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Flexural strength behavior in pultruded GFRP composites reinforced with high specific-surface-area biochar particles synthesized via microwave pyrolysis

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ABSTRACT

This research focuses on the development of novel biocomposites with improved flexural strength properties, obtained from merging conventional pultruded glass FRP (GFRP) composites with carbon-based biochar particles synthesized via microwave MW) pyrolysis method. A comprehensive design-of-experiments is carried out by varying: (1) biomass feedstock, (2) MW processing parameters, and (3) biochar vol.% in the pultrusion biocomposites manufacturing process. Results show over two times flexural strength gain in biocomposites reinforced with a 10 vol% biochar, from 450 MPa to 970 MPa, without compromising tensile strength. The increase in flexural strength is attributed to a combination of high SSA and the hardness of the biochar particles. High hardness enhanced the biocomposites compressive performance during bending, causing the failure mechanism to shift from compressive-dominant to tensile-dominant. High porosity of the biochar created a mechanical interlocking between the honeycomb structure of the biochar and the cured polymer matrix.

1. Introduction

Renewable biomaterials, and value-added products, produced via biomass conversion has gained significant interest in recent years. Concerns related to global warming, as well as declining fossil fuel reserves, have acted as a catalyst to promote studies and expand the research field. CO_2, the most prevalent greenhouse gas, has experienced an increase in atmospheric concentration from 280 to 396 ppmv from pre-industrial to current levels, respectively [1]. Greenhouse gas emissions, if not acted upon, will raise atmospheric temperatures substantially, yielding irreversible damage to the environment and human livelihood. With knowledge of environmental issues, as well as an understanding that they will only continue to grow, scientists and engineers are urged to begin to develop products that are not only functional, but also sustainable.

Biochar is a unique and versatile material, which has established value in various applications. The most developed include: soil amendment, carbon sequestration, and contaminant removal [2–4]. In order for a biochar-based system to be effective and resilient, it is necessary to develop multiple application routes. Research for the utilization of biochar as a reinforcing filler in polymer composites remains in its infancy, but early studies have shown promising results. The University of Auckland, New Zealand, is the leader in this field and has published several papers investigating the manufacturing, characterization and testing of biochar-polypropylene and biochar-wood fiber-polypropylene biocomposites [3–5]. Mechanical tests results showed validity to biochar use in composites, where increasing content of biochar continuously improved the tensile modulus and flexural strength/modulus of the resulting composite. The porous, honeycomb structure of biochar allowed the molten polymer to infiltrate the pores of the biochar, which created a mechanical interlocking upon curing [6]. Researchers have tested for carbon particles, such as spherical carbon black particles, reinforced in carbon fiber-GFRP/polymer matrix hybrid composites to assess their self-monitoring potential [7,8]. They showed that the use of graphite carbon flakes is particularly suitable for high sensitive functionalities, while the use of carbon black particles increases the composite capability to memorize maximum applied load. This presents promise of carbon-based particles as self-monitoring material that can correlate the change of electrical resistance of a conductive phase and the stress/strain occurring to the host composite [9].

The high porosity, along with high surface area, of biochar is what has enabled its success in many of the aforementioned applications. This unique structure is produced at high reaction temperatures with

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fast heating rates, which enables the rapid release of volatiles. Thus far, only conventional pyrolysis has been employed for producing biochar used in biocomposites fabrication, which has heating rates of < 20 °C/min. Microwave pyrolysis has significantly higher heating rates, commonly in excess of 140 °C/min. Further advantages include: selective and uniform heating, and instantaneous on/off control. Studies have verified that a higher quality biochar is produced from microwave pyrolysis, with higher surface area and porosity [10–12]. This study employs microwave pyrolysis for the production of biochar used in biocomposites fabrication.

To the best of authors' knowledge, no studies have been performed that introduce biochar as a particulate reinforcement in pultrusion manufacturing. It is obvious that wood-fibers cannot compare in strength to industry norms, such as glass fibers. Therefore, it is of interest to see how biochar will perform when added to the pultrusion process, to produce a composite with enhanced flexural strength, while maintaining tensile properties.

The objectives are to (a) assess the viability of microwave pyrolysis technique to synthesize high specific-surface-area biochar particles from woody and agricultural biomass and (b) the possibility of introducing these particles as a reinforcing filler material in pultruded glass-fiber-reinforced-polymers (GFRP) to enhance the flexural strength of the resulting composite structure. A custom-designed pultrusion machine is employed in this study.

2. Materials and methods

2.1. Biochar production

Microwave pyrolysis was performed at constant parameters while the feedstock source was varied. This enabled accurate comparison of the biochars produced from different biomass sources: maple, spruce and switchgrass. Table 1 shows the pyrolysis parameters that were employed. A total of ten microwave pyrolysis experiments were carried out for each feedstock, and the data presented represents average values and trends observed.

Reaction temperature is a dependent variable, based on the power level and amount of microwave absorber used. Therefore, 700 °C is an average value with ± 50 °C, during the duration of the pyrolysis experiment. Previously produced biochar was used as the carbon microwave absorber (CMWA) at a loading rate ten percent (wt.%). Fig. 1 shows the microwave pyrolysis and data acquisition schematic.

2.2. Biochar characterization

Based on literature, common biochar characterization tests were performed to determine quality of the produced biochars. Elemental analysis employed the use of a CHN Elemental Analyzer, and tests were performed according to ASTM D5373. The ash (dry-basis) contents were measured following the ASTM D1762-84 protocol, employing the use of a muffle furnace.

Porous properties of interest included: porosity distribution (cc/g) and BET (Brunauer-Emmett-Teller) surface area (m^2/g). These were obtained from nitrogen absorption isotherms at 77 K produced from physiosorption analysis, using a gas sorption analyzer (Autosorb 1). Further study of the biochar structure utilized SEM imaging (scanning electron microscopy), employing a model JEOL JSM 6400 SEM. The hardness and Young's modulus values of the biochar particles and biocomposites were obtained using a iMicro Nanoindenter (Nanoscience Instruments, Phoenix, AZ) using a 500 mN load. An average of 10 indentations was performed on cold-mounted biochar and biocomposite specimens separately.

Table 1
Microwave pyrolysis process parameters.

Raw biomass	Carbon microwave absorber (CMWA)	Microwave power	Reaction temperature	residence time
100 g	10 g	500 W	700 °C	60 min

2.3. Biocomposites manufacturing and testing

Biocomposites fabrication was central to this study, utilizing an in-house, custom pultrusion machine. Urethane modified, bisphenol vinylester was employed for use as the resin matrix, and fiber and particulate reinforcements were added via the pultrusion technique. Fig. 2 shows the pultrusion manufacturing schematic. Unidirectional E-glass fibers were used for fiber reinforcement, while varying biochar species were tested as a novel particulate reinforcement.

Reinforcing fibers were pulled from a creel system into a resin bath, through a system of fiber guides, and into a heated die for shaping and curing. The resin bath contained a uniform mixture of vinylester resin and biochar particles. Organic peroxide catalysts were introduced in the resin mixture in order to polymerize the resin while it moved through the shaping die. An internal lubricant, Technick Products 190-TG, was used to ensure that the biocomposites could move through, and release from, the die. A peroxide initiator, Norox Pulcat AMB, was used to initiate the polymerization. The fibers were thoroughly wetted with resin and biochar in the resin bath, and the polymerization took place in the heated die at a temperature of 150 °C. The pulling force was maintained by a set of counter-rotated wheels, which provided a consistent pulling speed of 30 cm/min. A rigid, cured biocomposite rod exited the die with a circular profile of Ø9.2 mm. Finished products were cut off to desired length by a cut-off saw. The quality of the rods was checked by visual inspection, with any defects being clearly visible. Volume fractions of E-glass fibers and vinylester matrix were set at 62% and 38% respectively, based on previous literature [13]. Species of biochar particles were introduced at five and ten percent volume fractions [6], of the biocomposites matrix. Table 2 shows the properties of the glass fibers and vinylester resin used in this study, respectively.

Pultruded biocomposites were tested for flexural strength and modulus properties using an Instron Model 1332 load frame driven by an Instron 8500 series controller. Test parameters for flexural testing, including strain rate, sample length, and span were set in accordance with the corresponding ASTM D790.

3. Results and discussion

3.1. Biochar properties

A main focus in biochar characterization was to analyze the highly porous, honeycomb-like structure of the biochars. Therefore, SEM images of various samples were taken, and are presented below in Fig. 3. Columns identify the feedstock source, while the rows indicate the magnification level. Spruce, maple, and switchgrass biochar SEM images are given by row one (images 'a' and 'd'), row two (images 'b' and 'e'), and row three (images 'c' and 'f'), respectively. Column one consists of images of magnification 1000×, while images in column two were taken at 2000× magnification. As evident, all biochar structures are highly porous, but contain significant variation in pore sizes. Biochar produced from maple showed the cleanest pores, being almost free of carbon-like adhesives; these results agree with SEM biochar structures seen in a study performed on cylindrical wood blocks [14]. Spruce images showed, on average, smaller pores but in a higher quantity.

The BET surface area and porosity distribution of biochars were found through physiosorption analysis, and are shown in Table 3 below. Biochar from spruce (softwood) showed the most promising results with a surface area of 200 m^2/g. Maple (hardwood) followed with a result of