated by the presence of hydroxyl functional groups. This fact validates the production method used.

The other peaks observed in the curves can be related to a failure of the material, evaporation and degradation of some volatile compound, since this resin is comprised by additives for improving its quality. Importantly, the last peak (sharper) is not related to the melt of the material, as it is at very low temperature to melt the epoxy.

IV. CONCLUSION

Through this study it was possible to determine a route for obtaining an epoxy/phenolic/graphene oxide nanocomposite by aqueous emulsion, without addition of emulsifiers and dispersants, for three different mass concentrations of nanoparticle (0.10 wt%, 0.25 wt% and 0.50 wt%), which was regarded as environmentally friendly and effective. It was also possible to determine thermal properties of nanomaterials by laboratory tests. The most suitable concentration of nanoparticle determined to be 0.10 wt% of reinforcement has an increased 2 °C in glass transition temperature.

ACKNOWLEDGMENT

The authors offer thanks and acknowledgment of the support of the Mauá Institute of Technology.

REFERENCES

- [1] Zhong, Yujia; Zhen, Zhen; Zhu, Hongwei. Graphene: Fundamental research and potential applications. *Flatchem*, (s.l.), v. 4, p.20-32, ago. 2017. Elsevier BV. <http://dx.doi.org/10.1016/j.flatc.2017.06.008>.
- [2] Rahim, Ishrat; Shah, Mutabar; IQBAL, Mahmood; Wahab, Fazal; Khan, Afzal; Khan, Shah Haider Fabrication and electrical characterizations of graphene nanocomposite thin film based heterojunction diode. *Physica B: Condensed Matter*, (s.l.), v. 524, p.97-103, nov. 2017. Elsevier BV. <http://dx.doi.org/10.1016/j.physb.2017.07.073>.
- [3] Yanik, Mahir Ozan; Yigit, Ekrem Akif; Akansu, Yahya Erkan; Sahmetlioglu, Ertugrul. Magnetic conductive polymer-graphene nanocomposites based supercapacitors for energy storage. *Energy*, (s.l.), v. 138, p.883-889, nov. 2017. Elsevier BV. <http://dx.doi.org/10.1016/j.energy.2017.07.022>.
- [4] Park, Saibom; Park, Saibom; He, Siyao; Wang, Jianeng; Stein, Andreas; Macosko, Christopher W. Graphene-polyethylene nanocomposites: Effect of graphene functionalization. *Polymer*, (s.l.), v. 104, p.1-9, nov. 2016. Elsevier BV. <http://dx.doi.org/10.1016/j.polymer.2016.09.058>.
- [5] Wang, Li; Zhang, Yujie; Wu, Aiguo; Wei, Gang. Designed graphene-peptide nanocomposites for biosensor applications: A review. *Analytica Chimica Acta*, (s.l.), v. 985, p.24-40, set. 2017. Elsevier BV. <http://dx.doi.org/10.1016/j.aca.2017.06.054>.
- [6] Velmurugan, R.; MOHAN, T. P. Epoxy-Clay Nanocomposites and Hybrids: Synthesis and Characterization. *Journal Of Reinforced Plastics And Composites*, (s.l.), v. 28, n. 1, p.17-37, 18 jul. 2008. SAGE Publications. <http://dx.doi.org/10.1177/0731684407081439>.
- [7] Koo, Joseph H. *Polymer Nanocomposites: Processing, Characterization and Applications*. 1st. ed. Two Penn Plaza, New York, NY, 10121-2298, USA: McGraw-Hill, 2006. 272 p.
- [8] Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Katsnelson, M. I.; Grigorieva, I. V.; DUBONOS, S. V.; Firsov, A. A. Two-dimensional gas of massless Dirac fermions in graphene. *Nature*, (s.l.), v. 438, n. 7065, p.197-200, nov. 2005. Springer Nature. <http://dx.doi.org/10.1038/nature04233>.
- [9] Lee, Hee-Jin; Song, Ye-Seul; An, Kyu Tae; Choi, Kook; Kim, Sung-Ryong. Ultraspeed transparent conductive hybrid films of reduced graphene oxide and single-walled carbon nanotube by ultrasonic spraying. *Synthetic Metals*, (s.l.), v. 221, p.340-344, nov. 2016. Elsevier BV. <http://dx.doi.org/10.1016/j.synthmet.2016.10.012>.
- [10] Patole, A. S.; Patole, S. P.; Yoo, Kang, H.; Ji-Beom; Hokim, Tae; Hoqhn, J. A facile approach to the fabrication of graphene/polystyrene nanocomposite by in situ microemulsion polymerization. *Journal Of Colloid And Interface Science*, (s.l.), v. 350, n. 2, p.530-537, out. 2010. Elsevier BV. <http://dx.doi.org/10.1016/j.jcis.2010.01.035>.
- [11] Hu H, Wang X, Wang J, Wan L, Liu F, Zheng H, Chen R, Xu C. (2010) Preparation and properties of graphene nanosheets-polystyrene nanocomposites via in situ emulsion polymerization. *Chemical Physics Letters*, n. 484, p. 247-253.
- [12] Ganguli, S.; Aglan, H.; Dennig, P.; Irvin, G. (2006) Effect of Loading and Surface Modification of MWCNTs on the Fracture Behavior of Epoxy Nanocomposites. *Journal Of Reinforced Plastics And Composites*, (s.l.), v. 25, n. 2, p.175-188, 16 ago. 2005. SAGE Publications. <http://dx.doi.org/10.1177/0731684405056425>.
- [13] DA Silva, L. V.; Pezzin, S. H.; Rezende, M. C.; Campos, A. S.. Glass fiber/carbon nanotubes/epoxy three-component composites as radar absorbing materials. *Polymer Composites*, (s.l.), v. 37, n. 8, p.2277-2284, 20 mar. 2015. Wiley-Blackwell. <http://dx.doi.org/10.1002/pc.23405>.