Increase of Mechanical and Thermic Performance of Polymers with Renewable-Base Nanomaterials to Develop Composite for Fiber Reinforced Polymers Industry

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Abstract. The objective of this research was to evaluate mechanical and thermal performance of a commercial adhesive with the incorporation of renewable-based nanomaterials. Renewable-based CNTs (carbon nanotubes) were synthesized using microwave irradiation of pyrolyzed oat hulls biochar and ferrocene as catalyst. CNTs were mixed with epoxy adhesive and TEPA (tetraethylene pentamine) which were used as curing agents. In the evaluation of mechanical and thermal properties of the composites studied, the samples contained between 0.02-0.1 wt% of CNTs. All composites were cured during 2 hours at 60°C. Mechanical properties (tensile strength and modulus) were tested in a Universal Testing Machine and were evaluated according to ASTM D638. Thermal properties were evaluated using a Thermogravimetric Analyzer. Of the results obtained an improvement of mechanical and thermal properties were observed. Thus, the incorporation of renewable-based CNTs can be a suitable alternative both to reduce fiber reinforced polymer manufacturing costs and in the valorisation of waste biomass.

1. Introduction
A fiber reinforced polymer (FRP) is a composite material consisting of a polymer matrix imbedded with high-strength fibers, such as glass, aramid and carbon. FRPs are known for their non-corrosive, strong, non-conductive nature and lightweight properties, having applications in important sectors, such as energy, construction and the automotive industry [1, 2].

In recent decades, nanostructures as reinforcement (or fillers) in polymer composites have attracted attention due to their advantages in improving mechanical, electrical, and thermal properties. Nanoscale fillers such as carbon blacks, silica, clays, carbon nanofibers and carbon nanotubes (CNTs) have been used [3-5].

CNTs are materials of increasing interest due to their excellent electronic properties as well as their physical and chemical properties. CNTs possess high flexibility, low mass density, large aspect ratio (typically ca. 300-1000) and high electrical conductivity to different applications. CNTs have been used for developing field emitters, transistors, solar cells, fuel cells, biosensors, and other applications as filler material in composites to improve mechanical properties or electrical conductivity [4, 6, 7].

According to reports CNTs’ reinforced epoxy composites have better mechanical properties such as modulus and strength, than neat polymer matrices[8]. However, their high manufacturing cost and...
effective dispersion in the polymer to ensure that CNTs are homogeneously embedded in the matrices[8, 9] are a great disadvantage. Even though various methods for the synthesis of CNTs have been reported such as laser ablation, chemical vapor deposition and arc discharge, all of these methods may present high production costs[10, 11], as they require expensive processing conditions including gases as feedstock, high vacuum levels, high temperature, inert atmosphere. Furthermore, the processing times for CNTs production is long [6].

Thus, new methods for CNTs synthesis have been studied, such as the use of microwave radiation. Microwave-assisted synthesis of CNTs is a low-cost alternative to produce CNTs using low temperature in short reaction times. Moreover, carbon residue materials such as biochar can be used as precursor materials for CNTs growth [9].

Biochar is a carbon-rich porous material obtained by the pyrolysis of lignocellulosic residues. Biochar is characterized as having a high surface area and porosity, and is used traditionally to improve organic matter content in soil [12]. For biochar production, sustainable sources such as lignocellulosic residuals biomass are used. Lignocellulosic residuals are a renewable and abundant material for large-scale conversion with added-value products. As such, biochar production has become a sustainable lignocellulosic residual biomass management solution.

The choice of a carbon precursor for CNTs synthesis has been mainly limited to graphite, so to find other sources of precursors for CNT such as biochar is a topic of interest in recent researches. Moreover, the behavior of CNTs obtained from biochar into polymeric matrices is unknown. Thus, in this research we evaluated mechanical and thermic performance of a commercial adhesive with the incorporation of CNTs obtained from microwave-assisted synthesis using biochar as the biological precursor, which could be a promising alternative to reduce FRP manufacturing costs with improved properties.

2. Methodology

2.1. Materials

The reagents and auxiliary materials used in the experimental work were biochar of oat hull (particle size of less than 75 μm); ferrocene (99% purity, Sigma-Aldrich); Industrial multiwall carbon nanotubes (NC7000, Nanocyl); Acetone (99% purity, SigmaAldrich); Bisphenol A diglycidyl ether (DGEBA) adhesive and tetraethylene pentamine (TEPA) from Britez LTD.

2.2. Experimental setup and procedure

In this study, renewable-based CNTs (CNR) and NC7000 were used. CNR were synthesized by microwave irradiation of pyrolyzed oat hulls biochar to 600°C, according to Hidalgo et al (2019) using ferrocene as a catalyst.

2.2.1. Dispersion of CNTs into epoxy adhesive

NTs were dispersed in acetone into an ultrasonic probe (Omni Sonic Ruptor 400) during 45 min at 60% of power handling capacity and then they were added to the epoxy adhesive. CNTs and the epoxy adhesive were mixed using a mechanical stirrer (Hsiangtai, Shear mixer) at 400 rpm for 10 h. The mixture was then degassed in a vacuum desiccator and used in preparation of composites.

2.2.2. Preparation of composites

The composites (Figure 1) were prepared using a dual asymmetric centrifugal speed mixer (Flacktek Inc. speed mixer DAC 150.1 FVZ), during 4 min at 3000 rpm. Between 0.02 y 0.1% wt of CNTs were added to adhesive. TEPA used as a curing agent, was added to adhesive-to-hardener weight ratio of 1:0.1. The composite was cured into a mold of silicone for 2 h at 60 °C in a curing oven (Memmert UHF-260).
2.2.3. Evaluation of effect of temperature on material properties
To determine the influence of temperature on the mechanical strength of the nanocomposites was measured. The test temperatures ranged from -10 to 60 °C. To perform this evaluation, an environmental chamber (Instron 3119-605) equipped with a CO₂ cooling module was used. Strain gauge extensometers (Instron 2630-100) were used to measure the fracture strain and eliminate errors caused by physical distortion.

2.3. Characterization methods
Mechanical properties (tensile strength, tensile deformation, and modulus) were carried out in a Universal Testing Machine (model 3369, INSTRON) and were evaluated according to ASTM D638. A test specimen with a thickness of 4 mm of the type IV, was used (Figure 2). Data acquisition and processing were made using Instron Bluehill® Lite (versión 2.24) software.

Thermal properties were evaluated using a Thermogravimetric Analyzer (TGA STA 6000, Perkin Elmer). The weight loss of the sample was recorded as function of temperature for obtaining the temperatures corresponding to 5, 10 and 50% (T₅%, T₁₀%, T₅₀%) mass loss and char content. Maximum decomposition temperature (Tₘₐₓ) was obtained from the first derivative (in function of the time) of the TGA curve.

3. Results and Discussion
3.1. Influence of CNTs contents on material properties
In order to homogeneously disperse nanoparticles in the epoxy adhesive, CNTs were dispersed previously in acetone which prevents the agglomeration by van der Waals-forces within the CNTs. Then, to disperse CNTs an epoxy matrix was performed with a mechanical stirrer. Tensile strength of all samples is summarized in Table 1. Of the results obtained it can be observed that the addition of low CNR dosage increases the tensile strength respect to epoxy neat.

Moreover, the relatively large improvement in adhesive by CNR compared to NC7000 could be due to the highest aspect ratio of the CNTs, or could be caused by poor interfacial adhesion leading to
a decrease in tensile strength[13]. Moreover, it is possible to find amino-groups in CNR that could improve the dispersibility in the polymeric matrix, thus reducing the agglomeration. This effect could contribute to a possible reaction between the introduced amino-groups of CNR and the epoxy resin, thus, integrating the CNTs into the epoxy-network structure. Furthermore, as higher filler content there is a reduction of tensile strength which can be attributed to an increasing amount of improper impregnated agglomerates [14].

The introducing of CNTs does not affect the initial decomposition temperature of the matrix, according to Figure 3 (a). In the neat epoxy curve, it can be observed all polymeric matrix is degraded while in the nanostructured composites curves (Epoxy/NC7000 and Epoxy/CNR) a residue of CNTs was observed. All specimens started to decompose around 370°C and completed decomposition around 400°C as shown in Figure 3 (b).

In Table 2, a reduction on degradation temperature with the inclusion of nanotubes was observed, possibly due to the physical hindrance of the nanotubes to the mobility of the monomer[15]. A lower mobility of monomers can result in a lower level of cross-linking and a decrease of total heat of reaction [8]. Total heat of reaction diminished with incorporation of CNR of 26.79 J/g to 20.28 J/g, according to Table 2. However, a slight increase of enthalpy value was observed with the incorporation of CN7000 to 27.89 J/g. Moreover, the residual mass (char) of the neat epoxy sample is about 4.36 wt% at 600°C, whereas the char of the Epoxy/NC7000 and Epoxy/CNR are approximately 5.47 and 5.11 wt%, respectively.

Table 1. Mechanical properties of nanoparticle reinforced composites

| Filler type/ content (wt%) | Tensile strength (Mpa) |
|----------------------------|------------------------|
| Epoxy                      | 0.00 60.29 ± 1.80      |
| Epoxy/NC7000              | 0.03 62.77 ± 0.24      |
|                           | 0.04 56.85 ± 0.41      |
|                           | 0.06 51.88 ± 6.37      |
|                           | 0.08 57.90 ± 1.85      |
|                           | 0.1 52.70 ± 1.43       |
| Epoxy/CNR                 | 0.03 63.88 ± 0.95      |

Table 2. Thermal properties of nanoparticle reinforced composites

| Sample        | Char (%) | T5% (°C) | T10% (°C) | T50% (°C) | Tmax (°C) | Enthalpy (J/g) |
|---------------|----------|----------|-----------|-----------|-----------|----------------|
| Epoxy         | 4.36     | 328.68   | 350.53    | 415.75    | 450.62    | 26.79          |
| Epoxy/NC7000  | 5.47     | 324.65   | 349.05    | 414.18    | 392.38    | 27.89          |
| Epoxy/CNR     | 5.11     | 329.56   | 351.81    | 415.47    | 377.44    | 20.28          |

* Filler content of 0.03wt%
3.2. Effects of temperature in material properties

The results of mechanical properties to the neat epoxy and the CNTs reinforced composites are summarized in Table 3. The specimens were tested at -10°C, 20 °C, 40 °C and 60 °C and according to the results, upon increasing the test temperature, a significant loss in tensile strength was observed. To raise the temperature, a ductile performance was observed followed by a decrease in the load bearing capacity[16].

In the specimens tested, a strong and marked temperature dependency was present. Moreover, between 40°C and 60°C for reinforced composites, a higher tensile strength than that of neat epoxy was reached. An improving in the mechanical properties with CNR-reinforced composites respect to NC7000-reinforced composites was observed.

As the temperature decreased, material rigidity increased, and tensile strength of nanoparticle reinforced samples diminished. In general, the tensile strength of specimens decreased due to the damage caused by the temperature decrease[17]. As shown in Figures 4 and Figure 5, the loss of load bearing capacity increases with temperature tested. This behavior is associated with a progressive loss of material stiffness, turning the brittle characteristics of the polymer into ductility.

Table 3. Mechanical properties of nanoparticles reinforced composites

| Temperature (°C) | Sample          | Tensile strength (MPa) | Max. deformation (mm/mm) | Young’s modulus (MPa) |
|-----------------|-----------------|------------------------|--------------------------|-----------------------|
| -10             | Epoxy           | 73.64 ± 1.90           | 0.0321                   | 2856.3                |
|                 | Epoxy/NC7000    | 53.45 ± 4.35           | 0.022                    | 2768.76               |
|                 | Epoxy/CNR       | 37.70 ± 2.78           | 0.0136                   | 2999.74               |
| 20              | Epoxy           | 60.29 ± 1.80           | 0.0493                   | 2531.81               |
|                 | Epoxy/NC7000    | 62.77 ± 0.24           | 0.0415                   | 2576.31               |
|          | Epoxy/CNR | Epoxy   | Epoxy/NC7000 | Epoxy/CNR |
|----------|-----------|---------|-------------|-----------|
| 40       | 63.88 ± 0.95 | 0.0395  | 43.23 ± 1.55 | 0.0548    |
|          | 46.34 ± 0.59 | 0.0433  | 51.16 ± 0.62 | 0.0401    |
| 60       | 26.98 ± 2.02 | 0.0928  | 28.36 ± 0.38 | 0.127     |
|          | 29.04 ± 0.89 | 0.0689  | 29.04 ± 0.89 | 0.0689    |

*Filler content of 0.03 wt%*

![Figure 4](image-url)

**Figure 4.** Effect of temperature on ultimate tensile strength of epoxy-based composites using CNTs.
- a) The specimens tested at -10 °C
- b) The specimens tested at 20 °C
- c) The specimens tested at 40 °C
- d) The specimens tested at 60 °C

*Filler content of 0.03 wt%*
Figure 5. Effect of temperature on Young’s modulus of epoxy-based composites using CNTs. * Filler content of 0.03wt%.

4. Conclusions
This work discusses the results of an experimental study that evaluated mechanical and thermal performance of a commercial adhesive with the incorporation of renewable-based nanomaterials. CNTs in general exhibit a certain potential to improve the mechanical properties of the polymer. To be compared with an industrial multiwall carbon nanotube, a greater improvement in tensile strength needs to be reached. This could be caused by poor interfacial adhesion leading to a decrease in tensile strength, or due to the presence of amino-groups in CNTs. Moreover, a reduction of degradation temperature with the inclusion of CNTs was observed. The reduction may have been due to the physical hindrance of the nanotubes to the mobility of the monomer.

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