EVALUATING THE POTENTIAL OF BIOCHAR AS REINFORCING FILLER IN GLASS FIBER-REINFORCED POLYMER COMPOSITES

Bowlby, L.K., Lander, J.J., Afzal, M.T., Saha G.C.*
Department of Mechanical Engineering, University of New Brunswick, 15 Dineen Drive, Fredericton, E3B 5A3, Canada
* Corresponding author (gsaha@unb.ca)

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ABSTRACT

This research project focuses on the design, manufacturing, characterization, and mechanical testing of a novel biocomposite by combining two materials research areas, namely fiber-reinforced polymer composites and renewable bioenergy materials, specifically biochar. This is the first study to attempt to utilize a biological based carbon source (biochar) as reinforcing filler in well-established glass fiber-reinforced polymers (GFRP). In industry, carbonaceous materials, including carbon black, carbon fibers, and more recently, carbon nanotubes and graphenes, have been widely used as reinforcing materials in polymer composites. Due to the renewable nature and cost effectiveness of biochar it is necessary to evaluate its potential in carbonaceous applications. In this research, two distinct biochars were synthesized from biological feedstocks, namely, hardwood (maple) and softwood (spruce) at a power level of 500 Watts, using the microwave pyrolysis technique. They were then characterized for porous properties, including BET surface area, and SEM imaging to analyze the structure. The biochar feedstocks were introduced to the biocomposite design-of-experiments to produce custom-designed biocomposite rebars using a modified pultrusion machine. The method is an advanced composites manufacturing technique, which is also one of the most cost-effective processes available. The three constituents of the composites are biochar, glass fiber, and vinylester resin. Finally, the three-point flexural bend tests were conducted to evaluate the flexural strength and modulus properties of the novel biocomposites and compare those to their conventional GFRP counterpart.

1 INTRODUCTION

Concerns related to the well-being of the environment are consistently growing and constantly publicized. Many processes and products used in major human activities today, such as energy generation, construction and manufacturing, are harmful through various means, and are unsustainable. 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. This research takes a step in this direction, by investigating a renewable material that could have application in composite fabrication.

Carbonaceous materials, including carbon black, carbon fibers, and more recently, carbon nanotubes and graphenes, have been widely used as reinforcing materials in polymer composites. These materials have shown to increase mechanical and thermal properties, as well as provide other functional features such as moisture resistance and electrical conductance [1]. Biochar is a carbonaceous material that is produced through the pyrolysis of various forestry and agriculture resources. Commonly, biochar is produced using waste from these industries, which allows it to be produced inexpensively. Due to biochars renewable nature and cost effectiveness, it is necessary to evaluate its potential in carbonaceous applications.

In order for a biochar-based system to be effective and resilient, it is necessary to develop multiple application routes. Biochar is a unique and versatile material, which has established its value in a few pertinent applications. These include: soil amendment, carbon sequestration, and contaminant remediation [2]. Biochar has a unique structure that is highly porous and thermally stable. The highly porous structure allows it to retain nutrients and water, while also increasing cation exchange and raising the pH level of the soil. This yields improved soil quality, making biochar an effective soil amendment. The high stability of biochar enables it to resist microbial degradation and mineralization, allowing it to remain in soil for hundreds, and even thousands of years. The plant matter that was pyrolyzed to produce biochar, absorbed CO_2 from the atmosphere while growing, but did not release CO_2 because the carbon became trapped in the biochar; this creates a carbon negative process. This technique is called carbon sequestration, and is an effective strategy to remove excessive greenhouse gases from the atmosphere. Contaminant remediation is achieved through the high specific surface area (SSA) and porosity of biochar. These properties allow it to absorb organic and inorganic contaminants from a contaminated media, restoring the media to its original composition [3].

Research for the utilization of biochar as a reinforcing filler in polymer composites remains in its infancy, but early papers have shown promising results. The University of Auckland has published several papers that investigated the manufacturing, characterization and testing of biochar biocomposites. Initial studies examined the effect of adding biochar, produced from landfill pinewood, into wood-fiber-reinforced polypropylene. Biocomposites were manufactured via injection molding, and the volume fraction of biochar was varied from 6 to 30 vol.%. One study, published January 2015, showed an increase in tensile moduli and flexural strength/moduli, while the tensile strength remained similar. The optimal volume fraction of biochar was found to be 24% [4]. A second study utilized the optimal loading fraction of 24% and investigated the effect of adding biochars pyrolyzed at different temperatures. It was found that a higher temperature of 900˚C produced a biochar with higher carbon content and surface area, 335 m^2/g, which resulted in better mechanical properties [5]. Additional studies investigated adding biochar to a neat polypropylene matrix. Mechanical tests results agreed with previous studies, where increasing content of biochar continuously improved the tensile modulus and flexural strength/modulus of the resulting composite [6]. Rationale for improved mechanical performance of biochar-enhanced composites reported in all

papers was the same. The highly porous structure, with high surface area, of biochar allowed pore infiltration of the molten polymer, therefore creating an elaborate matrix with mechanical interlocking [7].

Thus far, no studies have been performed that introduce biochar into a conventional, well established composite. It is obvious that wood-fibers cannot compare in strength to industry norms, such as glass or carbon fibers. Therefore, it is of interest to see how biochar will perform when added to a well-established composite [8]. This study examines that effect and is set to determine the potential of biochar as a reinforcing agent in well-established, glass-fiber-reinforced polymer (GFRP) composites. The structure of the current paper is as follows: Section 2 discusses the starting materials and their initial characteristics before manufacturing of the end biocomposites, as well as the methodologies and characterization/testing equipment involved; Section 3 exhibits the results pertinent to each phase of this experimental development intertwined with relevant discussions; important conclusions with follow-up research outline are drawn in Section 4.

2 MATERIALS AND METHODS

2.1 Biochar production

Biochar was produced from two biomass feedstocks obtained from local New Brunswick companies. Both feedstocks were wood-based, namely maple, a hardwood, and spruce, a softwood. Wood-based feedstocks were chosen due to the significant forestry industry in New Brunswick and the vast amount of waste wood that can be utilized. Moreover, from literature review, it was seen that wood produced a biochar with more optimal properties, including lower ash content and higher specific surface area (SSA). Prior to experiment, biomass was formed into briquettes of 25 grams each; four briquettes were used in each experiment, resulting in a total experiment weight of 100 grams. Biochar was produced at a power level of 500 Watt, yielding a reaction temperature of between 600˚C and 700˚C. The retention time was kept constant at one hour, to ensure full pyrolysis. Temperature measurement was performed using a high-temperature thermocouple, which was inserted directly into a briquette. Figure 1 shows the microwave pyrolysis system and reactor used in the experiment.

Figure 1: (a) microwave pyrolysis system and (b) reactor used in the experiment.

2.2 Biocomposite manufacturing

Central to this study was the fabrication of biocomposite rebars using an in-house, custom pultrusion machine. Urethane modified, bisphenol vinylester was employed for use as the resin matrix, and fiber and particulate reinforcement were added via the pultrusion technique (see Figure 2 below). Biochar was used as the particulate reinforcement, and continuous E-glass fibers were used for fiber reinforcement. The continuous glass fibers acted to greatly enhance the uniaxial strength of the composite. The porous structure of the biochar enabled a mechanical interlocking with the polymer, and yielded a more elaborate matrix for fiber bonding.

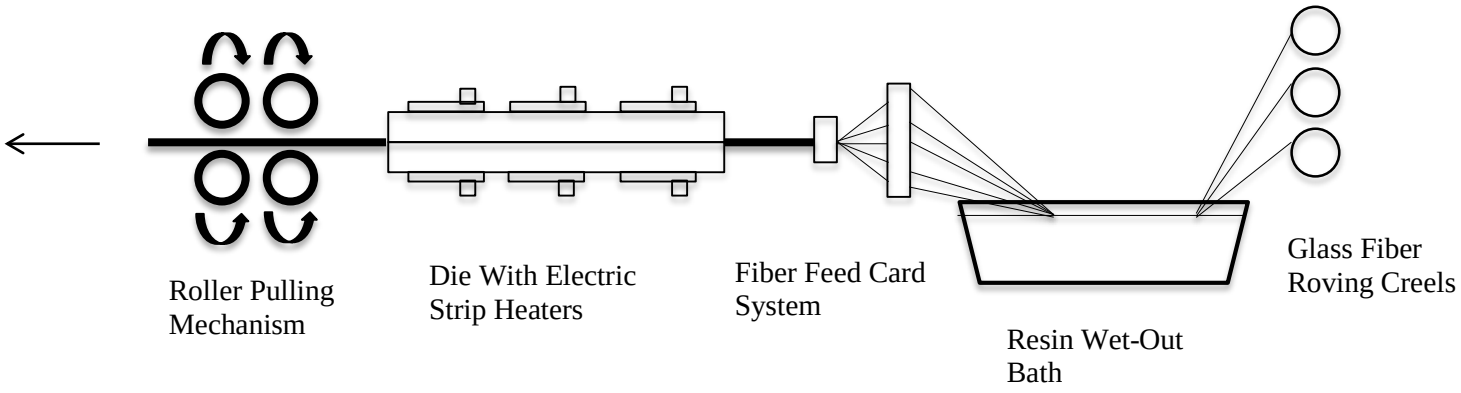

Figure 2: Pultrusion Manufacturing Schematic

As shown in Figure 2, reinforcing fibers were pulled from a creel system into a resin bath, and lastly, into a heated die for shaping and curing. The resin bath contained a uniform mixture of vinylester resin and biochar particles. An organic peroxide catalyst was introduced in the resin mixture in order to cure the resin while it moved through the shaping die. Moreover, an internal lubricant was used to ensure the composite would be able to move through, and release from the die. The fibers were thoroughly wetted with resin and biochar in the dipping tank, 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 composite rod exited the die with a circular profile of diameter 9.5 mm. The finished products were then 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. Table 1 shows the mechanical properties of the glass fibers and vinylester resin used in this study, respectively.

Glass Fibers		Vinylester Matrix	
Tensile Strength (MPa)	2760	Tensile Strength (MPa)	73
Tensile Modulus (GPa)	73	Tensile Modulus (GPa)	3.0
Poisson's Ratio	0.22	Poisson's Ratio	0.4
Diameter (microns)	23	Flexural Strength (MPa)	156
Density (g/cm^3)	2.54	Flexural Modulus (GPa)	3.2

Table 1: Matrix and Fiber Properties

2.3 *Biochar characterization*

The synthesized biochar was characterized using an Autosorb 1 gas sorption analyzer performing physiosorption analysis in the Chemistry Department at UNB for surface area and porosity analyses. To study the pore structures of

different biochars an SEM (scanning electron microscopy) of JEOL JSM 6400 model was used in the Microscopy and Microanalysis Facility at UNB.

2.4 Biocomposite testing

Pultruded biocomposite rebars were tested for flexural strength and modulus properties using an Instron Model 1332 load frame driven by an Instron 8500 series controller (see Figure 3 below). Table 2 below gives the test matrix for the specimens obtained from GFRP rebar, biochar-reinforced GFRP biocomposite rebars. The three-point bending (flexural) tests were carried out in accordance with ASTM D790. Three specimens of each group were tested to obtain a normalized value for both strength and modulus of the tested biocomposite rebars.

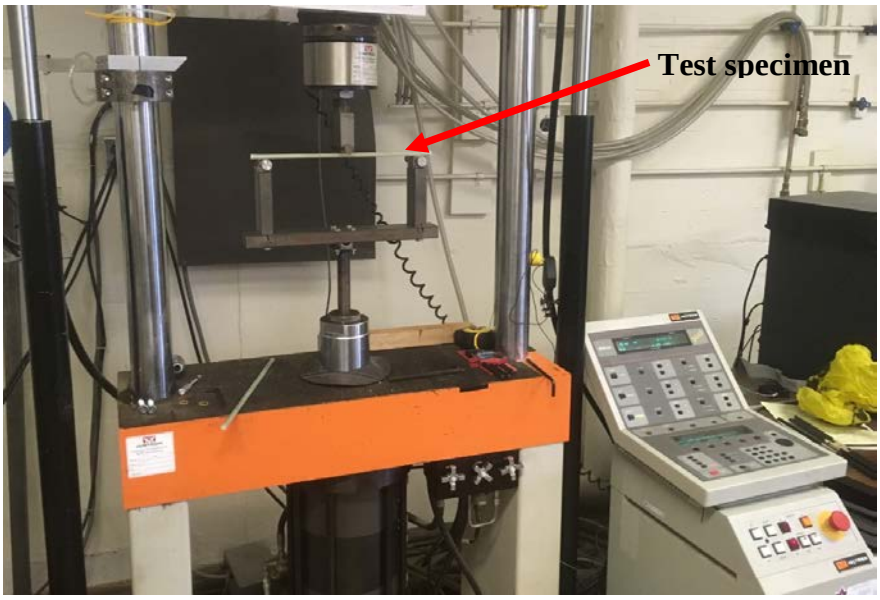

Figure 3: Instron machine used to perform 3-point flexural tests in Mechanical Testing Lab at UNB.

3 RESULTS AND DISCUSSION

3.1 Biochar properties

The addition of the biochar particles causes a mechanical interlocking to occur with the polymer matrix. The unique, highly porous structure of the biochar, allows the molten polymer to infiltrate these pores and then set. This yields a more elaborate structure, which could be optimal for fiber bonding within the matrix. In order to quantify the biochars ability to cause this effect, the BET surface area of biochars were found through physiosorption analysis, and are shown in Figure 4 below. As evident, biochar from spruce wood (softwood) showed the most promising results with a surface area of 200 m^2/g, with hardwood following with 150 m^2/g. It was of interest to

better visualize the porous biochar structure. SEM images of samples were taken, and are presented below in Figure 4. The images below show the porous structure of softwood and hardwood biochar, respectively; images were taken at 2000x.

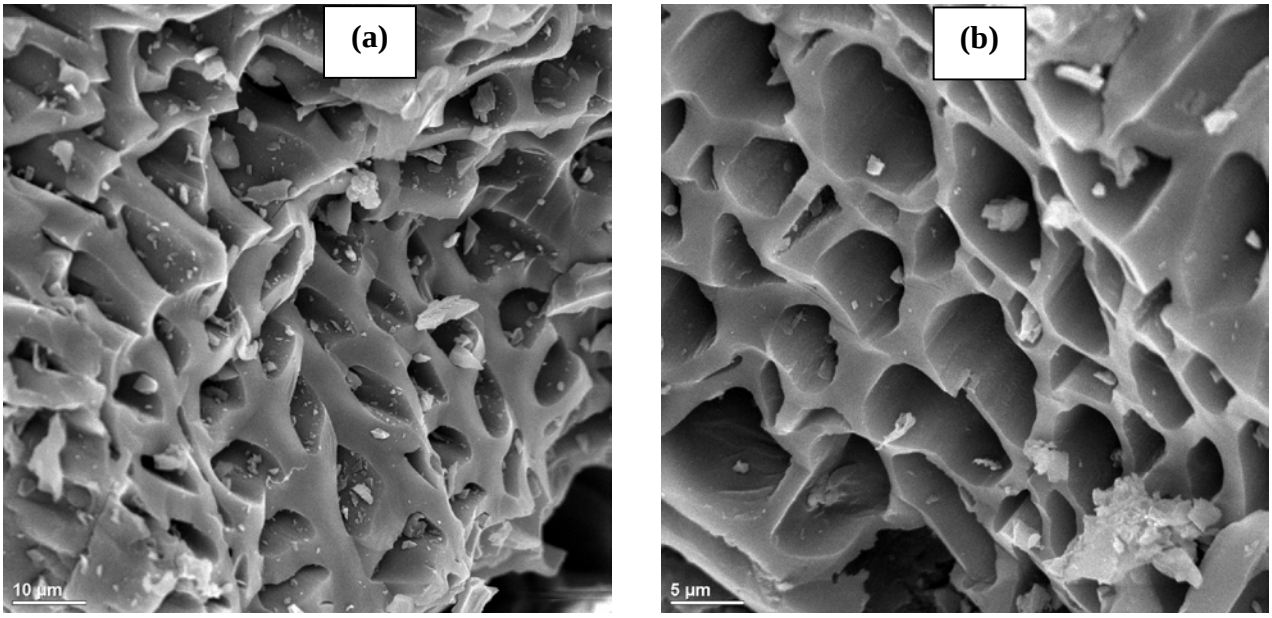

Figure 4: SEM micrographs taken for (a) softwood and (b) hardwood biochar structures.

3.2 Flexural properties of biocomposites

As-pultruded biocomposite and conventional GFRP composite rebars are shown in Figure 5 below.

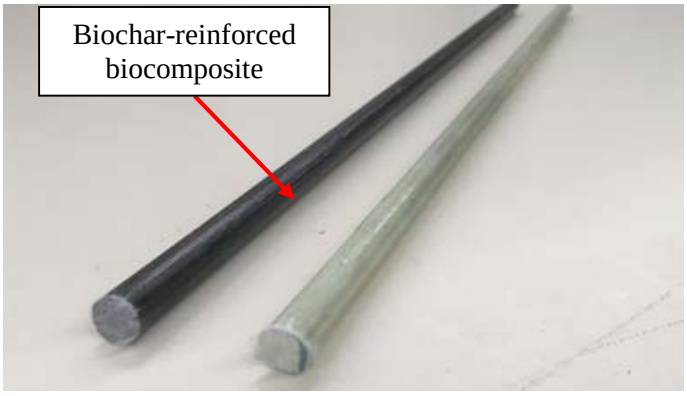

Figure 5: Pultruded biocomposite and conventional GFRP composite rebars.

It was mentioned earlier that the pultruded rebars were subjected to three-point bending (flexural) loading under a ramp rate 20 mm/minute. Figure 6 shows a standard load vs. displacement graph recorded with a control specimen (S.1), while Table 2 gives the flexural strength and modulus properties with corresponding specimen description.

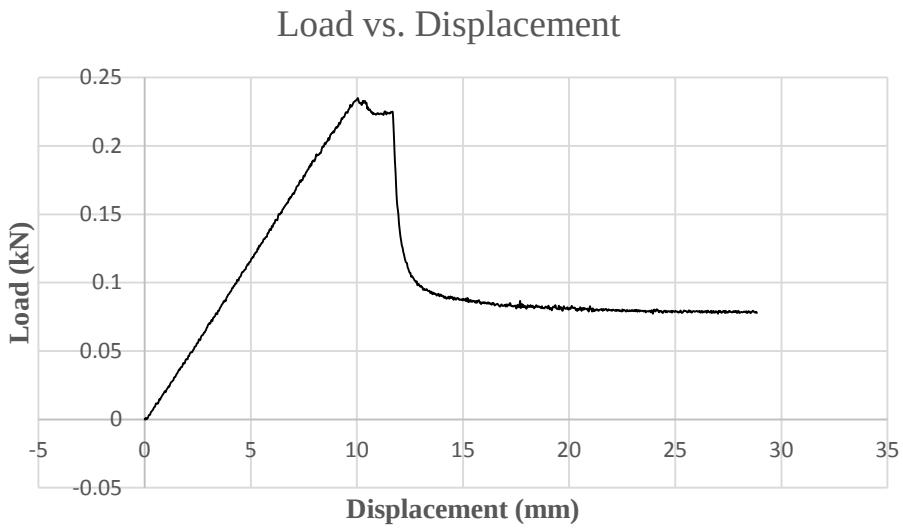

Figure 6: Load vs. displacement graph for a conventional GFRP rebar under flexural loading.

Specimen designation	Types of specimen	Flexural strength (MPa)	Flexural modulus (GPa)
S.1	Control GFRP rebar	167	33
S.2	Softwood biochar reinforced GFRP rebar	300	41
S.3	Hardwood biochar reinforced GFRP rebar	310	44

Table 2: Three-point (flexural) bending property of the biocomposites

Figure 7 shows the true stress-strain behavior of the tested rebars. It is evident from the graphs that all specimens started with a steep slope to a maximum stress level indicating their yielding point. From analytical calculation it was found out that the highest modulus was given by specimen S.3 (hardwood biochar-reinforced GFRP biocomposite), which stood at 44 GPa. When compared this value with the unreinforced conventional GFRP (S.1) this is an increase in flexural modulus of 33%. This was also evident in their corresponding flexural strength performance.

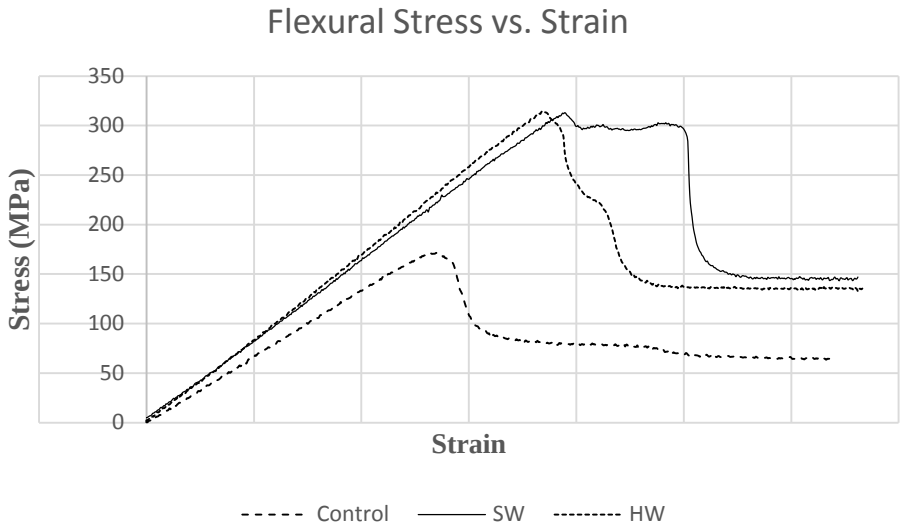

Figure 7: True stress-strain curves for tested rebars.

4 CONCLUSIONS

This study showed evidence for the potential of biochar as a particulate reinforcement in conventional fiber-reinforced polymer composites, hence the biocomposites. Biochar was produced from hardwood and softwood feedstock, and introduced into the GFRP via pultrusion process. The produced rebars were then tested for flexural modulus and strength and results were compared with a control rebar. The hardwood biochar produced the best results with a modulus increase of 33%. The porous structure of the biochar, seen in SEM imaging, created a mechanical interlocking with the polymer, and a more elaborate matrix for fiber bonding. Further testing will be conducted to evaluate additional mechanical and morphological properties, but initial results show great promise.

5 ACKNOWLEDGEMENTS

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