GRAPHENE BASED NANOCOMPOSITES FOR OCCCUPATIONAL THERAPY APPLICATIONS

Maria Gabriela R. Carvalho, mariagabrielacarvalho@yahoo.com.br
Universidade Federal de Minas Gerais, Graduate Program on Mechanical Engineering (PPGMEC-UFMG), 6627 Antonio Carlos Avenue , Belo Horizonte, MG 31270-901, Brazil

Adriana M.V Van Petten, avaladao@ufmg.br
Universidade Federal de Minas Gerais, Department of Occupational Therapy, 6627 Antonio Carlos Avenue, Belo Horizonte, MG 31270-901, Brazil

Eder C. Dias, edercesar01@gmail.com
Diego T.L. da Cruz, dtlcruz@gmail.com
Antonio F. Avila, aavila@netuno.lcc.ufmg.br
Universidade Federal de Minas Gerais, Department of Mechanical Engineering and Graduate Program on Mechanical Engineering (PPGMEC-UFMG), 6627 Antonio Carlos Avenue , Belo Horizonte, MG 31270-901, Brazil

Zilmar Lima Lula
Center for Development of Nuclear Technology (CDTN), Mineral Technology Laboratory, , 6627 Antonio Carlos Avenue , Belo Horizonte, MG 31270-901, Brazil

Abstract. *The goal of this paper is to investigate the use of nano-structured materials for Bio-Medical applications, in special, occupatioal therapy. To be able to understand the nanoparticle dispersion into the polymeric systems and later on their application to laminate composites, a set of nanographene based nanocomposites are synthetized using a high shear mixer. TGA, DSC, XRD, and SEM/TEM/AFM analysis were performed for nanoparticles dispersion evaluation. Furthermore, the results have showed that nano-structures formed are mostly into the exfoliated condition. The Hybrid laminates were evaluated using tensile and three point bending tests. The results have shown that nanogrpahene based hybrid nanocomposites lead to better performance than conventional laminate composites.*

Keywords*: Nano graphene, nanocomposite, bending tests, nanostructures materials*

1. INTRODUCTION

Composite materials for biomedical applications have been in use for years. In fact, the market share for such type of applications can be measured annually in billions of US dollars. The usage of orthesis on patients with limitation of mobility is a standard procedure. During the treatment, the therapist has to mold and remold the orthesis to adjust it to the patient's mobility evolution. The problem rises during the re-mold process and its final cost. The average cost of a treatment can easily relies on thousands of dollars. According to Fess (2002), among the large variety of materials used for orthesis manufacturing, the low temperature thermoplastics are the most efficient ones. Furthermore, Breger-Lee (1995) mentioned that thermoplastics great success is due to their easy manipulation during the orthesis preparation and good mechanical properties.

In Brazil, the availability of this material is very restricted since it is imported and its cost is high. A 3,2 mm x 45,7cm x 60,9 cm plate of thermoforming material costs from U$179,50 to U$260,95. Additionally, the number of orthesis resulting from this plate depends on the size and type required by the patient. Given the high cost involved in the import of this material, the sales representatives usually opt to work with the two less expensive options. This means that the materials available on the market may not be the best option for the patient's treatment. Still, the majority of the population is covered by the Universal Health System (SUS), a governmental organization, or by the Health Medical Organizations (HMO) that, many times, do not charge for this type of procedure or charge for some types of orthesis up to a pre-established price.

Another issue that must be addressed is the need of humid or dry heat during the orthesis preparation when thermoplastic materials are used. Studies developed by Rodrigues et al. (2007) show that successive heating can cause a process of material 'aging' characterized by the reduction of its mechanical properties up to 25% of the original ones, promoting a premature fracture. Even though, in Brazil, HMO and SUS are continuously pushing for the reusing of thermoplastic materials for economic reasons. Such policy can cause not only longer rehabilitation periods and after-effects to the patients, but it also affects the therapist work.

The need for an alternative material to the imported thermoplastics is urgent. The required characteristics of such "alternative" material are: low cost, large availability, good mechanical properties and easy mold ability. The possibilities for such materials are endless but there are certain characteristics that limit our choice. According to

Coppard and Lohman (2001), hand splints, a synonym for hand orthesis, are mainly loaded by bending moments. Furthermore, Giurintano (1995) called the attention to the fact that, considering biomechanics, hand splints as well as forearm splints are both subjected to bending stress due to the muscles activation. As we know, one of the most efficient composite materials for bending loads is the sandwich composite materials.

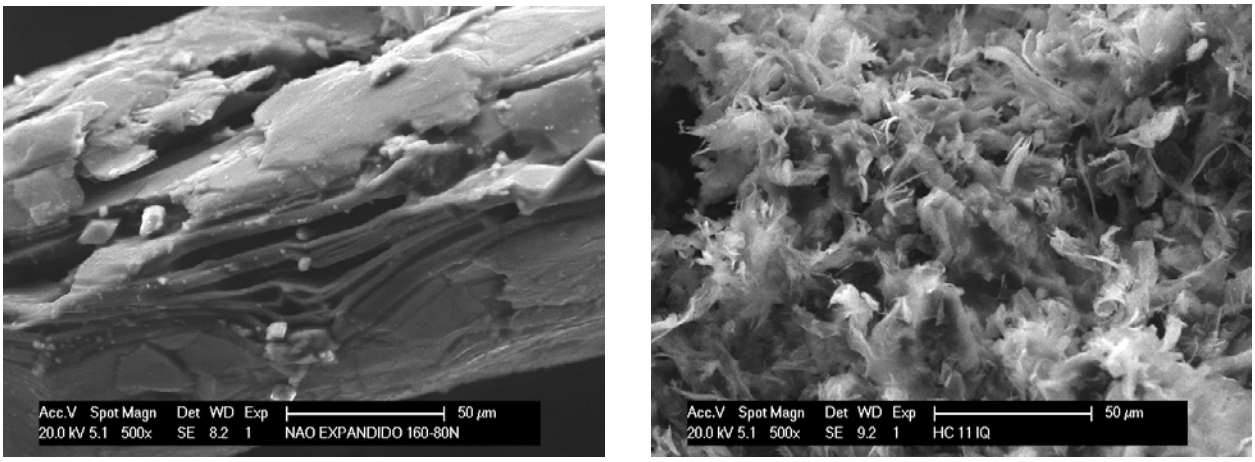
Ávila and co-workers (2007) defined composite materials as the ones composed of the blending of two or more organic or inorganic materials, in which one is used as matrix and the other as reinforcement. Vinson (1999) went further when mentioned that sandwich structures, a special class of composites, are distinguished by a low density kernel material surrounded by two external laminates. Sandwich composites have various advantages: the improvement of mechanical properties, i.e. stiffness, fatigue, heating resistance, among others, in addition to its low cost. Given the characteristics of these materials, seemingly compatible to orthesis preparation/manufacturing, and the need to implement studies related to this area, this research aims to: (*i*) develop a low cost and high performance nanocomposite to manufacture orthesis, (*ii*) test its mechanical characteristics in lab.

This work focuses on development of a graphene nanostructured hybrid composite to serve as main reinforcement of sandwich composites for occupational therapy applications.

2. NANOCOMPOSITE SYNTHESIS

2.1 Materials

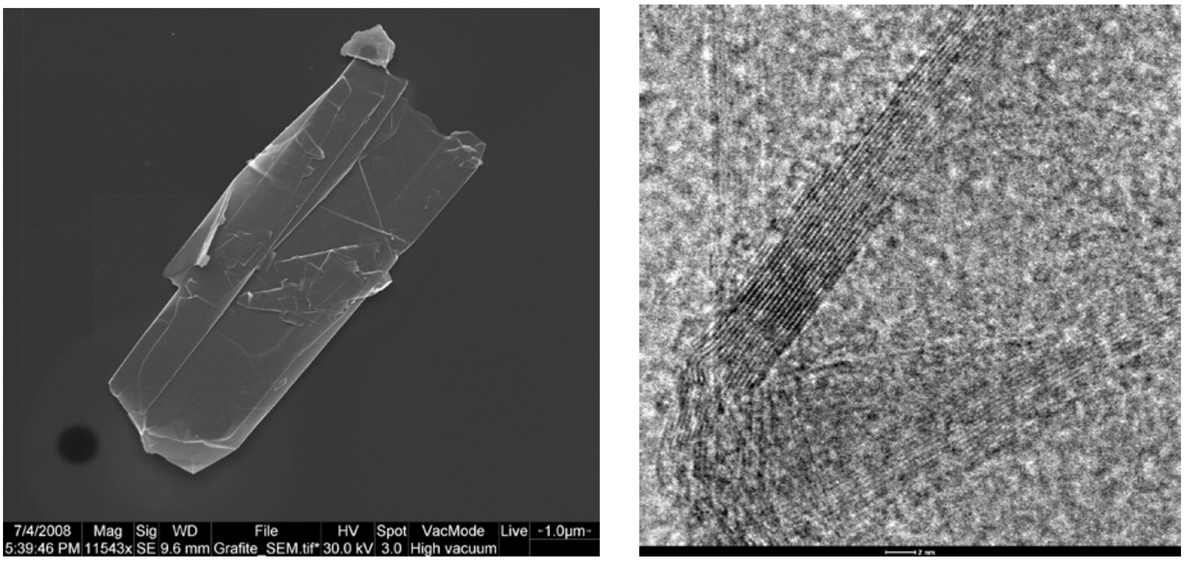
The hybrid nanocomposite is a fiber glass/nano-modified epoxy system laminates. The fiber reinforcement is a plain weave fiber glass fiber with arial density of 180 g/m^2. The epoxy system was made of *bisphenol A* resin and an amine hardener, i.e. RemLam M and HY956, from Hunstman Inc. The graphene used has its origin from an expandable graphite (HC 11 IQ) supplied by Nacional Grafite. When the HC 11 graphite is submitted to a 900 C thermal gradient in a 30 second period or less, the polymeric layers between the graphite plies volatilizes. This sudden reaction leads to the graphite speedy expansion. As the volume must remain constant, the graphite thickness approaches nanoscale. The graphite nanosheets are later on functionalized using a mix of sulfuric and nitric acid. Figure 1-A shows the expanded graphite before the thermal shock. As it can be noticed, the structure is multilayer, where the polymeric matrix is located between graphite layers. The flake like structure is formed after the thermal expansion as show in Figure 1B .



(a) (b)

Figure 1. Expandable graphite. (a) Before thermal expansion; (b) after thermal expansion

From previous results from Ávila´s research group, it is possible to demonstrate that a large amount of graphene is present into the nanographite. Figure 2A shows a scanning electronic microscope (SEM) observation of a single nanographite sheet. By using a transmission electronic microscope (TEM), Ávila and collaborators (2009) were able to observe clusters of graphene nanosheets piled up as described in Figure 2B.



(a) (b)

Figure 2. Single nanographite sheet observation. (a) SEM analysis; (b) TEM analysis

During the nanocomposite preparation, the graphene dispersion process into the epoxy system followed the procedure describe in Ávila et al. (2008). A dispersant agent, acetone, was employed to improve the mixing process. The degassing stage was required to eliminate bubbles generated during the mechanical mixing, as well as to eliminate the dispersant agent, i.e. acetone. After this procedure, the hand lay-up with vacuum assisted cure was performed. As mentioned by Ávila and collaborators (2007), the epoxy system has a saturation limit. For graphite nanosheets, this saturation limit is around 3 wt%. To be able to investigate the graphene effects, four different sets of specimens were prepared, i.e. 0 wt%, 1wt%, 2wt% and 3wt%.

2.2 Nanostructure characterization

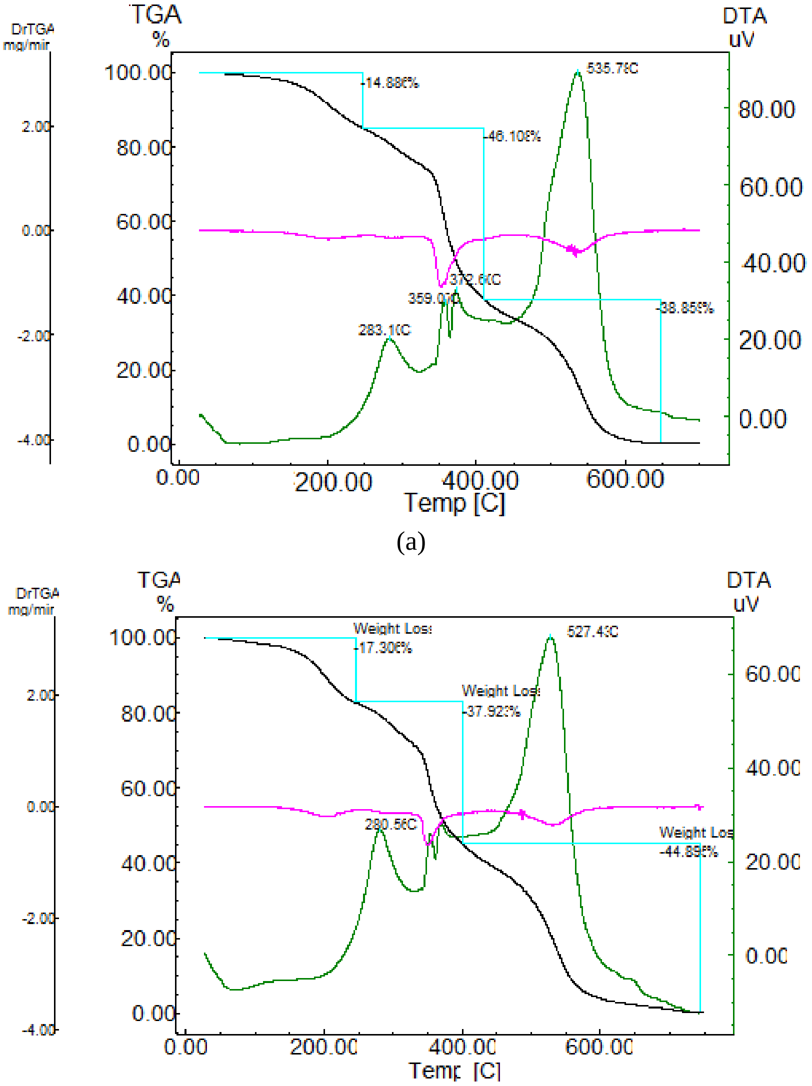
According to Koo (2006), during the nanoparticles dispersion into polymeric matrices nano-structures are formed. The two most common detection techniques to nano-structures identification are X-ray diffraction and electronic microscopy. In this research, X-ray diffraction (XRD) experiments were carried out on a Shimadzu XRD-6000 X-ray diffract meter with Cu (λ=0.154 nm) irradiation at 40 *kV* and 30 *mA* using a Ni filter. Data were recorded in the range from 2 to 80 deg in a continuous scanning at 2 degrees per minute and sampling pitch of 0.02 deg. The scanning electron microscope (SEM) used was a LEO model 1430VP. In all cases, a gold thin film was placed on the surface of the sample to able to scan its structure. Finally, a thermal stability analysis was also performed using a Shimadzu DTG 60 Thermogravimeter under nitrogen, at 10 C/min from 25 C to 750 C. As this research deals with dynamic loadings, in addition to the traditional nanoparticles dispersion analysis, information about the sandwich response under indentation must be supplied.

2.3 Mechanical tests

According to Rodrigues (2007), the most common loading into wrist orthesis is bending, Therefore, the mechanical characterization will focus on three point bending test following the ASTM standard D 790 (ASTM, 2003). The laminated prepared is composed of four layers of plain weave woven fabric with 50% volume fraction. This procedure leads to a 1.6 mm thickness. The three point bending test specimen dimensions can be described as: thickness of 1.6 mm, width of 12.7 mm, and length of 70 mm. All tests were performed using an INSTRON universal testing machine with a displacement rate of 1.53 mm/minute.

3. DATA ANALYSIS

Figure 3A-B show the DSC/TGA signature for the pure resin (0wt%), 3 wt% nanographite, respectively. The addition of nanoparticles, i.e. nanoclay, seems to delay the weight loss. Taking the 410 C temperature, it is possible to observe a weight loss reduction from 46.10% for the pure resin to 37.92% for the 3wt% nanographite addition. Based on these results, it is possible to conclude that an improvement in thermal stability similar to that reported by Gilman (1999) is noticed. This increase on thermal stability can be explained by the nanostructures formed inside the epoxy system. Still, an increase into glass transition temperature (t_g) was noticed when the nanoparticles are added, i.e. 380 C for the pure epoxy and 395 C for the 3wt% nanographite content. These variations into glass transition temperature (t_g) can be explained by the nanographite/ graphene large superficial area which can acts as nucleation sites for polymeric chains. As explained by Ávila et al. (2008), the epoxy system has a saturation limit; it is possible to observe the formation of clusters of immiscible structures.



(a)

(b)

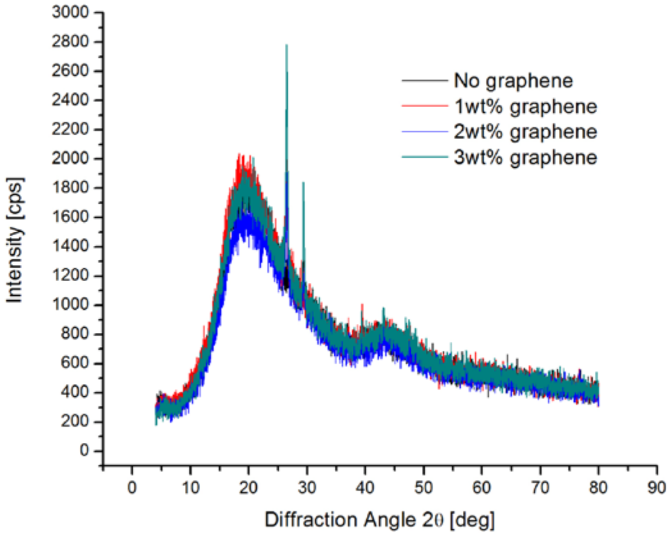
Figure 3. TGA and DTA signatures for nanocomposites with 0 wt%, 3 wt% nanographite

The XRD signature indicates a high exfoliation rate. The fiber glass amorphous part is represented by the smooth curve into figure 4A. As shown in figure 4B, for pure expanded nanographite the highest peak leads to a 0.34 nm basal spacing, which is the distance between two carbon atoms in a covalent bond. For the 1wt%, a 2wt% and 3wt% nanocomposite, the 0.34 nm spacing is also detected. However, no other peak was noticed, a clear indication of exfoliation. Based on these results, a hypothesis can be formulated. The dispersion process was able to exfoliate clusters of graphene sheets into the epoxy system. The secondary peak observed for the 3wt% graphene can be explained by precipitation due to the epoxy system saturation limit as described in Ávila et al. (2008). To be able to obtain a complete exfoliation of individual graphene nanosheets the C-C covalent bonds must be somehow broken. However, as described in Saito et al. (2005), those individual graphene nanosheets have the tendency to roll up.

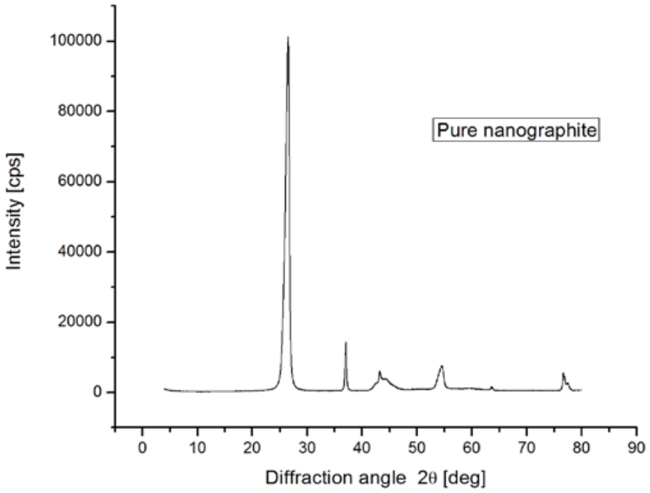
Once the exfoliation process is analyzed, the mechanical characterization must be performed. As described before, three point bending tests were done following the ASTM standard. At least 12 specimens were tested for each configuration. Figure 5A-D describes representative stress-strain curves for 0wt%, 1wt%, 2wt% and 3wt% graphene content. Table 1 described the average peak stress, maximum strain and the Young´s modulus.

Table 1. Average three point bending data

Graphene [wt%]	Peak stress [MPa]	Maximum strain [mm/mm]	Young´s modulus [GPa]
0	333.214	0.0259	14.523
1	336.202	0.0245	15.046
2	339.138	0.0247	15.420
3	318.599	0.0261	13.774

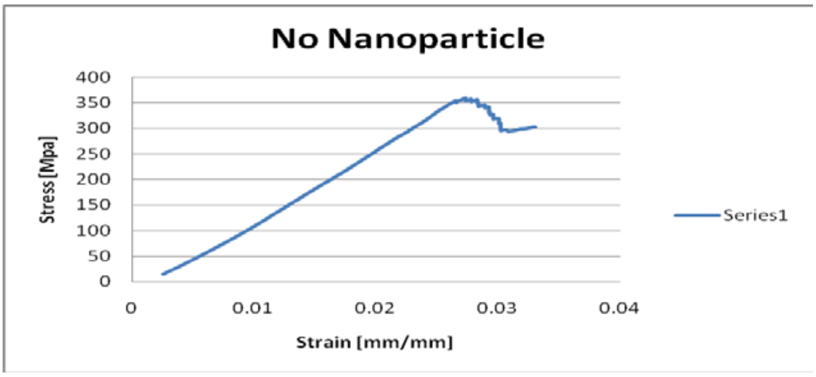


(a)

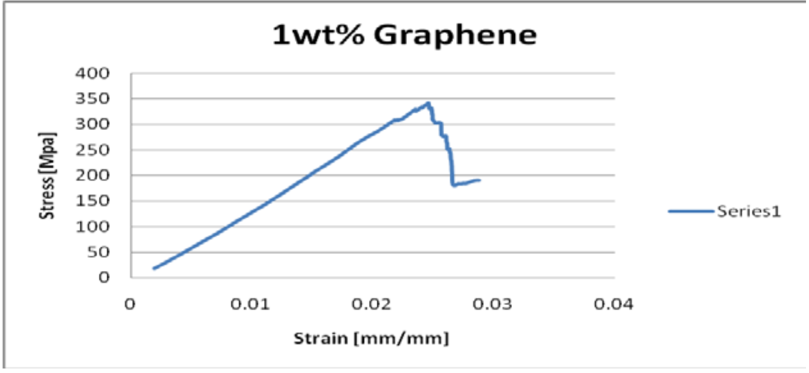


(b)

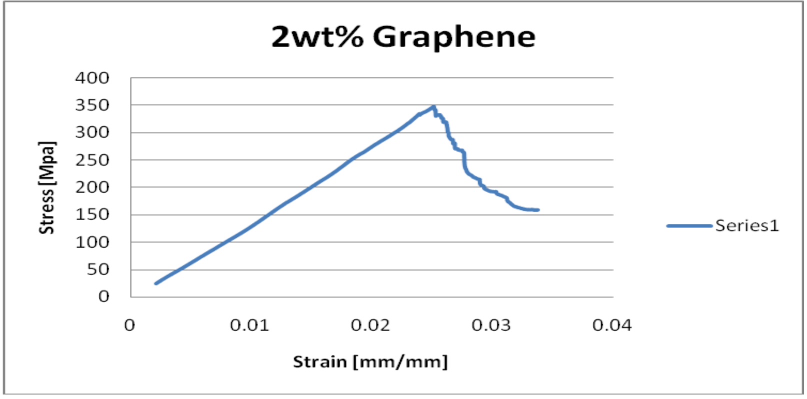
Figure 4. XRD signature. (a) Nanocomposites; (b) Pure nanographite



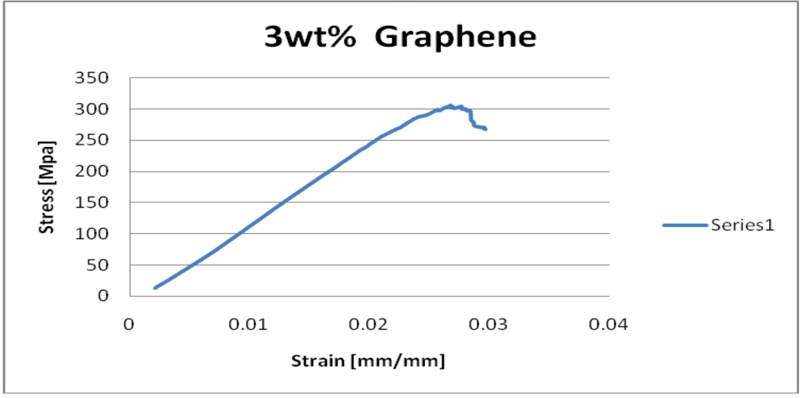
(a)



(b)



(c)



(d)

Figure 5. Stress-strain curves for three-point bending tests. (a) 0wt%; (b) 1wt%; (c) 2wt%; (d) 3wt%

From the data described in Table 1, it is possible to observe a decrease on average stiffness when the graphene concentration reached the 3wt%. As discussed in Ávila and co-workers (2008), the epoxy system has a saturation limit.

Once this limit is reached, any further amount of nanoparticles dispersed is precipitated. These precipitated nanoparticles, in our case graphene clusters, acts as stress concentration locus and crack sources. Those cracks generated during the bending tests lead to a decrease not only on stiffness but also on strength. The 2wt% specimens presented an average increase on stiffness of 6.19%. The average strength was 1.78% higher for the 2wt% nanocomposite. A nonlinear relationship between stiffness and strength seems to be the case for all groups of nanocomposites studied. Such nonlinearity can be attributed to the graphene dispersion inside the epoxy system and their dispersion between the laminate layers, as the damage mechanism for the three point bending tests is based on shear deformation.

4. CLOSING COMMENTS

The first step for the development of a new material for orthesis applications was done. The hybrid nanocomposites developed is based on graphene nanosheets dispersed into an epoxy system and later on infused into fiber glass woven fabrics. The addition on graphene nanosheets into the epoxy system brought as consequence a better thermal stability and an increase on glass transition temperature. By performing high magnifications observations using SEM and TEM, the graphene cluster formation was detected. The X-ray diffraction tests indicate a fully exfoliation process of graphene nanosheets clusters. The best mechanical results were obtained for a 2wt% graphene nanosheets concentration. For concentrations higher than 2wt%, the epoxy system was not capable of absorb and retain the additional nanoparticles dispersed. As consequence, an immiscible third phase precipitated was formed.

Increases on thermal and mechanical properties were obtained using the high shear mix technique described. The new family of nanocomposite seems to be a promising class of material not only for biomedical applications but also in different areas.

5. ACKNOWLEDGEMENTS

We would like to acknowledge the financial support provided by the Brazilian Research Council (CNPq) under grants 470511/2006-0, 472213/2007-5 and 300434/2008-1, and the CAPES Foundation.

6. REFERENCES

ASTM D 790 2003, “Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials”, Annual Book of ASTM Standards.Vol.08 pp 109-121.

Ávila, A.F. Soares, M.I. Neto, A. S. 2007. “A Study on Nanostructured Laminated Plates Behavior under Low Velocity Impact Loadings,” International Journal of Impact Engineering, Vol. 34, n. 1, pp.28-41.

Ávila, A.F. Donadon, L.V. Duarte, H.V. 2008. “Modal Analysis of Nanocomposites Plates,” Composite Structures, Vol. 8, n. 3, pp.324-330.

Ávila, A.F., Andrade, M.C., da Cruz, D.T.L., Dias, E.C., Sousa, D.G. 2009, “Nano-Modified Sandwich Composites under Dynamic Loading Conditions”, In: Proceedings of the 50th AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics, and Materials Conference and Exhibit, Palm Springs, CA, CDROM.

Breger-Lee, D. 1995. “Objective and Subjective Observations of Low Temperature Thermoplastic Materials,” Journal of Hand Therapy, Vol. 8, No. 3, pp. 138-143.

Coppard, B.M. and H. Lohman. 2001. Introduction to Splinting: A Clinical Reasoning and Problem-Solving Approach, Saint Louis: Mosby Publishing Company.

Fess, E.E. 2002. “A History of Splinting: To Understand the Present, View the Past,” Journal of Hand Therapy, Vol. 15, No. 2, pp. 97-132.

Giurintano, D.J. 1995. Basic Biomechanics. Journal of Hand Therapy, Vol. 8, No. 2, pp. 79-84.

Gilman JW. 1999, “Flammability and Thermal Stability Studies of Polymer Layered-Silicate (Clay) Nanocomposites”, Applied Clay Science, Vol. 15, No. 1, pp. 31-49.

Rodrigues, A. M. N. V., 2007, Development of Sandwich Composites for Orthesis Applications and the Effect of Composite’s Orhtesis into Hand Function and Muscle Activation. Doctoral thesis. (Mechanical Engineering) - Universidade Federal de Minas Gerais (in Portuguese)

Rodrigues, A. M. N. V., Miranda, A.D., Pereira, G.S., Leal, V.A., Ávila, A.F., 2007. “A Study on Effect of Usage of Wrist Orthesis into Forearm Muscles” Journal of Therapy Occupational of the Universidade of São Paulo, Vol. 18, pp. 30-37. (in Portuguese)

Saito, R., Dresselhaus, G., & Dresselhaus, M.S., 2005, Physical Properties of Carbon Nanotubes. Imperial College Press.

Vinson, J.R. 1999. Behavior of Sandwich Structures of Isotropic and Composite Materials, Lancaster: Technomic Publishers.

7. RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material included in this paper.