NANOMODIFIED MATERIAL TO ORTHESIS MANUFACTURING

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Abstract
This work focuses on the development and mechanical characterization of a hybrid nanocomposite material to orthesis fabrication. The analyzed hybrid composite was a carbon/nanomodified epoxy system. The reinforcement was a plain fiber wave and the epoxy system was DGEBA. The glass fiber volume fraction was around 60%. The graphene sheets were obtained from expandable graphite. The nanoparticles concentrations were 1 wt%, 2 wt% and 3 wt%, respectively. Nanocomposites were made using a high shear mixer and ultrasound. Mechanical characterization was performed considering the ASTM D 790 three point bending test. Results show that all graphene based hybrid composites have much better mechanical properties than Ezeform®, the conventional material used in orthotic fabrication.

1 Introduction
Orthesis are orthopedic devices used for immobilization, restraint or support of ay part of the body with the intent to restore maximum function, being a standard procedure on patients with motor and sensitive disorders of the hand and upper extremity [1].

Low temperature thermoplastics are the most efficient material for orthesis manufacturing due to their easy manipulation during the orthesis preparation and good mechanical properties [2]. The materials are considered low temperature because they soften in water heated between 57 and 82°C and the therapist can safely mold them directly against a person's skin.

In most of the developing countries, including Brazil, the availability of low temperature thermoplastic materials is very restricted since it is imported and its cost is high. A 3.2mm x 457mm x 601mm 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.

Even though, during the treatment, the therapist has to mold and remold the orthesis to adjust it to the patient's mobility evolution. However, studies [2] show that successive heating can cause reduction of its mechanical properties up to 25% of original ones, promoting a premature fracture. Thus, the need for an alternative material to conventional low temperature thermoplastics is urgent. The new material must present low cost, good mechanical properties and easy mold ability.

Composites materials are an interesting option to solve this problem. These materials are composed of a blending of two or more organic materials in which one is used as matrix and the other as reinforcement [3]. This class of material shows higher specific mechanical properties, i.e. stiffness-to-weight and strength-to-weight than conventional materials. For this reasons, it has being widely used in various engineering applications.

Polymer nanocomposites are a new class of composite materials containing extremely small particles with thickness around 1nm, dispersed in a polymeric matrix. Polymeric nanocomposites possess unique properties that are not shared by conventional composites, because of their large interfacial area per unit volume [4]. A large number of nanoparticles have been used to reinforce polymer materials: carbon nanotubes, clay, silica and carbon nanowires. Among this, carbon-based fillers are of great significance in scientific research and product development.

Graphite nanoparticles have attracted increasing interest, being a promising and cheaper alternative to carbon nanotubes in nanocomposites fabrication. This kind of nanoparticles consists of a stacking of nanosized graphene sheets formed by sp2 carbon atoms, while the carbon sheets are bounded by van der Waals forces [5]. Graphene nanosheets have excellent electrical properties and the same stiffness as single walled carbon nanotubes, which is around 1.0 TPa [6] . Figure 1, clearly shows the several layers of graphene nanosheets.

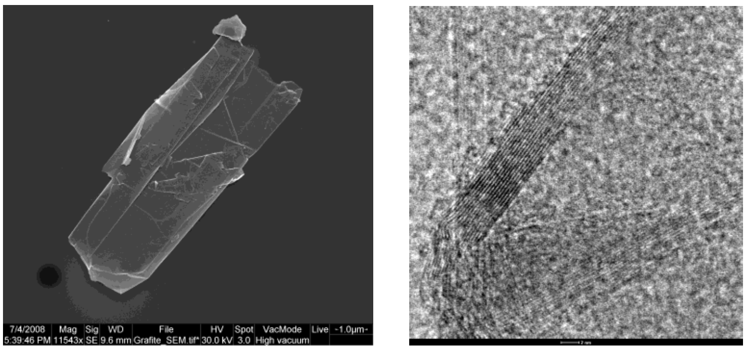

Figure 1. Graphene nanosheets. (a) SEM analysis; (b) TEM analysis

Fibrous composites and nanocomposites can be associated, forming a new type of composite, named hybrid nanocomposite. As described by Ávila et al. [7], hybrid nanocomposites can be defined as multi-reinforced laminated composites. Such multi-reinforcement can be divided in three different levels: the first one is due to nanostructures formation when nanoparticles were dispersed into the polymeric matrix. The second level of reinforcement can be described as the bonds formed between clusters of nanostructures and the macroscopic fibers. Finally, fibers themselves can be defined as the last level of reinforcement. The combination of nanocomposites and fibrous composites improves composites materials properties.

Due excellent mechanical properties of graphene nanosheets and the possibility of make an composite reinforced with this kind of nanoparticles, this research aims to: develop a low cost and high performance hybrid nanocomposite to manufacture orthesis, test its mechanical characteristics and comparing to a conventional low temperature thermoplastic material.

2 Materials and testing methods

Nanomodified composite orthesis material structure (Figure 2) is formed by a kernel region, which was a fiber/glass nanomodified epoxy system laminate.

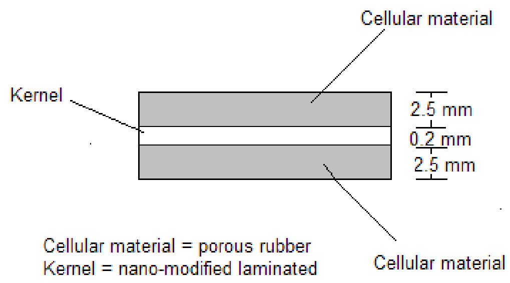

Figure 2. Schematic representation of Hybrid nanocomposite orthesis

The epoxy system was made DGEBA and the graphene nanosheets used has its origin from an expandable graphite (HC-11 IQ) supplied by Nacional Grafite. The nanoparticles concentrations in this research are 1wt%, 2wt% and 3wt%. The fiber reinforcement was a plain glass fiber with density of 180 g/m^2. To properly disperse graphite nanosheets stacks into the polymer, it was used a high shear mixer and an ultrasound. A degassing stage was required to eliminate bubbles generated during the shear mixing.

Hand lay-up technique was used to impregnate and laminate the composite structures. The fiber volume fraction was around 60%. Four glass fiber plies were impregnated with graphene nanocomposites and stacked. After the lamination procedure, composites were cured at 80^{o}C and then, a post cure at 100^{o}C, was applied for 1h. New composites thickness was almost 0.7mm.

The kernel was involved by two layers, one above and another below, of cellular materials. These cellular materials have purpose to allow a perfect fitting between the patient’s skin and the orthesis. Figure 3 shows wrist extension orthosis made with Ezeform® and with the new material.

Figure 3. Schematic representation of hybrid nanocomposite orthesis

Stiffness and strength were appraised by bending test (Figure 4) following the ASTM Standards [8] and compared to a conventional low temperature thermoplastics material called Ezeform®, which thickness was 3.2 mm. All tests were performed using an INSTRON universal testing machine with a displacement rate of 1.53 mm/minut. At least 12 specimes were tested for each experimental condition. ANOVA was conducted to verify statistical difference among the groups and *Bonferroni* test was performed to localize these differences.

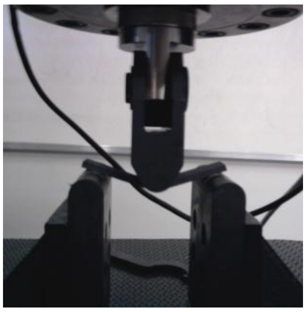

Figure 4: Three point bending test

2 Results and Discussion

Figures 5 and 6 show the flexural modulus and maximal strength values, respectively, for the experimental conditions.

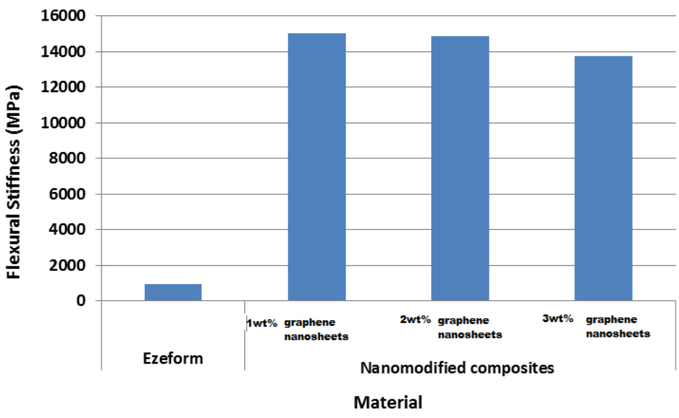

Figure 5: Flexural stiffness of Ezeform® and hybrid composites with different graphene nanosheets loadings

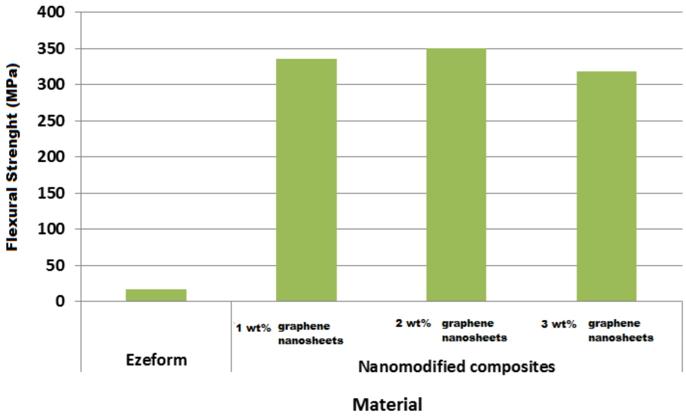

Figure 6: Flexural strenght of Ezeform® and hybrid composites with different graphene nanosheets loadings

As shown, all hybrid composites showed a dramatic improvement in mechanical properties compared to Ezeform®. Significant increase (α=0.00) in the composites maximal strength and flexural modulus was observed for all hybrid composites when compared to the Ezeform® group. For 1wt% group, the superiority was almost 1500% on flexural strength and 1400% on flexural modulus. It can due glass fibers math used as macroscopic reinforcement. These materials are important constituents of composites, providing strength and stiffness. Moreover, the presence of nanosheets located at the surface of the glass fibers can enhance the interfacial properties between the matrix and the fibers, allowing better stress distribution [4,9,10].

Nanomodified composites made with 1 and 2 wt% nanographite showed similar stiffness and strength ($p<0.05$). This can be due to the fact that the same dispersion process was performed in all cases. It suggests that the dispersion process parameters should be modified according to the graphene concentration, allowing better nanoparticles dispersion.

Nanomodified composite made with 3 wt% nanographite showed poor stiffness and strength compared to other nanomodified composites. This can result of nanoparticles precipitation and voids that act as stress concentration locus, leading to cracks and decreasing not only on stiffness but also on strength, as showed by Carvalho et al. [4].

Table 1 shows Ezeform® and Hybrid Composite costs. In addition to elevated mechanical properties, Hybrid Composites costs are at least 60% less than conventional thermoplastics, being useful in orthotic manufacturing in Public Health Service.

Material (45,7 cm x 60,9 cm plate)	**Costs (U$)**
Ezeform®	260
Hybrid Composite	104

Table 1: Materials Costs

4 Conclusions

The first step for the development of a new nanostructured 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. All nanocomposites tested presented better mechanical properties than Ezeform®, the conventional material used to orthotic production.

Among tested nanocomposites, 3wt% showed the worst performance. It suggests that for graphene concentrations higher than 2wt%, the epoxy system were not capable of absorb and retain the additional nanoparticles dispersed, leading to premature fail.

Due excellent mechanical properties associated with low costs, the nanocomposites developed seem to be a promising material not only for biomedical products, like orthotic and prosthetic devices, but also in automotive and aerospace industries.

5 References

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