Experimental/Numerical Modeling of Microwave-Pyrolysis-Biochar Reinforced GFRP Biocomposites

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ABSTRACT

This study focuses on developing high-strength biocomposites through the addition of biochar particulate reinforcement in the conventional fiber-reinforced polymer composites. The novel biocomposites, consisting of E-glass fiber, microwave-pyrolysis synthesized biochar, and polymer matrix, are manufactured in a modified pultrusion process. The high-specific-surface-area of biochar particles along with their nanoscale hardness/Young's modulus are attributed up to 25% flexural strength gain in the biocomposite rebars, among others. This research paper presents results from biocomposites tensile-compressive, 3-point bending tests conducted following a design-of-experiments. Experimental results are assessed against computational values derived from a hybrid composite theory on the basis of Halpin-Tsai theory

KEYWORDS: Microwave pyrolysis; Biochar; Pultrusion; Biocomposites; Effective properties

1 INTRODUCTION

Sustainable materials are becoming an important focus of research and innovation as awareness of the changing global environment increases and the availability of non-renewable resources declines. One effective method for the development of sustainable materials is the thermal conversion process known as pyrolysis, in which organic biomass is heated in an anaerobic environment causing devolatilization of the feedstock into biofuels and bio-products. Biochar, the solid byproduct of pyrolysis is a unique renewable material known for its porous, honeycomb-like structure, and high carbon content (Li et al., 2016). Current utilization of biochar employs the unique material structure for assistance in carbon sequestration and filtration applications, as well as soil remediation in agriculture (Luque et al., 2012). Recent considerations have been on the potential for expanded fields of biochar use such as high-power batteries (Saavedra et al., 2018), and advanced composite materials (Bowlby et al., 2018).

Recently, biochar as a particulate material has been considered in various epoxy and wood-laminate composites for increased mechanical and thermal properties (Das et al., 2016A). These studies report a favorable increase in flexural and tensile mechanical properties owing to addition of biochar causing a reinforcing effect due to the particle hardness and mechanical interlocking with the polypropylene matrix (Das et al., 2015). Mechanical interlocking is a favorable interaction between the char and matrix that occurs as the resin flows through the porous biochar prior to hardening during the curing stage. It is the novelty of this paper that by combining the mechanical reinforcing properties of biochar with high tensile strength glass-fiber reinforced polymer (GFRP) composites there is high potential for mechanically superior three-part biocomposites, which utilize sustainable materials.

Therefore, the objective of this research was to further the knowledge of biochar as a particulate-reinforcement through pultrusion manufacturing and mechanically testing of GFRP biocomposites consisting of various matrix volume weights of biochar (5, 10, 20%) in the novel material. Two separate feedstocks were processed through microwave pyrolysis to create biochars, followed by their use in a pultrusion process to manufacture the unidirectional GFRP/biochar biocomposites. Both flexural and tensile mechanical testing was conducted to compare effects of biochar feedstocks and additive volume weights on the biocomposites. Predictive modeling is another important concept for composite materials in order to better understand the impact of various loading conditions prior to use. The ‘Rule of Mixtures’ (RoM) composite theory was first used as a predictive model development tool to estimate both flexural and tensile moduli by combining the known mechanical properties of the E-glass fiber and vinyl-ester resin, with the biochar modulus found through nanoindentation tests. ABAQUS finite element was further used to create a representative volume element (RVE) model of the three-part biocomposites. Applying a uniform plane-strain along the fiber direction and solving for the RVE stress/strain values, allowed for homogenization of the values through MATLAB software in order to calculate the effective tensile modulus of the biocomposites. Both the RoM and homogenized tensile modulus values were compared against the experimentally-obtained tensile modulus to assess the validity of the RoM and RVE models when applied in novel three-part biocomposites.

2 MATERIALS AND METHODS

2.1 Biochar production and characterization

Biochar was produced from two separate feedstocks through pyrolysis using a 0.051 m^3 single-batch microwave reactor capable of 3,000 Watts microwave power. The chosen feedstocks were hemp straw, and softwood (spruce and fir mixture) chips. Each feedstock underwent pyrolysis at a microwave power level of 2,700 watts, for a run time of 60 minutes and biomass loading of 1,000 grams. Pyrolysis was carried out under N_2 environment. Each experiment was run three times in order to gain a statistical significance in the collected data. To capture and understand the real-time temperature profile during pyrolysis, K-type probe thermocouples and a data logger were used. Table 1 gives the captured heating rates and residence temperatures during pyrolysis of each feedstock.

Table 1: Microwave pyrolysis heating results

Feedstock	Temperature, ^{o}C	Heating rate, ^{o}C/min
Softwood	659.8 ± 59.9	38.7 ± 13.3
Hemp	604.2 ± 3.3	49.2 ± 10.8

In order to understand the effects of biochar as a particulate reinforcement for unidirectional fiber-reinforced composites and to aid in the predictive modelling of the composites, the Young’s modulus and hardness values of the biochar were obtained from an iMicro Nanoindenter using a 1mN load. An average of ten indentations was performed on cold-mounted biochar samples, polished with decreasing grit sizes from 500 to 1,200 microns. The results of nanoindentation are displayed in Table 2. Finally, prior to biocomposites manufacturing, biochar was grinded and sieved with an average particle size of 190 to 230 microns used for biocomposites manufacturing.

Table 2: Nanoindentation testing results

Biochar Sample	Young’s Modulus (GPa)	Hardness (GPa)
Softwood	5.64 ± 0.93	0.51 ± 0.19
Hemp	5.98 ± 1.05	0.26 ± 0.11

2.2 Biocomposites manufacturing and testing

The composites for this study were manufactured in a pultrusion process. Roving from 22 spools of E-glass fiber was pulled from a creel system through the vinyl-ester resin bath, then through the heated die by the end pulleys. The finished rebars exited the pulley with an approximate diameter of 9.3 mm, were cut to preferred lengths, and tested. Biocomposites were manufactured by keeping the fiber volume percentage set at 62% and decreasing the resin volume percentages as the biochar volume percentage increased. For both softwood and hemp char samples biocomposites were created at 5, 10, and 20% matrix volume loading. Control rods containing no biochar were also created from comparison.

Biocomposites mechanical testing consisted of both flexural and tensile tests. flexural testing was accomplished in an Instron Model 1332 load frame driven by an Instron 8500 series controller, performed in a three-point bending jig. Test parameters for flexural testing, including strain rate, sample length, and span were set in accordance with the corresponding ASTM D790-17. Composite stress and strain data were gathered and analyzed, for six tests per sample, to discuss a statistical average of the effects from biochar loading on the flexural yield strength and modulus of the biocomposites.

Tensile testing was performed with an Instron universal testing machine, Model 5985 with 250 kN capacity electromechanical device. Displacement controlled testing was performed at a strain rate of 2 mm/min. An integrated load cell measured tension force while a 50 mm gauge length Instron extensometer placed at mid-span of the rebars measured strain. Tensile testing was performed for three tests per sample.

2.3 Biocomposite micromechanical modelling

An important aspect of composite application is the ability to accurately predict how a composite will behave under various mechanical loadings. For two-part composites, a common predictive method is the ‘Rule of Mixture’ or RoM, shown in Equation 1. This theory builds off of the iso-stress model and indicates that the composite modulus (E_c) is a combination of the fiber and matrix constituents’ individual moduli (E_f, E_m, respectively) versus their individual composite volume fractions (V_f, V_m, respectively) (Daniel and Ishai, 2005).

$$E_c = E_f V_f + E_m V_m \tag{1}$$

Assumptions made when using the RoM theory include uniform dispersion of fiber, perfect bonding between fiber and matrix, and matrix is free of voids. In order to apply the RoM method for the novel three-part biocomposites, further assumptions were made that the mixture of biochar particle into the vinyl-ester resin prior to pultrusion created a new complex matrix for which RoM could also be used to calculate the ‘convoluted’ matrix modulus as in Equation 2. The subscripts bc and r represent the biochar and resin contributions, respectively. Using the new matrix modulus, the total biocomposites modulus was calculated from the RoM as in Equation 1.

$$E_m = E_{bc} V_{bc} + E_r V_r \tag{2}$$

A more advanced predictive method used for finding the effective elastic moduli of the biocomposites was through the homogenization of a representative volume element (RVE) of the biocomposites structure. First, an RVE model representing the convoluted matrix was created, which was then superimposed periodically to obtain the complete biocomposites RVE. ABAQUS finite element (FE) software was used to compile and analyze, by imposing a uniform strain to each RVE and solving for individual nodal stress and strain of the RVE mesh. Homogenization calculations (Kalamkarov, 1992) were completed, according to Equations 3 and 4, to find the effective stress (σ_{11}) and strain (ε_{11}) in the fiber direction of the models, where v^k is the integration point volume of the mesh, and V is the total volume of each RVE.

$$\sigma_{ij} = \frac{1}{V}\int_V^1 \sigma_{ij}\, dV = \frac{1}{V}\sum_{k=1}^{N_p} \sigma_{ij}^k v^k \tag{3}$$

$$\varepsilon_{ij} = \frac{1}{V}\int_V^1 \varepsilon_{ij}\, dV = \frac{1}{V}\sum_{k=1}^{N_p} \epsilon_{ij}^k v^k \tag{4}$$

The effective elastic modulus of the biocomposites was then found by dividing the homogenized stress by the homogenized strain. In order to use these micromechanical models, the individual moduli of the E-glass fiber and vinyl-ester resin (provided by the supplier) were used in conjunction with the experimental modulus of biochar material found through nanoindentation technique.

2.4 Biocomposite finite element modelling

Biocomposites modelling consisted of two stages, the first being the biochar-matrix RVE model, and the second being the single fiber biocomposites RVE model. Some assumptions were made in-order to simplify the FEA model, including periodic and regularly spaced fibers and biochar particles, all constituents are elastic in nature, fibers and particles are homogeneous and perfectly bonded to the matrix, biochar particles are spherical and solid, the composite is free of voids or irregularities (Potluri, 2018). Assuming a homogenous and periodic biochar mixture inside the resin, a square RVE model was chosen for the biochar/resin (or the convoluted) matrix model. ABAQUS model was then rendered by using a 100 unit^3 cubed matrix model and adjusting the spherical biochar particle dimensions to represent 5, 10, and 20% biochar volume inside the matrix.

For homogenization of unidirectional fiber-reinforced composites, single fiber unit-cell models are often chosen due to the simplicity of the RVE model allowed by the assumption of periodically spaced fibers (Kalamkarov, 1992). Figure 5 displays the unit-cell RVE model, containing a single cylindrical fiber surround by matrix material. The fiber-matrix model was created in ABAQUS, as a cubic RVE of dimensions 50x50x10 units^3, and the fiber diameter calculated to represent 62% of the composite volume fraction. The length of the fiber was chosen as 10 units in order to reduce computational time by reducing the total mesh size (Potluri, 2018). In order to develop the RVE into the biocomposites model, the biochar/resin model was positioned periodically to create the cubic shape into which the fiber is centred (Figure 1).

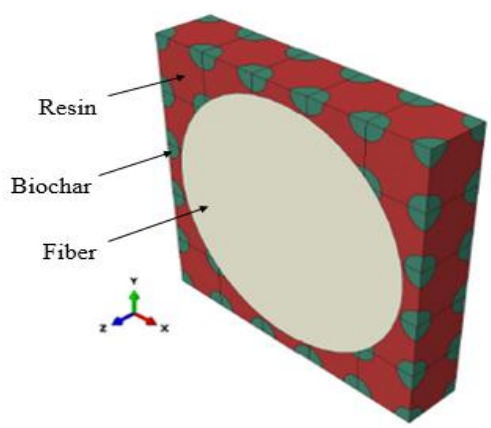

Figure 1: Biocomposite finite element analysis model

The biocomposites unit-cell model was created representing 5, 10, and 20 vol.% biochar, and material properties (Young's modulus, Poisson's ratio) were assigned to all the components based on their individual constitute properties. Owing to the spherical shape of the biochar particles, a tetrahedron mesh was assigned to the model. Assuming perfect bonding of all the biocomposites constituents, cohesive bonding constrains were added to the model components. Finally, in-order to facilitate the usage of Hook's Law to solve for the effective modulus in the fiber-direction, a uniform strain was given according to Equation 5

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ z \end{pmatrix} \tag{5}$$

Upon solving the model in ABAQUS, data files were processed and compiled in MATLAB through the usage of the Abaqus2Matlab plug-in (Papazafeiropoulos et al., 2017). MATLAB code was included to first extract the stress (E_{33}), strain (ε_{33}), and integration point volume (IVOL) data for the solved RVE model, which was then used for homogenization calculations to compute the composite model effective stress, strain, and finally homogenized modulus.

3 RESULTS

3.1 Biocomposite flexural properties

Unidirectional fiber reinforced composites are characteristically strong in tension due to the high tensile strength of the fiber reinforcements. As flexural strength is a more elaborate property, with dependence on both tensile and compressive regions, many unidirectional pultruded composites are much weaker in flexure than tension, relying on the weaker matrix for support in the compression region of flexural bending. Adding biochar as a particulate reinforcement provides the opportunity to improve the flexural behavior of the overall biocomposites as the hard, porous particles contribute to a more elaborate and stiffer biocomposites matrix (Ogunsona el al., 2016). To further investigate the benefit of biochar as a reinforcement, three-point bend tests were carried out six times and statistically averaged for each biocomposites sample, as well as the control samples lacking biochar. While three-point bending failure still occurred in the compressive region for all samples, the results displayed in Figure 10 reinforce the theory the biochar provides strong support in the compressive region and increases the overall flexural strength of the biocomposites.

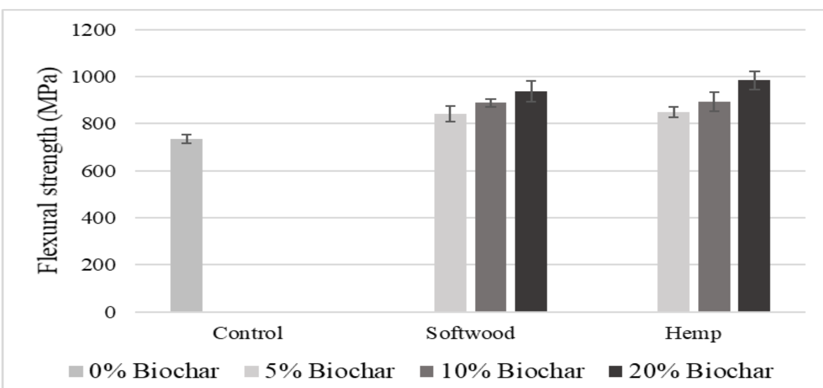

Figure 2: Composite flexural strength results

It is evident from Figure 2 that as the biochar loading (in vol.%) increased, going from 5% to 20%, the flexural strength increased along with it; however, the increment is not linear. The largest gain in strength was recorded at 985 ± 38 MPa in HM_20, which when compared with the FRP composite (control) strength is about 34% higher.

Table 3 compares the flexural modulus performance recorded via three-point bend testing and computationally-obtained using RoM technique. Hemp biochar biocomposites are found to have higher theoretical flexural modulus owing to the larger modulus of the hemp biochar, and there is no statistically-significant difference among HM_5, HM_10, and HM_20. Looking at the difference (in %) column in Table 3, it is apparent that while the RoM model gives a 'fairly-accurate' effective flexural modulus, it however overestimates the same, in comparison with experimental flexural modulus. This finding bodes well with the generally-accepted notion where RoM is considered to be the upper-bounds estimate of the composite modulus, as it does not take into consideration composite defects such as bonding or voids (Bakis and Ripepi, 2015).

Table 3: Comparison of experimental and rule of mixtures flexural modulus

Specimen nomenclature	Flexural modulus (experimental), GPa	Flexural modulus (RoM), GPa	Difference, %
Control	42.63 ± 0.52	46.48	9.03
SW_5	44.26 ± 0.82	46.52	5.11
SW_10	44.76 ± 1.44	46.57	4.04
SW_20	45.21 ± 1.10	46.66	3.21
HM_5	43.98 ± 1.05	46.53	5.79
HM_10	44.42 ± 0.64	46.58	4.86
HM_20	45.38 ± 1.17	46.69	2.89

3.2 Biocomposite tensile properties

The averaged tensile strength results are displayed in Figure 13. Evidently, the addition of biochar to the GFRP composites increase the ultimate strength; nevertheless, any apparent connection between biochar loading variation and tensile strength is not there. This overall increase in ultimate tensile strength in the biocomposites can be explained from the viewpoint that addition of biochar to the GFRP matrix created a convoluted matrix, from which to hold some of the tensile stress during longitudinal loading. The largest tensile strength gains were recorded at 10.1% and 12.5% (in comparison with GFRP) respectively in softwood- and hemp-reinforced biocomposites.

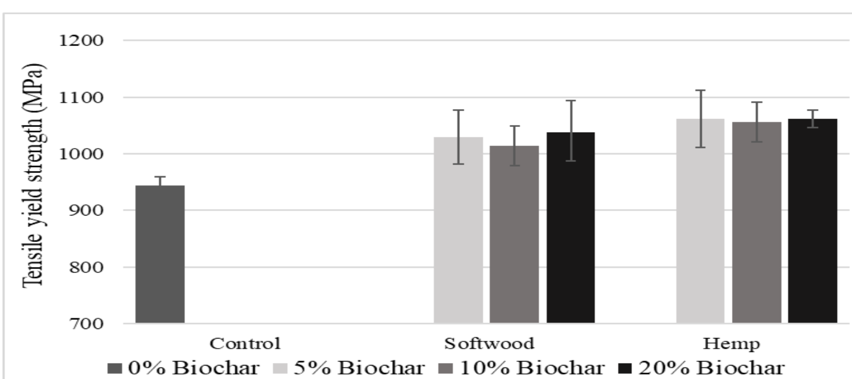

Figure 3: Composite tensile strength results

Table 5 compares the RoM modulus versus the experimental modulus, complementing the percentage difference between them. Observing the experimental modulus results there is a small tensile modulus gain from the addition of biochar to the composite material. This gain in tensile modulus is not as large as the flexural modulus increase due to the effect of the stiffest component (E-glass), holding the majority of resistance to deformation in longitudinal loading. Studies on composite matrix, combining neat polypropylene and biochar reported that biochar addition can increase the overall tensile modulus due to enhanced stress transfer properties between the polypropylene and stiffer biochar from mechanical interlocking (Das et al., 2016B). As to the decline of tensile modulus between 10 vol.% to 20 vol.% biochar in both species, this trend is inconclusive to the proportionality between tensile strength and tensile modulus. A possible explanation can be that as the biochar load increases, concern on the quality of interfacial bonding arises, due to potential agglomeration of particles inside the matrix decreasing overall bonding strength.

It is evident that RoM modulus dominates in both softwood and hemp biocomposites in comparison with respective experimental modulus, which again is linked to the fact that RoM is considered an upper-bounds limit of the modulus found through ideal conditions and neglecting composite defects such as voids or non-perfect bonding. Moreover, from comparison of the control GFRP results with the RoM, it can be argued that there could be additional defects in the fibers themselves which have had a lengthy storage life.

Table 4: Comparison of experimental and rule of mixtures tensile modulus

Specimen nomenclature	Tensile modulus (experimental), GPa	Tensile modulus (RoM), GPa	Difference, %
Control	42.24 ± 0.89	46.40	9.85
SW_5	42.35 ± 0.24	46.45	8.05
SW_10	42.99 ± 0.23	46.50	8.16
SW_20	41.20 ± 0.33	46.60	13.11
HM_5	41.71 ± 0.54	46.46	11.39
HM_10	42.80 ± 0.49	46.51	8.67
HM_20	41.90 ± 0.76	46.63	11.29

3.3 Biocomposites tensile modulus obtained via FE computational modeling

To the best of authors' knowledge, there is no clear consent among scientific communities when it comes to micromechanical modeling of composite flexural behaviour. Therefore, the following section describes the results pertaining tensile modulus of biocomposites via homogenization of an FE model.

When comparing the micromechanical modeling results to the experimental results found through tensile testing (reported in Table 10 below), it is apparent that the finite element model also overestimates the tensile modulus of the biocomposites. Explanations owing to the ideal assumptions of the models compared to potential defects of the composites have been stated throughout this study. The FE model could also further be improved through advanced modeling of the porous properties of the biochar and flow of the resin through said pores. It is further noted that results may improve by adopting a model that better represents the randomness of the biochar particle distribution inside the resin matrix [14].

Table 5: Comparison of experiment and finite-element model tensile modulus

Specimen nomenclature	Tensile modulus (experimental), GPa	Tensile modulus (FE), GPa	Difference, %
Control	42.24 ± 0.89	46.417	9.89
SW_5	42.35 ± 0.24	46.465	9.72
SW_10	42.99 ± 0.23	46.519	8.21
SW_20	41.20 ± 0.33	46.628	13.17
HM_5	41.71 ± 0.54	46.472	10.25

HM_10	42.80 ± 0.49	46.532	8.72
HM_20	41.90 ± 0.76	46.656	11.35

4 CONCLUSIONS

The goal of this study was to further understanding of the potential of biochar particle as a reinforcement to the matrix of continuous glass-fiber reinforced polymer composites. The novel three-part biocomposites were created by first synthesizing biochar from two separate feedstocks in a microwave pyrolysis thermal conversion process, then manufacturing the rebars in a pultrusion process, with increasing volume additions of biochar. The biochar from two different feedstocks was separately characterized for aid in the investigation of their effects on the biocomposites flexural and tensile properties. The composite 'Rule of Mixture' theory was employed to analytically calculate the flexural and tensile moduli of the novel biocomposites. Finally, a representative volume element (RVE) model was created and analyzed through ABAQUS software, with the results used through homogenization over RVE unit-cell volume to calculate the effective tensile modulus of the biocomposites. In summarizing, the following conclusions are drawn:

1. The addition of biochar as a reinforcement to the matrix of GFRP composites significantly increased the flexural strength of the biocomposites (up to 34% at 20% hemp biochar volume loading).
2. The addition of biochar significantly increased the flexural modulus of the biocomposites (up to 6.5% at 20% hemp biochar volume loading).
3. When comparing the hemp and softwood biocomposites mechanical performance, main contributors to the increase of flexural properties were the biochar modulus and high specific surface area, accommodating superior mechanical interlocking of the biochar/resin creating a stiffer matrix.
4. The addition of biochar increased the tensile strength of the biocomposites by creating an elaborate matrix for bonding (up to 12.5% at 20% hemp biochar volume loading).
5. The addition of biochar did not significantly change biocomposites tensile modulus as the majority of stress was held by the stiff fibers during tensile loading.
6. Composite RoM theory was successfully used for both flexural and tensile moduli prediction, but it overestimated the behavior over experimental properties due to the ideal-case assumptions of the model (up to 9 and 13 % difference for flexural and tensile modulus respectively).
7. The developed biocomposites RVE model was able to predict the homogenized tensile modulus of the novel biocomposites with some success (up to 13% difference), with potential for refinement by incorporation of the biochar porous properties.

Based on the results and conclusions of this study it is apparent that biochar can be used to create mechanically superior glass-fiber reinforced polymer composites, through the utilization of renewable biomass waste. This novel biocomposite material has vast industrial potential, due to the increased flexural strength. Aerospace, defense, construction, and manufacturing could all benefit from the adaptation of this sustainably strengthened biocomposite.

The micromechanical modeling usage and comparison throughout this paper was also highly important as it proved the validity of these two common modeling techniques when used for our novel three-part composite. These predictive models will be important in furthering the adaptation of this material by industry and can both be further improved upon with refined biochar modeling conditions.

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