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Development of polyvinyl alcohol/wood-derived carbon thin films: Influence of processing parameters on mechanical, thermal, and electrical properties

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**DEVELOPMENT OF POLYVINYL ALCOHOL/WOOD-DERIVED CARBON
THIN FILMS: INFLUENCE OF PROCESSING PARAMETERS ON
MECHANICAL, THERMAL, AND ELECTRICAL PROPERTIES**

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**Dissertation submitted
to the Davis College of Agriculture, Natural Resources and Design
at West Virginia University**

in partial fulfillment of the requirements for the degree of

**Doctor of Philosophy in
Forest Resources Science**

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Division of Forestry and Natural Resources

**Morgantown, West Virginia
2016**

**Keywords: Biochar, Polyvinyl Alcohol (PVA), Electrically Conductive Polymer
Composite (ECPC), Piezoresistive Pressure Sensor
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ABSTRACT

DEVELOPMENT OF POLYVINYL ALCOHOL/WOOD-DERIVED CARBON THIN FILMS: INFLUENCE OF PROCESSING PARAMETERS ON THE MECHANICAL, THERMAL, AND ELECTRICAL PROPERTIES

Nan Nan

The first goal of this research was to explore the potential value of hardwood-derived carbon materials as fillers for reinforcing polymer materials, and investigate the effect of filler content on various properties of reinforced composites. Three loading levels of biochar particles, 2wt%, 6wt%, and 10wt% (by weight) were added to a 10wt% polyvinyl alcohol (PVA) solution (by weight) and composites were formed via the film-casting method. The morphological, tensile, thermal, and dynamic mechanical properties of PVA/biochar composite films were tested and analyzed. Tensile tests indicated that the addition of biochar reduced the tensile strength and elongation at break of the films. The tensile modulus, however, was improved through the addition of biochar. Dynamic mechanical analyses (DMA) indicated when the temperature was above 83°C (melting point of PVA) the storage modulus of the composite films was higher than the PVA films. Also, the addition of biochar particles increased the thermal stability of the PVA films. Results of this study indicated that the combination of PVA with biochar has a potential to produce film materials with improved thermal and tensile properties.

Further evaluation was conducted to investigate the electrical conductivity and piezoresistive behaviors of the developed PVA/biochar films for the use of piezoresistive pressure sensor. The PVA/biochar films exhibited a similar electrical conductivity as most carbon nanotube and graphene reinforced PVA composites. Additionally, with increased pressure from 0 to 358kPa, the average electrical resistance of PVA/biochar composite films with 8wt%, 10wt%, and 12wt% biochar content decreased by 92%, 98%, and 99%, respectively. Additionally, the effect of film thickness (0.40mm to 0.60mm) and temperature (-20°C to 70°C) were investigated. Results indicated that the effect of thickness was most

influential in the PVA/biochar films with 8wt% biochar. Higher temperature (40°C to 70°C) enhanced the piezoresistive effect, while lower temperature (-5°C to -20°C) reduced the piezoresistive effect.

To further develop conductive bio-based carbon material, research was conducted on biochar preparation. The biochar was made from red oak, yellow-poplar, and willow by pyrolysis at different heating temperatures (HTTs). The electrical conductivity of these biochar particles was measured under compression. Additionally, scanning electron microscope, Brunauer-Emmett-Teller (BET) test, fourier transform infrared spectroscopy, X-ray diffraction, and raman spectroscopy analysis were performed to investigate the physicochemical properties of carbonized biochar. Results showed that the electrical conductivity of wood-derived carbons was markedly influenced by the applied pressure, feedstock, and HTT. Specifically, the biochar obtained at 1000°C HTT exhibited the highest electrical conductivity among all HTTs tested under pressure. The results of the physicochemical tests show that the increase of HTT significantly increased carbon content, decreased chemical groups, increased both of D-band and G-band of the carbon structure, and increased the surface area of biochar. These results may indicate that via changing the physical and chemical properties of biochar, the HTT and feedstock impacted the electrical conductivity of biochar.

Finally, to investigate the effect of feedstock and particle size distribution of the biochar filler on the conductivity and piezoresistive behavior of PVA/biochar composites, biochar was prepared from red oak, yellow-poplar, and willow feedstock at 1000°C HTT with two particle size distributions. Results indicated that the percolation threshold of the composites was between 16wt% and 18wt%. The impact of particle size on conductivity and piezoresistive behavior depended on the biochar content and feedstock. Additionally, applied temperature increased the conductivity of all the specimens, specifically at lower biochar contents (6wt% and 8wt%). These results indicated that the electrical conductivity and piezoresistive behavior of PVA/biochar composite films strongly depended on the feedstock, particle size, and temperature.

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1. INTRODUCTION

An electrically conductive polymer composite (ECPC) is a composite material which incorporates insulating polymer matrices with electrical conductive fillers (Hussain et al. 2001; Knite et al. 2004; Hwang 2011). ECPCs have been evaluated for their mechanical and electrical properties, and been used in the packaging, automotive, construction, aerospace, biomedical, and electronic industries (Kuilla et al. 2010; Tjong 2012). Because of their excellent tensile and thermal properties, and electrical conductivity, carbon-based fillers such as carbon nanotubes (CNTs), graphene, carbon fibers, and carbon black are one of the most widely used conductor groups. Among these carbon-based fillers, CNTs and graphene sheets are very effective as conductive fillers. One drawback, however, of CNTs and graphene sheets as filler for ECPCs is their high production cost. The cost of CNTs is even higher than graphene because of the complex operations during production (Coleman et al. 2006; Kilbride et al. 2002). Another popular carbon-based filler is carbon black. Carbon black requires lower cost to produce, but the tensile and electrical properties of carbon black fillers are lower than most other conductive fillers. Therefore, carbon black is most often used to reinforce rubber (Park et al. 2003; Wang and Ding 2010), and epoxy (Fournier et al. 1997; EI-Tantawy et al. 2002). Since the mass production of conventional carbon-based functional composite material is very difficult, low-cost and high-performance conductive materials are needed to meet the rising demand. Biochar has potential to be an alternative filler material. The advantages of biochar mainly are the high carbon content, excellent electrical conductivity, adjustable physical and chemical structure, and a large amount of sustainable and low-cost bio-resources.

Biochar is the remaining solid product obtained after biomass pyrolysis which is a thermochemical decomposition of organic material at elevated temperatures in the absence of oxygen (Joseph and Lehmann, 2010). Biochar, as a high carbon content material, may have potential to be used as filler to reinforce the mechanical and thermal properties of polymers. Ahmetli et al. (2013) reported that biochar obtained from wood shavings significantly improved the thermal stability, tensile strength, modulus, and surface hardness of the epoxy resin matrix. However, to date, there is limited research on using biochar in the enhancement of polymers.

Biochar as an excellent conductor may also have potential as a conductive filler for ECPCs. Joseph and Lehmann (2010) reported biochar can be a good conductor of electricity depending upon the processing conditions. The structure of biochar consists of essentially amorphous carbon and some crystalline areas formed by the turbostratical stacks of graphene sheets, which is the conductive phase of biochar (Xie et al. 2008). Moreover, there are studies that indicated the electrical conductivity of biochar can be influenced by feedstock and pyrolysis conditions via changing the physical and chemical structure of biochar (Pandolfo and Hollenkamp 2006; Bourke et al. 2007; McBeatch et al. 2014). This feature of biochar may provide more possibilities for the creation and application of biochar fillers.

Biochar as a bio-resource material allows sustainable mass-application of biochar based ECPCs at a relatively low cost. Biomass, the precursor of biochar, is a renewable material, which has been widely recognized as the third primary energy sources after coal and oil (Kirubakaran et al. 2009). The potentially available biomass in the current bio-economy are agricultural resources and forest resources. The 2005 Billion-Ton Study (BTS) performed by the United States Department of Agriculture (USDA) estimated the potential biophysical availability of biomass and identified the potential of biomass resources to produce more than one billion tons per year of agricultural and forest biomass resources which is sufficient to produce enough biofuel to displace 30% of current petroleum consumption (DOE 2012). Currently, agricultural biomass is mainly used for fuels and bio-based chemicals. Biomass resources include various energy crops, crop residues, and waste from plants and animals. Forest biomass is used to produce heat and power for industrial and residential use, comes mainly from purposely grown plantations, wood wastes from forests, mills, landfills, and harvesting from silvicultural treatments such as thinning, fuel reduction, and regeneration cuts. The 2016 Billion-Ton study (BTS) evaluated the most recent estimates of potential biomass that could be available for new industrial uses for production of renewable energy and bio-products in the future. The biomass resource, which is available at \$60/dry ton or less, in 2016 only is 365 million dry tons. From 2017 to 2040, the base-case scenario for the potential biomass resources is 343 to 826 million dry tons including forestry resources at 103 to 97 million dry tons (DOE 2016).

Building upon the widely available amount of biomass, the overall goal of this study was to explore biochar as filler to improve the mechanical, thermal, and electrical properties of polymer composites, and to develop biochar from low-value hardwood materials and use it for electrical sensor applications. The polymer evaluated in this study was polyvinyl alcohol (PVA) which is an ideal model polymer matrix for studying the effects of various fillers due to its lower cost, non-toxicity, durability, and ease of processing. In the first section of the study, the capability of commercial biochar as filler to enhance the mechanical and thermal properties of PVA composite films is investigated. The second section explores the electrical conductivity and piezoresistive behavior of PVA/commercial biochar composite films to investigate the probability of biochar-filled polymer-composite thin films for use as piezoresistive pressure sensors. The third section evaluates the effects of feedstock and pyrolysis temperature on the conductivity, physical, and chemical properties of biochar carbonized from three species of wood including red oak, yellow-poplar, and willow under compression. The forth section investigates the influence of both biochar feedstock and particle size on the conductivity and piezoresistive behavior of PVA/biochar composite films.

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2. BIOCHAR AS FILLER FOR POLYVINYL ALCOHOL COMPOSITE FILMS

ABSTRACT

This study was conducted to explore the potential value of hardwood-derived carbon materials (woody biochar) as filler to reinforce polymer materials and the effect of filler content on various properties of the reinforced composites. Three loading levels of biochar particles, 2wt%, 6wt%, and 10wt% (by weight) were added to a 10wt% polyvinyl alcohol (PVA) solution (by weight) and formed composites via a film-casting method. The morphological, tensile, thermal, and dynamic mechanical properties of PVA/biochar composite films were tested and analyzed. Tensile tests indicated that the addition of biochar reduced the tensile strength and elongation at break of the films. The tensile modulus, however, was improved through the addition of biochar. Dynamic mechanical analyses (DMA) indicated when the temperature was above 83°C (melting point of PVA) the storage modulus of the composite films was higher than the PVA films. Also, the addition of biochar particles increased the thermal stability of the PVA films. Results of this study indicated that the combination of PVA with biochar has a potential to produce film materials with improved thermal and tensile properties.

2.1 INTRODUCTION

Biochar is produced by the pyrolysis of biological residues, including agricultural and forestry biomass, and various waste, under low oxygen at temperatures of less than 700°C (Beesley et al. 2011; Joseph 2010). Presently, biochar is widely considered as a tool to improve soil productivity (Galinato et al. 2011; Sohi et al. 2010), and to remove pollutants like heavy metals, pesticides, and herbicides (Kookana et al. 2011). In addition, research found that biochar could be promising renewable filler for composites as well. Peterson (2012) used the co-filler of corn starch and corn stover biochar, instead of carbon black, to enhance styrene-butadiene rubber composites. This research indicated that the rubber composites filled with 10wt%, 3:1 blend of starch and biochar showed better tensile strength, elongation at break, and toughness than those filled with carbon black. Ahmetli et al. (2013) reported that biochar obtained from wood shavings can significantly improve the thermal stability, tensile strength, modulus, and surface hardness of the epoxy resin matrix. However, to date, there has been limited research on using biochar produced from wood in composite material applications.

Polyvinyl alcohol (PVA) is widely used in packaging industry due to its water solubility, nontoxic, high clarity and gloss, excellent durability and film forming property, and low permittivity coefficient. (Tripathi et al. 2009; Kulanthaisami et al. 1995) Furthermore, PVA is a biodegradable polymer that can be degraded by enzymes and microorganism at a relatively low rate (Luo et al. 2012). Therefore, PVA has potential as a material that can be used for developing biodegradable plastics with excellent tensile properties and hydrophobicity. Recently, numerous low-cost and renewable bio-additives combined with PVA polymer have been reported to produce various biodegradable composites for special applications. For instance, composite films of PVA blended with eelgrass (*Zostera marinas*) flakes enhanced gas barrier behavior (Sapalidis et al. 2007), and films of PVA blended with chitosan improved antimicrobial capability, a function that could be useful in the food packaging industry (Tripathi et al. 2009). PVA/starch films have also been widely studied since they are able to be completely biodegradable at an inexpensive cost (Liu et al. 2012; Luo et al. 2012; Yao et al. 2011). To improve the mechanical properties

of PVA films, researchers have focused on adding varied nanoparticles such as nano spherical cellulose (Ibrahim et al. 2010), nano silica (Wang et al. 2013), and jute nano particles (Baheti and Militky 2013).

Based on the past research performed by DeVallance et al. (2015) at West Virginia University, the addition of biochar improved both mechanical and physical properties of the wood-plastic composites (WPCs). Given past experiences with adding biochar for the reinforcement of WPCs, it was hypothesized that biochar has potential as a filler to reinforce PVA composites. The purpose of the study in this section was to investigate the effect of biochar particle filler on the morphological, tensile, thermal, and dynamic mechanical properties of PVA/biochar composites, and to compare the influence of biochar content (including 2wt%, 6wt%, and 10wt%) on the various properties of PVA/biochar composite films.

2.2 MATERIALS AND METHODS

2.2.1 Materials

Mixed hardwood biochar manufactured by Charcoal Green® (Crawford, NE) was used in filling the composite films. The biochar was ground using a Thomas Scientific Wiley mill (Swedesboro, NJ) equipped with a 1 mm sieve and screened using a 60 mesh (250 microns) shaker (USA Standard Sieve Series, Model 11). The mean particle size and distribution of the biochar powder were measured by laser diffraction (Mastersizer 2000, Malvern).

PVA solution at 10wt% by weight was made from PVA crystals (Acros Organics, MFCD-00081922). Distilled water (360 ml) was heated to approximately 85°C, and then 40g of PVA crystals were added to the hot water and stirred with a magnetic stirring device. The mixture was then heated and stirred for 2-4 h at 85°C until the solution became clear. Once the material cooled to room temperature, it was stored in a laboratory refrigerator (4°C) before the composite preparation.

2.2.2 Composites Preparation

Three loading levels of biochar were used in this study: 2wt%, 6wt%, and 10wt% (to PVA 10wt% solution by weight). The prepared PVA 10wt% solution and biochar particles were mixed manually until there was an even black color distribution. The solution was then dispersed by ultrasonic treatment (Sonics & Materials, 20 kHz, Model VCX 750) for 1 min at 50% power. The mixtures were degassed in a desiccator with a vacuum (Welch, 60 Hz, Model 2546B-01) and evaporated at room temperature (approximately 25°C and a relative humidity of approximately 30%) until films were formed (Figure 2.1). The films were dried in an oven (Thermo Fisher Scientific, Model 6524) at 55°C for 6 h. Upon cooling, the films were placed in sealed bags until testing.

Figure 2.1 Film casting in a desiccator for degassing purpose.

2.2.3 Proximate Analysis

Proximate analysis (moisture, volatile matter, fixed carbon and ash) of biochar was carried out using a proximate analyzer (Model: LECO 701, LECO Corporation, St. Joseph, MI, USA) following the ASTM D7582 (2015).

2.2.4 Scanning Electron Microscope analysis

Scanning electron microscopy (SEM) was performed to investigate the surface morphology of biochar particles and the PVA/Biochar composite films with a JEOL JSM 7600F scanning electron microscope.

2.2.5 Mechanical Testing

The mechanical properties of composite films were tested following the procedures outlined in ASTM D1708 (2013) and ASTM D638 (2014). Dog-bone shaped specimens were prepared for the tensile tests using a Qualitest die and press (Model 038446). The specimens were 5mm in width at the narrow section and measured 40mm in overall length. The specimens were placed in a pneumatic tension grip fixture and tested over a gauge length of 20mm. A universal test machine (UTM-MTS, Model 810 with a load cell capacity of 2.5kN, 550lb) was used for the tests (Figure 2.2), and the load was applied at a constant rate of 1mm/min. Stress vs. strain data were collected at a rate of 10 samples per second to determine the modulus of elasticity.

Figure 2.2 Tensile test specimens under applied load.

2.2.6 Dynamic Mechanical Analysis

DMA was performed to investigate the viscoelastic behavior of the composite films using a TA Q800 Instrument. The pure PVA film and the composite films were tested in a tensile mode over the temperature range from -30°C to 150°C with a heating rate of 5°C/min and upon a frequency of 1Hz. The specimen dimensions were 20mm × 5mm × 0.50 mm.

2.2.7 Thermal Gravimetric Analysis

The thermal degradation behaviors of biochar particles, PVA, and composite films were investigated using thermal gravimetric analysis (TGA, TA Q50 Instrument). A 2-3mg sample was placed in the TGA and heated from room temperature to 400°C at a heating rate of 20°C/min in nitrogen.

2.2.8 Differential Scanning Calorimetry Analysis

Differential scanning calorimetry (DSC) was performed to investigate the melting, crystallization, and decomposition behavior of the composite films using a TA Q20 Instrument. For each test, 8mg of each sample was heated from -90°C to 400°C at a heating rate of 10°C/min in nitrogen.

2.2.9 Statistical Analysis

JMP-software was used for all statistical analysis in this study. Analysis of variance (ANOVA) and the Tukey–Kramer multiple comparison test (alpha level = 0.05) were applied.

2.3 RESULTS AND DISCUSSION

2.3.1 Characterization of Biochar

Due to the difference of raw materials and processing parameters, the features of biochar can differ significantly. Table 2.1 shows the results of the proximate and elemental analysis of the commercial hardwood derived biochar used in this study.

Table 2.1 Proximate and elemental analysis of biochar used in this study.

Sample	Proximate analysis (% , dry basis)			Elemental analysis (%)			
	Ash	Fixed carbon	Volatile matter	C	H	N	O
Biochar	14.9	65.1	20	63.2	1.9	0.4	30.3

Figure 2.3 shows the surface morphology of biochar particles at gradually enlarged magnification from $\times 75$ to $\times 20,000$. These particles have irregular shape and size in the range from micro to nano scale. The average volume weighted mean Diameter[4,3] of biochar particles is $22.9\mu m$, and the distribution of particle size is normal (Figure 2.4). The pores with heterogeneous size were distributed on the biochar surface. These porous structures likely came from the decomposition of wood cells during the process of pyrolysis and may influence the properties of the biochar and final composites.

Figure 2.3 SEM surface images of biochar powder. Showing the shape and size distribution of biochar particles used in this study.

Figure 2.4 Particle size distribution of biochar particles.

2.3.2 Mechanical Properties of PVA/Biochar Composite Films

Figures 2.5-2.7 and Table 2.2 show the effect of biochar content on the tensile properties of PVA/biochar composites films. Compared with the pure PVA, the tensile strength of the PVA/biochar films with 2wt%, 6wt%, and 10wt% biochar decreased by 58%, 75%, and 81%, respectively. Results from a Tukey–Kramer multiple comparison test ($P < 0.05$) indicated that the mean tensile strength of PVA/ biochar films with 6wt% and 10wt% biochar were significantly lower than the mean values of pure PVA and PVA/ biochar films with 2wt% biochar. In contrast, the tensile modulus of PVA/biochar films with 2wt%, 6wt%, and 10wt% loading increased by 129%, 271%, and 429%, respectively. Results from a Tukey–Kramer multiple comparison test ($\alpha = 0.05$) indicated that the mean tensile modulus of PVA/biochar films with 6wt% and 10wt% biochar were significantly higher than the mean values of pure PVA and PVA/biochar films with 2wt% biochar.

Figure 2.5 Tensile strength of PVA and PVA/biochar composite films.

Figure 2.6 Tensile Modulus of PVA and PVA/biochar composite films.

Figure 2.7 Elongation at break of PVA and PVA/biochar composite films.

Table 2.2 Tensile properties of pure PVA and PVA/biochar composites films.

Sample	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)
PVA	31.75±3.38	0.07±0.02	212±26
PVA/2wt% biochar	13.49±2.04	0.16±0.03	56±11
PVA/6wt% biochar	7.98±1.10	0.26±0.10	13±5
PVA/10wt% biochar	5.93±1.40	0.37±0.09	6±1

Similar to the results in other research, the addition of various CNTs (Spitalsky et al. 2010; Mallakpour et al. 2014; Li et al. 2013) and graphene (Shang et al. 2015; Layek et al. 2012; Tang et al. 2012; Yang et al. 2011; Yang et al. 2010; Yu et al. 2014) nanoscale fillers dramatically improved the tensile strength and modulus of composites. The results of this study indicated that the bio-carbon filler was able to improve the tensile modulus as well as most modified and/or functionalized CNTs and graphene fillers. However, the biochar used in this research resulted in a reduced tensile strength for the PVA composites. There are research indicated that the mechanical properties of reinforced polymeric composite material mainly depend on adhesion between filler and polymer matrix, dispersion and distribution of

filler, filler aspect ratio, and orientation of filler (Al-Saleh et al. 2011). In this study, the reduction in tensile strength may be caused by that the addition of biochar particles destroyed the links among polymer molecules and the links built between biochar and polymer were not as strong as that of polymer molecules. Figure 2.8 shows the effects of the addition of biochar filler on both the tensile stress and the tensile modulus (tensile stress versus strain). The addition of biochar particles appeared to have interrupted the original cross-linked polymer network and formed new connections between the filler particles and the polymer matrix. Due to the biochar filler's relatively wide particle size distribution and apparent lower adhesion within the polymer matrix, the increase in biochar content resulted in a decline in tensile strength, along with a reduction in overall ductility. However, due to the high rigidity of biochar filler, an increase in tensile modulus of composites was evident.

Figure 2.8 Example of tensile stress–strain relation for pure PVA and PVA/biochar composite films.

The dynamic mechanical properties of PVA/biochar composites with different biochar content were also investigated, and the results are showed in Figures 2.9-2.11. The storage modulus of the PVA films decreased with increasing biochar content below the glass transition temperature (T_g), but increased with increasing biochar content above the T_g . Similarly, this phenomenon happened to the loss modulus. When temperature was below the T_g , the storage and loss modulus of biochar composites was lower than the pure PVA film, which may be caused by the addition of biochar that broken the original network interaction between PVA chains. However, with increasing temperature, the components of composites turned to form more frequent and stronger bonds, and the modulus of the composites gradually increased. This increase in storage modulus continued until the temperature was above the T_g , where the storage modulus of the composites exceeded the storage modulus of pure PVA films. Additionally, the positions of the tan delta peaks were slightly reduced with the addition of biochar, indicating that the T_g (83°C) of the films were slightly reduced when biochar was added. Wang et al. (2013) indicated that the decrease of T_g may be caused by the amount of intermolecular hydrogen bonding of PVA being reduced which resulted in the decrease of crystallinity of PVA. Research on modified CNTs (Sitalsky et al. 2010) and graphene (Yu et al. 2014) reinforced PVA composites showed that modified carbon fillers were able to improve the storage modulus and T_g through increased the degree of crystallinity. As indicated previously, proper modification of bio-carbon filler could help to improve the interaction between filler and PVA and improve the storage modulus and increase the T_g of reinforced PVA composites.

Figure 2.9 Storage modulus curves of pure PVA and PVA/biochar films.

Figure 2.10 Loss modulus curves of pure PVA and PVA/biochar films.

Figure 2.11 Tan Delta curves of pure PVA and PVA/biochar films.

2.3.3 Morphology of PVA/Biochar Composite Films

Figure 2.12 shows the SEM images of the surface of the PVA/biochar films with different biochar loading levels. In all biochar loading levels, biochar particles were randomly and evenly distributed throughout the surface of films. However, in the 10wt% PVA/biochar films, the particles appeared to have a higher amount of aggregation and tended to form more random partial clusters. Furthermore, due to the increase of particle content the particles tended to distributed both in the polymer matrix and on the surface of the matrix. The increase of particles on the surface resulted in a decrease in the smoothness of the film surface. Additionally, the non-uniform particle sizes, shape, and broad distribution of the biochar filler may cause a lower tensile strength of PVA/biochar films. A reduction in tensile strength when adding fillers was observed by Paiva et al. (2004) who found that the addition of pristine CNTs decreased the tensile strength of PVA/SWCNTs by 5% because of poor dispersion, distribution, and interaction of nano fillers and PVA matrix.

Figure 2.12 Surface images of PVA/biochar composite films with different biochar content.

2.3.4 Thermal Properties of PVA/Biochar Composite Films

Figure 2.13 shows the weight loss of PVA/biochar composites, biochar, and PVA film under heating from 25°C to 400°C. The results of the TGA test indicated that the weight loss of biochar was less than 5% up 400°C. The pure PVA, however, had a significant weight loss in the range of 230°C to 360°C. The total weight loss of the film containing 2wt% biochar was lower than that of PVA film, but the weight loss speed was faster than that of PVA film. The increase in weight loss rate of the 2wt% films was likely caused by that the addition of biochar interrupted the hydrogen bonding of PVA and the amount of 2wt% biochar was not enough to develop the thermal advantage of biochar itself. However, with the increase of biochar content, both the total weight loss and weight loss rate were reduced. These findings

indicated that the addition of biochar to the PVA films can improve the thermal stability of the composite films. Similarly, the same type of thermal degradation results have been obtained from CNTs and graphene reinforced PVA composites (Shang et al. 2015; Dassios et al. 2012; Hasan et al. 2013; Yang et al. 2010).

Figure 2.13 TGA curves of PVA/biochar composite films, pure PVA, and biochar.

The results of the DSC tests are summarized in Figure 2.14 and Table 2.3. As shown in Figure 2.14, the addition of biochar particles (2wt% to 10wt%) decreased the melting temperature (T_m) from 215°C to 192.8°C, increased the decomposition temperature (T_d) from 290.1°C to 337.1°C, and decreased the crystallinity from 58% to 33%. The crystallinity of a PVA is the ratio of its melting enthalpy to the enthalpy of the pure PVA crystal, which is 138.6J/g. Similarly, a decrease of T_m and crystallinity was reported for graphene nanoribbon reinforced PVA composites (Shang et al. 2015) and graphene oxide reinforced PVA composites (Yang et al. 2011). In these prior studies, the interactions between graphene and

PVA were found to have led to a decrease in the crystallinity. However, other research has indicated that CNTs and PVA can form an extremely strong interfacial interaction due to the nucleation of crystalline PVA (Cadek et al. 2002). In addition, the DSC results exhibited two degradation peaks T_{d1} and T_{d2} , corresponding to the melting and complete decomposition. The addition of biochar delayed the complete decomposition of the composites. Therefore, the biochar filler was able to improve the thermal stability of the PVA material.

Figure 2.14 DSC of PVA/biochar composite films and pure PVA.

Table 2.3 DSC results of PVA/biochar composite films.

Sample	T_m (°C)	T_{d1} (°C)	T_{d2} (°C)	Heat of melting (J/g)	Crystallinity (%)
PVA	215	239.5	290.1	64	58
PVA/2wt% biochar	198	228.9	324.3	36.2	33
PVA/6wt% biochar	197.2	230.9	333.2	45.2	41
PVA/10wt% biochar	192.8	231.3	337.1	46.4	42

2.4 CONCLUSIONS

In this study, the biochar reinforced PVA composites were investigated by tensile, DMA, TGA, and DSC tests. The addition of biochar increased the tensile modulus and storage modulus above the T_g but resulted in a reduced tensile strength. The results of the thermal testing indicated that the addition of biochar improved the thermal degradation and decomposition (T_d) of the PVA/biochar composites but lowered the T_g and T_m . These experimental results indicate that wood-derived carbon materials have potential for use as an alternative to carbon-based fillers to improve the mechanical and thermal properties of polymer composites. Specifically, wood-derived carbon could be utilized in future research to investigate the electrical properties of biochar as alternatives to conventional carbon-based fillers in electrical applications. Additionally, future research on the improvement in feedstock, particle size, and carbon percentage would assist in the development of biochar as potential filler.

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3. ELECTRICAL CONDUCTIVITY AND PIEZORESISTIVE BEHAVIOR OF POLYVINYL ALCOHOL/BIOCHAR COMPOSITE FILMS

ABSTRACT

The composites of polyvinyl alcohol (PVA) and biochar were prepared by a solution casting method to investigate their electrical conductivity and piezoresistive behaviors for use as piezoresistive pressure sensors. The PVA/biochar films exhibited a similar electrical conductivity as most carbon nanotube and graphene reinforced PVA composites. Additionally, with elevated pressure from 0 to 358kPa, the electrical resistance of PVA/biochar composite films with 8wt%, 10wt%, and 12wt% biochar content decreased by 92%, 98%, and 99%, respectively. The effects of film thickness (0.40mm, 0.50mm, and 0.60mm) and temperature (-20°C to 70°C) were investigated as well. Results indicated that thickness was most influential parameter in the PVA/biochar films with 8wt% biochar addition. Higher temperature (40°C to 70°C) enhanced the piezoresistive effect, while lower temperatures (-5°C to -20°C) reduced the piezoresistive effect. These results suggest that the developed PVA/biochar composite films show potential as piezoresistive pressure sensors. The results of the research also provided data for the application and design of biochar-based polymer composite pressure sensors.

3.1 INTRODUCTION

An electrically conductive polymer composite (ECPC) is a composite material which incorporates insulating polymer matrices with electrical conductive fillers (Hussain et al. 2001; Knite et al. 2004; Hwang 2011). ECPCs have been evaluated for their mechanical and electrical properties, and been used in various sensor and electrical devices. Because of their excellent tensile, thermal, and electrical properties one of the most widely used conductor groups is carbon-based fillers, such as carbon nanotubes (CNTs), graphene, carbon fibers, and carbon black. CNTs and graphene have been recognized as excellent fillers for the production of polymer composites with enhanced tensile properties, thermal stability, and electrical properties. The electrical properties of carbon-based polymer composites provides the potential for use in sensors, capacitors, batteries, and many other electrical applications (Castell et al. 2013; Hawarin et al. 2013; Kuilla et al. 2010; Shang et al. 2015; Spitalsky et al. 2010).

The piezoresistive effect is a phenomenon where the electrical resistance of an ECPC material changes as external pressure is applied to the material (Hwang 2011). Due to their excellent electrical, mechanical, and thermal properties, carbon-based ECPC materials have been considered as promising candidates for piezoresistive pressure sensors applied in robotic skin applications (Lacasse et al. 2010; Wang and Ye 2013), medical health monitoring (Schwartz et al. 2013), and other cutting-edge electric devices (Dusek et al. 2014). However, it is very difficult to obtain a usable piezoresistive pressure sensor, since the sensor product has to be sensitive, repeatable, and stable in certain conditions.

The design of effective sensors can be influenced by many factors including conductor content, mechanical and thermal properties of the polymer matrix, range of pressure, and temperature. For example, Wang et al. (2009) reported that carbon black content had a significant influence on the piezoresistivity of carbon black (CB) filled silicone rubber (SR) composites. They found that under applied pressure from 0 to 1MPa, the content of CB had influence in the resistance of SR/CB composites. Moreover, the properties of a polymer are important factor in the sensitivity and reliability of piezoresistive pressure sensors. Wang and Ding (2010) compared CB filled polymers and found that under applied

pressures from 0 to 3MPa, the piezoresistivity of SR/CB composites were significantly higher than that of high density polythene (HDP)/CB composites, because of the better elastic property of SR. Another critical factor is the range of applied pressure. Most piezoresistive pressure sensor materials can only sense changes in electrical resistance within a specific range of pressure, and the change could be positive or negative. For example, Wang et al. (2007) found the electrical conductivity of SR/CB composites increased under pressure in the range from 0MPa to 0.37MPa. In contrast, the electrical conductivity decreased under higher pressure in the range from 0.37MPa to 0.7MPa. Furthermore, the variation of temperature should be avoided for piezoresistive pressure sensors. However, this effect is very difficult to eliminate as most flexible polymers are influenced by temperature, with the exception of a few thermal-proof polymers. However, it is possible to determine a relatively stable range for a variety of polymers. Knite et al. (2004) reported that the piezoresistivity of carbon black filled polyisoprene nanocomposite sensors was relatively stable in the temperature from 20°C to 70°C, under applied pressure from 0 to 0.3MPa.

Additionally, research indicated that depending on the processing temperature, biochar can be a good conductor of electricity (Lehmann and Joseph 2010). Biochar is obtained from the pyrolysis of biomass, and mainly consists of amorphous carbon structures and turbostratically stacked graphene sheets, which form the conductive phase of the material (Xie et al. 2008). Therefore, biochar may be able to provide a consistent renewable supply for ECPCs due to its excellent electrical properties and cost-performance ratio.

Research presented in Chapter 2 investigated the mechanical, and thermal properties of biochar filled polyvinyl alcohol (PVA) composite films. To further investigate the potential of PVA/biochar composite films for electrical applications, especially for use as piezoresistive pressure sensors, the study in this section investigated the electrical conductivity of PVA/commercial biochar composite films with 8wt%, 10wt%, and 12wt% biochar content (to PVA 10wt% solution, by weight). The films were then evaluated for investigating the effects of biochar content, film thickness, and temperature on the piezoresistive behavior.

3.2 MATERIALS AND METHODS

3.2.1 Materials

Mixed hardwood biochar manufactured by Charcoal Green® (Crawford, NE) was used in making the composite films. The biochar was ground using a Thomas Scientific Wiley mill (Swedesboro, NJ) equipped with a 1 mm sieve and screened using a 60 mesh (250 microns) shaker (USA Standard Sieve Series, Model 11). The mean particle size and distribution of biochar powder were measured by laser diffraction (Mastersizer 2000, Malvern). The average volume weighted mean Diameter [4,3] of biochar particles was $22.9\mu\text{m}$, and their distribution was normal.

PVA solution at 10wt% by weight was made from PVA crystals (Acros Organics, MFCD-00081922). Distilled water (360 ml) was heated to approximately 85°C, and then 40 g of PVA crystals were added to the hot water and stirred with a magnetic stirring device. The mixture was then heated and stirred for 2-4 h at 85°C until the solution became clear. Once the material cooled to room temperature, it was stored in a laboratory refrigerator (4°C) before the composite preparation.

3.2.2 Composites Preparation

Three loading levels of biochar were used in the study: 8wt%, 10wt%, and 12wt% (added to PVA 10wt% solution). The prepared PVA 10wt% solution and biochar particles were mixed manually until there was an even black color distribution. The solution was then dispersed by ultrasonic treatment (Sonics & Materials, 20 kHz, Model VCX 750) for 2 min at 50% power. The mixtures were degassed in a desiccator with a vacuum (Welch, 60 Hz, Model 2546B-01) and evaporated at room temperature (approximately 25°C and a relative humidity of approximately 30%) until films were formed. The films were dried in an oven (Thermo Fisher Scientific, Model 6524) at 55°C for 4 h. Upon cooling, the films were placed in sealed bags until the start of testing.

3.2.3 Electrical Conductivity Measurement

The conductivity of the films was measured by placing them between two clamps of a dynamic mechanical analysis (DMA) instrument (TA Instruments, Q800) with the holding force between the two clamps set at 99.5kPa, as shown Figures 3.1(a and b). The electrical response was recorded with a NI USB-6210 16-bit DAQ system, using a 5Vdc power source. The absolute accuracy of the 16-bit DAQ system is $\pm 0.003V$. The circuit was depicted in Figure 3.1c. According to this circuit, $5V = R \times I + V_0$ and $I = \frac{5V}{R+R_{ref}}$, the resistance of sample (R) was calculated using equation 3.1:

$$R = \frac{5V \times R_{ref}}{V_0} - R_{ref} \quad (3.1)$$

where:

R_{ref} = resistance of the reference resistor (15k Ω)

V_0 = output voltage of the sample (V)

The 5V represents the input voltage of this circuit.

The test was performed at room temperature, and the conductivity (σ) of composites was calculated using equation 3.2:

$$\sigma = \frac{1}{R} \times \frac{l}{A} \quad (3.2)$$

where:

l = film thickness (cm)

A = area under loading (cm²)

R = resistance of the sample (Ω)

Five replicated films were prepared for each particle loading level, with each sample being 8mm in diameter and approximately 0.50 ± 0.01 mm in thickness.

Figure 3.1 (a) Schematic of the piezoresistive sensor test setup. (b) DMA setup for PVA/biochar pressure sensor tests. (c) Circuit used for piezoresistive sensor testing.

3.2.4 Piezoresistive Test and Analysis

The prepared film samples were cut into samples with a diameter of 8mm. Tests were performed by setting a film sample between two clamps of a dynamic mechanical analysis (DMA) instrument (TA Instruments, Q800) with the holding force between two clamps elevated from 0 to 358kPa at the rate of 1kPa/second, as shown Figures 3.1(a and b). The electrical response was recorded with a NI USB-6210 16-bit DAQ system, using a +5Vdc power source. The circuit was depicted in Figure 3.1c. According to this circuit, According to this circuit, $5V = R \times I + V_o$ and $I = \frac{5V}{R + R_{ref}}$, the resistance of sample (R) was calculated using equation 3.1:

$$R = \frac{5V \times R_{ref}}{V_o} - R_{ref} \quad (3.1)$$

where:

R_{ref} = resistance of the reference resistor (15k Ω)

V_0 = output voltage of the sample (V)

The 5V represents the input voltage of this circuit.

For testing the effects of biochar content on piezoresistive behavior of PVA/biochar films, the films containing three biochar contents including 8wt%, 10wt%, and 12wt% were prepared. Nine replicated films were prepared for each biochar content, with each sample being 8mm in diameter and approximately 0.50 ± 0.01 mm in thickness. Test performed ten times for each individual film continuously at room temperature.

For testing the effects of thickness on piezoresistive behavior of PVA/biochar films, the films with three thickness level including 0.40mm, 0.50mm, and 0.60mm were prepared. Three replicated films were prepared for each thickness level, with each sample being 8mm in diameter. Tests performed at room temperature.

For testing the effects of temperature, the piezoresistive test was performed via the DMA temperature control accessory at different temperatures -20°C, -5°C, 10°C, 25°C, 40°C, 55°C, and 70°C, respectively. The temperature range selected considered the thermal properties of PVA/biochar sensors that were reported by Nan et al. (2016). Three replicated films were tested for each biochar content level, with each sample being 8mm in diameter and approximately 0.50 ± 0.01 mm in thickness.

Analysis of variance (ANOVA) was performed to analyze the data obtained from piezoresistive tests, and Tukey-Kramer multiple comparison tests were performed to determine statistically significant differences between means ($\alpha = 0.05$).

3.2.5 Scanning Electron Microscope Analysis

Scanning-electron microscopic (SEM) analysis of the microstructure of the PVA/biochar composite films were performed using a Hitachi S-4700 Scanning Electron Microscope fitted with an X-ray energy dispersive spectrometry (EDS) detector.

3.3 RESULTS AND DISCUSSION

3.3.1 Morphology of PVA/Biochar Composite Films

The morphology of PVA/biochar composite films was investigated by the SEM method. Figure 3.2 shows the surface and cross-sectional images of sensors with different biochar content. These images revealed the network of conductors, and provided more accurate information to deduce the real conductive paths. Figures 3.2(a-c) show that particles distributed in the surface randomly and were inclined to be homogenous. Figures 3.2(d-f) show that particles were distributed randomly in the cross-section. Results indicated that biochar particles were almost evenly distributed into the polymer matrix, and formed networks in the polymer matrix randomly. Since the space between particles decreased with increased particles content, higher biochar content formed more compact networks, and compact networks helped to form more and shorter paths for electron transfer.

Figure 3.2 SEM images of PVA/biochar composite films with different biochar content. (a-c) surface images. (d-f) cross-section images.

3.3.2 Electrical Conductivity of PVA/Biochar Composite Films

The electrical conductivity of the PVA/biochar composites with the addition of biochar is shown in Figure 3.3. There was no conductivity in the pure PVA films and little to no conductivity in the PVA/biochar composites with 2wt% biochar. The PVA/biochar composites with 6wt% and 10wt% biochar exhibited a mean conductivity of 0.24×10^{-6} S/cm and 1.83×10^{-6} S/cm, respectively. The conductivity of PVA/biochar films increased with increasing addition of biochar due to the reduced insulated space between biochar particles. The results are similar with CNTs and graphene filled PVA composites. Hawarin et al. (2013) reported that the conductivity of ozone treated single-walled carbon nanotubes (SWCNTs)/PVA composite was 2.5×10^{-6} S/cm, and the conductivity of untreated SWCNTs/PVA composite was 5×10^{-8} S/cm for 1wt% SWCNTs. Hu et al. (2010) reported that the conductivity of electrochemically modified graphite nano-sheets reinforced PVA was 10^{-7} S/cm for 6wt% graphene. Layek et al. (2012) reported that PVA/sulfonated graphene composites with 0.5, 1, 3, and 5wt% graphene have conductivity 6.1×10^{-10} S/cm, 1.2×10^{-5} S/cm, 0.9×10^{-4} S/cm, and 1.5×10^{-5} S/cm, respectively. Given these comparisons and the results of this study, it appears that the biochar is a promising filler to improve the electrical conductivity of PVA type composites and has potential for being used in the production of electrical type sensor materials.

Figure 3.3 Electrical conductivity of PVA/biochar composites at different biochar content.

3.3.3 The Effect of Biochar Content on Piezoresistive Behavior

Piezoresistive responses of PVA/biochar composite films with different biochar content are shown in Figure 3.4. With the increase of pressure, the voltage output (V_0) of PVA/biochar films with 8wt%, 10wt%, and 12wt% biochar content increased gradually, when pressure reach at 358kPa, the V_0 increased by 1,848%, 3,365%, and 4,785%, respectively, as compared to no pressure being applied. Correspondingly, the resistance of the PVA/ biochar films with 8wt%, 10wt%, and 12wt% biochar content decreased rapidly from 0 to 50kPa and then leveled off. When pressure reach 358kPa, the resistance of the 8wt%, 10wt%, and 12wt% biochar content films decreased by 92%, 98%, and 99%, respectively. Furthermore, the films containing 8wt% biochar content exhibited the highest resistance, followed by 10wt% and 12wt% films, respectively. Results indicated that biochar content influenced the conductivity and piezoresistive effect of PVA/biochar films. The decrease of resistance of PVA/biochar films with the increase of pressure indicated that the applied pressure resulted in sensor film deformation and the formation of more conductive paths, and an increased conductivity. Moreover, the increase in biochar content decreased

the resistance of PVA/biochar films through adding more conductors to form conductive paths.

Figure 3.4 (a) The resistance of PVA/biochar films under pressure, at different biochar content. (b) The voltage output of PVA/biochar films under pressure, at different biochar content.

Results from the Tukey-Kramer multiple comparison test ($\alpha=0.05$) indicated that when pressure was applied at 358kPa, the mean V_0 of 8wt%, 10wt%, and 12wt% PVA/biochar films were significantly different, as shown in Table 3.1. All results indicated that the piezoresistive behavior of PVA/biochar films were significantly enhanced as the continuous increase of the biochar content from 8wt% to 12wt%. The higher amount of biochar particles formed more conductive paths under pressure. Additionally, the 12wt% biochar content was not reach the percolation threshold of PVA/biochar films. Therefore, increased biochar content from 8 to 12wt% increased the piezoresistive behavior of films under pressure 0 to 358kPa.

Table 3.1 Turkey-Kramer multiple comparison of the V_0 of PVA/biochar films with different biochar content, at 358kPa pressure.

Level	$\alpha=0.05$	Level - Level	p-Value
12wt%	A ¹	12% - 8%	<.0001*
10wt%	B ¹	12% - 10%	0.0003*
8wt%	C ¹	10% - 8%	0.0472*

¹ In the comparison, if the same letters (e.g. As or Bs) occurred, there is no significant difference, but if different letters (e.g. A and B) occurred, there is significant difference.

Also, the analysis of surface and cross-section images supported the results about the effect of biochar content on piezoresistive behaviors of PVA/biochar films. As the pressure elevated from 0 to 358kPa, the PVA/biochar films with 8wt% biochar exhibited the smallest change in resistance and V_0 , due to their large space between particles (Figure 3.2a and d), and the applied pressure can only partially reduce the space. The PVA/biochar films with 10wt% biochar had the second higher change in resistance and V_0 , due to their space distance between particles was smaller than that of the films with 8wt% and larger than that of the films with 12wt% (Figure 3.2b and e). The PVA/biochar films with 12wt% biochar exhibited the largest change in resistance and V_0 , because of their smallest space between particles (Figure 3.2c and f).

To test the reliability and sensitivity of PVA/biochar composite sensors, pressure increase and release tests were performed ten times continuously. Figures 3.5-3.7 show the

results of the V_0 changes of the PVA/biochar films with 8wt%, 10wt%, and 12wt% biochar, respectively. The release tests indicated that all sensors exhibited favorable recovery capability, which benefits from the excellent elasticity of PVA polymer matrix. Specifically, when the pressure was removed the V_0 returned to the original voltage (0Pa) within 3 seconds. It was noted that the maximum voltage for the first cycle was slightly lower than the following cycles, which means that the first cycle likely enhanced the sensor stability. For each biochar content level, from the second cycle to the tenth cycle sensors showed similar piezoresistive response. Additionally, higher biochar content sensors benefited through the formation of more stable conductive paths, therefore the films with higher biochar content had more uniform curves. Wang et al. (2008) reported that the repeatability of the piezoresistivity in carbon black filled silicon rubber composites can be improved with the increase in the number of compression cycles. The result of this test also indicate the excellent restorability and flexibility of PVA polymer matrix material. Additionally, this capability is evident regardless of film thickness.

Figure 3.6 Compression increase and release repeat test of PVA/biochar composite films with 10wt% biochar content under applied pressure range from 0 to 358kPa.

Figure 3.7 Compression increase and release repeat test of PVA/biochar composite films with 12wt% biochar content under applied pressure range from 0 to 358kPa.

3.3.4 The Effect of Thickness on Piezoresistive Behavior

Figure 3.8-3.10 show the data of V_0 versus applied pressure of the PVA/biochar films with 0.40mm, 0.50mm, and 0.60mm thickness at different biochar contents. Test results indicate that the 10wt% PVA/biochar films were least affected by thickness. Tukey-Kramer multiple comparison test ($\alpha=0.05$) indicated that under a pressure of 350kPa, there were no statistically significant differences among the mean V_0 of films with 0.40mm, 0.50mm, 0.60mm thickness (Table 3.2). For films with 8wt% biochar, the average V_0 decreased with the increase of thickness from 0.40mm to 0.60mm. Multiple comparison indicated that under a pressure of 358kPa, the mean V_0 of 0.40mm and 0.50mm were significantly higher than 0.60mm thickness films. However, there was no statistically significant difference in V_0 between 0.40mm and 0.50mm films. Multiple comparison also indicated that under a pressure of 350kPa, there were no statistically significant difference among the mean V_0 of films with 12wt% biochar at different thicknesses. However, the p-value (0.0853) of the comparison between 0.50mm and 0.60mm was very close to 0.05, which means some difference did exist, but was not significant under $\alpha = 0.05$.

Table 3.2 Turkey-Kramer multiple comparison of the V_0 of PVA/biochar films with different biochar content and different thickness, at 358kPa pressure.

	Level	$\alpha=0.05$	Level- Level	p-Value
8wt%	0.40mm	A ¹	0.40mm -0.60mm	0.0041*
	0.50mm	A	0.50mm -0.60mm	0.0362*
	0.60mm	B ¹	0.40mm -0.50mm	0.1832
10wt%	0.40mm	A	0.40mm -0.60mm	0.9888
	0.50mm	A	0.40mm - 0.50mm	0.9945
	0.60mm	A	0.50mm -0.60mm	0.9990
12wt%	0.40mm	A	0.50mm - 0.60mm	0.0853
	0.50mm	A	0.50mm -0.40mm	0.3515
	0.60mm	A	0.40mm - 0.60mm	0.5311

¹ In the comparison, if the same letters (e.g. As or Bs) occurred, there is no significant difference, but if different letters (e.g. A and B) occurred, there is significant difference.

Figure 3.8 Piezoresistive test of PVA/biochar films with 8wt% biochar content at different thickness. (a) Average results. (b) All results.

Figure 3.9 Piezoresistive test of PVA/biochar films with 10wt% biochar content at different thickness. (a) Average results. (b) All results.

Figure 3.10 Piezoresistive test of PVA/biochar films with 12wt% biochar content at different thickness. (a) Average results. (b) All results.

Results from these tests showed that thickness was one of the important factors for PVA/biochar thin films. However, the impacts of thickness depended on the biochar content. For example, even a 0.10mm difference in thickness can lead to the change in V_0 , as shown in the films with 8wt% and 12wt% biochar. The films with 8wt% biochar showed that an increased thickness increased the distance of each single conductive path, therefore, the same pressure was not enough to sustain the similar number of the paths, and resulted in declined conductivity. However, due to the relatively higher biochar content in the films with 10wt% and 12wt% biochar, particles had more chance to form new conductive paths to compensate the effect of increased distance. However, when both the thickness and biochar content were at higher levels, the high stiffness of films caused by the high biochar content could require a higher pressure to form effective conductive paths.

3.3.5 The Effect of Temperature on Piezoresistive Behavior

Figures 3.11-13 show the V_0 of PVA/biochar films with different biochar content at different temperatures (-20°C to 70°C). In general, the V_0 of composite films significantly increased with increased applied pressure for each temperature, and the V_0 slightly increased with increased temperature. Results indicated that under different temperatures, the piezoresistive effect of films still existed, as the higher temperature enhanced the piezoresistive effect of films (40°C to 70°C). The piezoresistive effect was extremely low when the temperature was at -5°C, and -20°C. The higher temperature enhanced the deformation of the polymer matrix and resulted in a thermo-dynamic response, an increased speed to form conductive paths, and increased amount of conductive paths. Conversely, the low temperature blocked the deformation of polymer matrix and reduced the rate in forming conductive paths and also the amount of conductive paths, specifically at temperatures between -20°C and -5°C. The V_0 responses clearly showed the changes of piezoresistive behavior of PVA/biochar films under different temperatures. However, the results from the Tukey-Kramer multiple comparison test ($\alpha=0.05$) (Table 3.3) indicated that under pressure 358kPa, for all three content films, there is no significant difference among the temperature from 10°C to 70°C. Therefore, the changes in this temperature range was likely not enough

to reach the significant value when α is 0.05. This relative stability of PVA/biochar composite films at temperature from 10°C to 70°C provides more potential for electrical uses and for the development of more stable sensor devices.

Figure 3.11 Piezoresistive test of PVA/biochar films with 8wt% biochar content at different temperature.

Figure 3.12 Piezoresistive test of PVA/biochar films with 10wt% biochar content at different temperature.

Figure 3.13 Piezoresistive test of PVA/biochar films with 12wt% biochar content at different temperature.

Table 3.3 Turkey-Kramer multiple comparison of the V_0 of PVA/biochar films with different biochar content under different temperature, at 358kPa pressure.

	Level	$\alpha=0.05$			Level	$\alpha=0.05$		Level	$\alpha=0.05$	
8wt%	70°C	A ¹		10wt%	70°C	A		12wt%	70°C	A
	55°C	A	B ¹		55°C	A			55°C	A B
	40°C	A	B		40°C	A			40°C	A B
	25°C	A	B		25°C	A			25°C	A B C ¹
	10°C	A	B		10°C	A			10°C	A B C
	-5°C		B		-5°C	A			-5°C	B C
	-20°C		B		-20°C	A			-20°C	C

¹ In the comparison, if the same letters (e.g. As or Bs) occurred, there is no significant difference, but if different letters (e.g. A and B) occurred, there is significant difference.

3.4 CONCLUSIONS

The mean conductivity of PVA/biochar with 6wt% and 10wt% biochar composites was found to be 0.24×10^{-6} S/cm and 1.83×10^{-6} S/cm, respectively and resulted in bio-carbon reinforced composites that have a similar electrical conductive ability as most CNTs and graphene reinforced PVA composites. For the piezoresistive tests, with the increase of pressure (0 to 358kPa), the resistance of the PVA/biochar composite films with 8wt%, 10wt%, and 12wt% biochar content gradually decreased by 92%, 98%, and 99%, respectively. Results indicated that the increase of biochar content from 8wt% to 12wt% significantly improved the conductivity and piezoresistive behavior of PVA/biochar films. The piezoresistive behaviors of PVA/biochar composite films were found to be repeatable and stable. Moreover, the effect of thickness on piezoresistive behavior of PVA/biochar films was important and depended on the biochar content. Additionally, the piezoresistive behaviors of the PVA/biochar films influenced by temperature. Since the low percolation and high performance are the major requests to develop piezoresistive devices, the further investigation was related to the development of wood-derived biochar with high electrical conductivity and the influence of feedstock and particle size on the piezoresistive property of polymer composites filled with wood-derived biochar materials.

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4. THE ELECTRICAL CONDUCTIVITY OF HARDWOOD-DERIVED CARBON PARTICLES UNDER COMPRESSION

ABSTRACT

For the application of biochar fillers in electrical conductive composites, the electrical conductivity and physicochemical properties of biochar from hardwood species were determined. The biochar was made from red oak, yellow-poplar, and willow by pyrolysis at different heating temperature (HTT). The electrical conductivity of these biochar particles was measured under compression. Additionally, scanning electron microscope, Brunauer-Emmett-Teller test, fourier transform infrared spectroscopy, X-ray diffraction, and raman spectroscopy analyses were performed to investigate the physicochemical properties of carbonized wood (i.e., biochar). Results showed that the electrical conductivity of wood-derived carbons was markedly influenced by the applied pressure, feedstock, and HTT. Specifically, the biochar obtained at 1000°C HTT exhibited the highest electrical conductivity among all HTTs tested under pressure. The results of the physicochemical tests showed that the increase of HTT significantly increased carbon content, decreased the chemical groups, increased both of D-band and G-band of carbon structure, and increased the biochar surface area obtained from the different feedstocks. These results indicated that changing the physicochemical properties of hardwood feedstock through varying HTT impacted the electrical conductivity of biochar.

4.1 INTRODUCTION

The measurement of the electrical conductivity of powder materials under compression is a very traditional method for characterizing powder material. This method has also been used study the electrical conductivity of various carbonaceous powders due to its simplicity and reproducibility. For example, studies were described for the electrical conductivity of carbon black under compression (Probst and Grivei 2002; Sanchez-Gonzalez et al. 2004) and the electrical resistivity of submicron-diameter carbon-filament under compression (Shui and Chung 2001). Schematic diagrams of the methods used to measure the electrical conductivity of carbon materials in recent research are showed in Figure 4.1.

Figure 4.1 Experimental setup for measuring the electrical conductivity of powders under compression, (a) Celzard et al. (2002) for measuring carbonaceous powders, (b) Probst and Grivei (2002) for measuring carbon black, (c) Marinho et al. (2012) for measuring graphene, multi-wall carbon nanotubes, carbon black, and graphite powders.

The advantages of this method are that it is simple, reproducible, rapid, and low cost (Celzard et al. 2002). More importantly, this method is appropriate for the comparison among diverse materials. The electrical conductivity exhibited by compressed particles is the result of a combination of a number of factors, including the conductivity of the individual particles, the degree of contact between the particles and particle packing (Sanchez-Gonzalez et al. 2004). For instance, Marinho et al. (2012) compared the electrical conductivity of different carbons, including multi-walled carbon nanotubes, graphene, carbon black, and graphite, by powder compression. Like most methodologies to evaluate conductivity there are advantages and disadvantages to compaction type tests. Specifically, the broad particle distribution and possible morphological changes during the compression are variable when estimating both the degree of contact and the packing of particles. However, this method still is an effective way to measure the electrical conductivity of particles, especially to compare the conductivity of the particles with different surface morphologies.

Biomass carbonized at high temperature has been widely researched as a conductive material for various electrical applications, such as electrodes for microbial fuel cells, due to their excellent electrical conductivity, porosity, and bound oxygen and/or nitrogen groups within their structure (Qian et al. 2015). The structure of biochar consists essentially of amorphous carbon and some crystalline areas formed by turbostratical stacks of graphene sheets, which is the conductive phase of biochar (Xie et al. 2008). Lehmann and Joseph (2010) reported that biochar can be a good conductor of electricity depending upon the processing temperature. Moreover, there are studies indicating that the electrical conductivity of biochar directly depends on the properties of intrinsic feedstock and pyrolysis conditions, especially temperature (Bourke et al. 2007; McBeatch et al. 2014).

Past research reported that as the final pyrolysis treatment temperature increases, the crystallites of the biochar structure can be enlarged and more ordered (Figure 4.2). However, wood-based carbons are typically non-graphitizable because during carbonization, the process only reaches a state of continuous aromatic carbon production with increasing temperature (Figure 4.2, stage b) likely due to wood materials inherent cellulosic structure (Franklin 1951; Cheng et al. 1999; Pappacena et al. 2009). Instead of forming large ordered

graphene sheets (Figure 4.2, stage c), during wood carbonization, when temperatures are higher than 2500°C, turbostratic carbon is formed as misaligned graphene sheets, and the average lattice space of turbostratic carbon is larger than the space of graphite.

Figure 4.2 Ideal biochar structure development with highest treatment temperature (HTT). (a) Increased proportion of aromatic C, highly disordered in amorphous mass. (b) Growing sheets of conjugated aromatic carbon, turbostratically arranged. (c) Structure becomes graphitic with order in the third dimension (Lehmann and Joseph, 2010).

Furthermore, pyrolysis temperature has a significant influence on the conductivity of the final carbon materials. Specifically, Pandolfo and Hollenkamp (2006) reported that conductivity increased rapidly with temperature up to 700°C, but become less influenced at temperatures above 700°C. McBeath et al. (2014) reported that the increase of temperature produced larger and more condensed aromatic ring structures for biochar. Past research also found that during biochar formation, an increase in aromaticity occurred first at low

temperatures, followed by structural rearrangement and an increase in aromatic condensation at high temperatures (McBeath et al. 2014; McBeatch et al. 2011).

To develop the potential of hardwood biochar as a conductive filler for electrical conductive composites (ECPCs), the purpose of the study in this chapter was to optimize the biochar material for use in ECPC. Biochar produced from red oak, yellow-poplar, and willow were prepared at pyrolysis temperatures (HTT) of 700°C, 800°C, 900°C, and 1000°C and evaluated for electrical conductivity and physicochemical properties. Additionally, the relationship between conductivity and the changes of physicochemical properties caused by parameters feedstock and HTT were investigated.

4.2 MATERIALS AND METHODS

4.2.1 Materials

Biochar was prepared from red oak (*Quercus rubra*), yellow-poplar (*Liriodendron tulipifera*), and willow SV1 (*Salix × dasyclados*). Willow ‘SV1’ is a high yield, disease resistant, and moderately pest resistant shrub willow that was grown on marginal cropland. The raw particles were first prepared by grinding chips using a Pulverisette mill outfitted with a 1mm mesh sieve. These wood particles were carbonized in a three-heating-zone furnace at a heating rate of 5°C/minute to various highest heating temperatures (HTTs) of 700°C, 800°C, 900°C, and 1000°C for 1 hour. During heating a constant flow of nitrogen was sent through the furnace. Additionally, mixed hardwood biochar manufactured by Charcoal Green® (Crawford, NE) was used as comparison.

4.2.2 Electrical Conductivity Measurement

The dc electrical conductivity of biochar under compression was measured by the four-point method (Marinho et al., 2012; Probst and Grivei, 2002; Celzard et al., 2002) using a device fabricated at West Virginia University (Figure 4.3). The device consists of a non-electrical conducting and high-thermal conducting polytetrafluoroethylene (PTFE) die, oxygen-free high-conductivity copper (with 99.99% copper content) base support, and a copper piston rod. The piston moved down in the cylinder under an applied force that was

controlled by a universal test machine (MTS Model 810). The electrical power was provided by a HP 6205C dual dc power supply (Hewlett Packard, 0-40V, 0.3A/20V, 0.6A), while the current and voltage were measured by digital electrometers (Keithley 2000), separately. The conductivity was estimated according to equations 4.1 and 4.2 as follows:

$$R = V/I \quad (4.1)$$

where:

V = voltage of the sample (volt)

I = current of the sample (ampere)

$$\sigma = l/AR \quad (4.2)$$

where:

l = height of the sample (cm)

A = area of the cross-section of the piston (cm²)

Ten specimens were tested for each kind of biochar and the final exported results are the average of the ten measurements.

The volume of samples was estimated according to equations 4.3:

$$volume = \pi r^2 h \quad (4.3)$$

where:

$\pi = 3.14$

$r = 0.64$ cm, the inner semi-diameter of the device

h = height of the sample (cm), the initial height is 3.81cm

Therefore, the initial volume of samples was 4.9cm³.

Figure 4.3 Schematic of the experimental setup for measuring the electrical conductivity of biochar particles under compression.

4.2.3 Proximate Analysis

Proximate analysis (moisture, volatile matter, fixed carbon and ash) of biochar obtained from red oak, yellow-poplar, and willow was carried out using a proximate analyzer (Model: LECO 701, LECO Corporation, St. Joseph, MI, USA) following ASTM D7582 (2015).

4.2.4 Particle Sizes Analysis

The mean particle size and distribution of biochar were measured by laser diffraction (Mastersizer 2000, Malvern).

4.2.5 Scanning Electron Microscope Analysis

Scanning electron microscopic (SEM) analysis of the microstructure of the biochar particles was performed using a Hitachi S-4700 Scanning Electron Microscope fitted with

an X-ray energy dispersive spectrometry (EDS) detector. All specimens used in this research were tested by SEM.

4.2.6 Brunauer-Emmett-Teller Test

The specific surface area and pore size and distribution of the biochar were estimated by applying the Brunauer-Emmett-Teller equation (BET) to the nitrogen adsorption and desorption isotherms was measured at -196°C using an ASAP 2020 analyzer (Micromeritics Co.Ltd.).

4.2.7 X-ray Diffraction Analysis

X-ray diffraction (XRD) patterns were obtained on an X-ray diffractometer (PANalytical X'Pert Pro, Almelo, Netherlands) with a Cu K α X-ray source, operating at 40 kV and 10 mA.

4.2.8 Fourier Transform Infrared Spectroscopy Analysis

Fourier transform infrared (FTIR) spectroscopy was performed on a Nicolet iS10 spectrometer.

4.2.9 Raman Spectroscopy Analysis

Raman spectroscopy analysis was performed on ground samples with a Renishaw RM1000 microscope (argon ion laser) at 514 nm. A power of 25mW was used with an acquisition time of the 30s and a total of 5 scans per sample.

4.3 RESULTS AND DISCUSSION

4.3.1 Characterization of Biochar

The purity of carbon and the presence of functional groups are critical factors that influence conductivity. The proximate analysis results are shown in Table 4.1. The results show that the fixed carbon and ash content increased significantly at higher pyrolysis temperatures. Also, the results showed that the increase in fixed carbon and ash content

varied by feedstock. The fixed carbon content of red oak, yellow-poplar, and willow biochar were above 89%, 86%, and 81%, respectively. Additionally, the fixed carbon content of commercial biochar (65%) was much lower than biochar obtained by carbonization, but the ash and volatile matter content were much higher. The very low carbon and high ash contents could be dominating factors resulting in a low electrical conductivity of the commercial biochar evaluated. Thus the following tests mainly focused on the biochar carbonized at high temperatures.

Table 4.1 Proximate analysis and yield of wood and biochar (wt%, dry basis).

Sample	HTT (°C)	Ash (%)	Fixed carbon (%)	Volatile matter (%)	Yield (%)
Red oak	untreated	0.2	16.9	83	
	700	0.5	89.7	10	24.5
	800	0.3	90.8	8.9	22.7
	900	0.4	91.3	8.3	23.8
	1000	0.9	93.7	5.5	21.9
Yellow-poplar	untreated	0.3	14.8	84.9	
	700	1.5	86.8	11.6	21.6
	800	1.8	90	8.12	21
	900	1.7	91	7.3	19
	1000	1.7	90.4	78	18.1
Willow SV1	untreated	0.9	16.4	82.7	
	700	4	81.7	14.3	23.2
	800	4.5	85.5	10	22.1
	900	4.2	86.1	9.7	21.6
	1000	4.7	85.3	10.	18.4
Commercial biochar	~300	14.9	65.1	20	

Table 4.2 shows the elemental analysis of various biochar. In general, the oxygen content of willow biochar was higher than the red oak and yellow-poplar biochar. The carbon content of willow biochar was slightly lower than red oak and yellow-poplar biochar. The elemental carbon content likely formed conductive carbon structure. Therefore, the biochar with higher elemental carbon should exhibit a higher conductivity. Furthermore, the content of hydrogen, nitrogen, and oxygen elements likely formed non- or low-conductive ash and volatile matter. Therefore, the biochar with higher ash and volatile content would likely have

a lower conductivity. Table 4.2 also shows the effect of the HTT on particle size and density. For each individual feedstock, all biochar particles were produced from the same original size. The results indicated that different particle sizes were produced under different HTT (Figure 4.4). This occurrence was likely caused by the structural change during carbonization at different conditions. The average density of red oak biochar was the highest, followed by willow biochar and yellow-poplar biochar, respectively. The density of biochar may relate to their conductivity under compression.

Table 4.2 Elemental analysis, particle size and density of biochar.

Sample	HTT (°C)	C (%)	H (%)	N (%)	O (%)	Vol. Weighted Mean D[4,3] (µm)	Density (g/cm³)
Red oak	untreated	45.8	5.9	0.1	40.3		
	700	89.6	1.7	0.1	4.6	309.3	0.17
	800	86.0	0.6	0.1	8.2	277.6	0.18
	900	91.5	0.7	0.1	5.2	495	0.22
	1000	91.4	0	0.2	6.6	385.6	0.20
Yellow-poplar	untreated	45.3	5.8	0.1	41.8		
	700	89.6	1.9	0.1	5.2	207.6	0.11
	800	87.6	0.7	0.1	9.1	239.3	0.11
	900	88	0.5	0.1	8.7	259.8	0.10
	1000	92.8	0	0.5	6	258.2	0.12
Willow	untreated	45	5.9	0.4	40.7		
	700	84.5	1.7	0.5	11.0	323.4	0.15
	800	82.6	0.6	0.5	14.1	394.8	0.13
	900	86.3	0.5	0.4	9.8	453.7	0.14
	1000	87.3	0	0.3	9.12	495.1	0.14
Commercial biochar	~300	63.2	1.9	0.4	30.3		0.29

Figure 4.4 Particle sizes and volume weighted mean diameter of biochar particles produced at each HTT.

The electrical conductivity of biochar under compression can be influenced by morphological properties, as the conductivity depends on the degree of contact and the packing of particles during compression. Figures 4.5-4.7 show the surface texture of the biochar particles at 500x magnification. For all biochar types the surface texture roughness increased with increasing carbonization temperature. The roughness facilitates the contact among particles, and may increase the electrical conductivity or form stronger interfaces with the polymer matrix. At macro scale, the red oak biochar had bigger size pores and more ordered pore distribution (Figure 4.5). The pores in yellow-poplar biochar was smaller than the red oak biochar pores (Figure 4.6) and larger than the willow biochar pores (Figure 4.7).

Figure 4.5 SEM surface images of biochar particles obtained from red oak at different HTT.

Figure 4.6 SEM surface images of biochar particles obtained from yellow-poplar at different HTT.

Figure 4.7 SEM surface images of biochar particles obtained from willow at different HTT.

4.3.2 BET Analysis

Table 4.3 shows the surface area, pore size, and pore volume of the prepared biochar. The surface area of biochar significantly increased with the increase of HTT. At 700°C, the surface area was the highest for the red oak biochar, followed by yellow-poplar and willow biochar, respectively. However, for yellow-poplar, the dramatic increase of surface area resulted when the HTT was higher than 800°C. For willow, the increase occurred when the HTT was higher than 900°C. The pore diameter decreased from 700°C to 900°C. Also, the increase of HTT increased the micropore volume of all feedstocks, increased the mesopore volume of yellow-poplar and willow, and increased the macropore volume of red oak

significantly. These results may correspond to the original porous structure of different feedstock and the unique degradation reaction of different feedstock during carbonization.

Table 4.3 BET surface area, pore size, pore volume of biochar.

Sample	HTT (°C)	BET surface area (m ² /g)	BET average pore diameter (nm)	Pore Volume		
				Micropore (cm ³ /g)	Mesopore (cm ³ /g)	Macropore (cm ³ /g)
Red oak char	700	213.5	2.1	0.079		0.517
	800	304.4	1.7	0.116	0.032	0.013
	900	348.3	1.9	0.121	0.049	0.032
	1000	428.2	2.2	0.156	0.044	0.075
Yellow-poplar char	700	110.2	2.8	0.030		0.062
	800	348.2	1.9	0.117	0.050	0.037
	900	443.6	1.9	0.148	0.092	0.011
	1000	634.3	1.9	0.211	0.139	0.016
Willow char	700	16.5	3.9	0.003		0.019
	800	32	2	0.013	0.002	0.007
	900	225.2	2	0.069	0.003	0.086
	1000	526.4	2.3	0.154	0.189	0.032
Commercial biochar	~300	45.4	3	0.011	0.005	0.022

Figure 4.8 shows the Nitrogen adsorption and desorption isotherms for the carbonized biochar of the three feedstocks at different HTT. The adsorption and desorption capacity towards N₂ was strongly influenced by the precursor material and HTT, specifically the higher the HTT the higher adsorption capacity for each feedstock. This result was likely caused by the increase in surface area of the biochar. Furthermore, the adsorption isotherms of all biochar were seen to be type I and type IV. A type I isotherm shows the characteristic of microporous materials, while a type IV shows the characteristic of materials consisting of both micro and meso-pores. Red oak biochar at 800°C and 900°C were type I, but more closely resembled type IV when produced at 700°C and 1000°C. For yellow-poplar, biochar produced at all HTTs were type I. Willow biochar produced at 700°C, 800°C, and 900°C were type I, and at 1000°C were type IV. Also, the isotherm of willow biochar produced at 1000°C was flatter than the red oak biochar produced at 1000°C. The flatter isotherm meant that the micropores dominated.

Figure 4.8 Adsorption and desorption isotherms for N_2 at -196°C determined for biochar at different HTTs.

4.3.3 FTIR Analysis

FT-IR analyses are showed in Figure 4.9. The peaks between 3600 cm^{-1} and 3200 cm^{-1} corresponded to O-H stretching vibration, the peaks between 2950 cm^{-1} and 2850 cm^{-1} corresponded to aliphatic CH_3 asymmetric and symmetric stretching vibration, the absorbance peaks between 1800 cm^{-1} and 1415 cm^{-1} represent C=C stretching vibrations for alkanes and aromatics, the peaks between 1000 cm^{-1} or 1030 cm^{-1} and 1350 cm^{-1} occurred due to the presence of primary, secondary and tertiary alcohols, phenols, ethers and esters showing C-O stretching and O-H deformation vibrations, and the peaks between 900 cm^{-1} and 700 cm^{-1} represent aromatic C-H out of plane vibrations (Angin 2013). These peaks were visible in raw materials, but not in all carbonized biochar. Results revealed that the functional groups of carbonized red oak, yellow-poplar, and willow were eliminated by pyrolysis for most levels of pyrolysis. However, the willow biochar produced at 700°C exhibited peaks at 1389.52 cm^{-1} and 871.70 cm^{-1} wavenumber location. Since these peaks appeared within the 700 cm^{-1} to 1000 cm^{-1} range, the results suggest that the willow biochar produced at the 700°C level may still contain some cellulose and lignin constituents. The diminished functional groups of biochar may increase the electrical conductivity since the majority of biochar could be ordered carbon. On the another hand, the small amount of functional groups, such as oxygen and nitrogen groups, may assist in forming better interfacial bonds between particles and a polymer.

(a) Red oak

(b) Yellow-poplar

(c) Willow

Figure 4.9 FTIR analysis of biochar.

4.3.4 XRD Analysis

X-ray diffraction patterns of biochar are shown in Figure 4.10. Peaks originating from cellulose were detected from the original wood material. These peaks disappeared when the wood was carbonized. Two broad diffraction peaks were detected for all types of biochar at 2θ equal to 23° and 43° . However, for willow biochar, there were more small peaks appearing in the curves. These small and sharp peaks may be caused by the inorganic components and higher ash contents. The similar pattern has been found in grass biochar (Keiluweit et al. 2010). What the willow and grass-based biochar have in common is that they all have relatively high ash content. Furthermore, results indicated that the ash of biochar obtained from red oak, yellow-poplar and willow all likely consists of calcium and silica-based inorganic compounds.

Additionally, the increased HTT from 700°C to 1000°C did not cause significant difference of diffraction data among the biochar obtained from each wood material. The highest heating pyrolysis temperature of 1000°C was not enough to generate the graphite crystalline structure in red oak, yellow-poplar, and willow. As mentioned above, the crystalline structure contributes to the conductive nature of biochar. Therefore, increasing the crystalline structure will increase the electrical conductivity. Results show the increased HTT didn't help biochar used in this study generate the graphite crystalline structure.

(a) Red oak

(b) Yellow-poplar

(c) Willow

Figure 4.10 X-ray diffraction patterns of different wood and carbon particles.

4.3.5 Raman Spectroscopy Analysis

Table 4.4 and Figure 4.11 show the carbon structure characters of the biochar. The Raman spectrum of the biochar exhibited three peaks two main peaks at 1580 cm^{-1} (G band), 1360 cm^{-1} (D band), and a less pronounced peak at 2500 cm^{-1} to 2900 cm^{-1} (2D band). Both G and D bands are generally caused by sp^2 -bonded (aromatic) carbon. The 2D band is related to the interaction of stacked graphene layers. Usually, an ordered carbon material has a strong and narrow 2D band in the spectra. Conversely, a carbon material with extensive disorder or very small crystal size has a weak and broad 2D band (Escribano et al. 2001). In this study, the weak and broad 2D peaks show that all biochar tested had extensive disordered structure.

The D-band is related to the existence of disordered, and turbostratic structures, and the G-band corresponds to an intermolecular shear vibration of carbon atoms between individual graphene sheets (Escribano et al. 2001, Zhao et al. 2013). The higher HTT increased the height of both D-band and G-band, which may be caused by the increase in both ordered and disordered structure during the reaction at higher temperatures. Therefore, the ratio between the intensity of the D band and the G band (I_D/I_G) is used to estimate the ratio of ordered/disordered structures in amorphous carbonaceous materials. An increase in I_D/I_G corresponds to a relatively higher ordered carbon structure. The I_D/I_G of red oak biochar increased with the increase of HTT. The I_D/I_G of yellow-poplar and willow biochar, however, increased initially and then decreased with further increase of HTT.

Table 4.4 Raman analysis of biochar.

Sample	HTT (°C)	Band	Centre	Width	Height	D band/G band ($I_{D/G}$)
Red oak biochar	700	D	1352	258	3262	2.4
		G	1590	81	4208	
	800	D	1352	229	1587	2.5
		G	1594	78	1887	
	900	D	1347	194	2865	2.8
		G	1591	80	2935	
	1000	D	1353	186	4361	2.9
		G	1593	85	4333	
Yellow-poplar biochar	700	D	1352	263	3800	2.6
		G	1591	83	4634	
	800	D	1351	254	6612	3.1
		G	1591	86	7131	
	900	D	1346	189	5512	2.8
		G	1595	76	5650	
	1000	D	1353	183	5366	2.5
		G	1593	75	6073	
Willow biochar	700	D	1357	256	7591	2.4
		G	1590	90	9048	
	800	D	1354	253	9092	2.7
		G	1587	93	9742	
	900	D	1357	246	10317	3.1
		G	1588	96	10121	
	1000	D	1352	197	8079	2.6
		G	1588	90	8041	
Commercial biochar	~300	D	1366	273	5495	2.1
		G	1595	86	7869	

(a) Red oak

(b) Yellow-poplar

(c) Willow

Figure 4.11 Raman spectra of biochar.

4.3.6 Electrical Conductivity of Biochar Particles

4.3.6.1 Conductivity versus volume and pressure

The measurement of electrical conductivity under compression was applied to the biochar obtained from different feedstocks and HTTs. Figures 4.12-4.14 show the variation of volume and conductivity of biochar samples under compression. In general, with an increase in the applied pressure, the volume decreased and conductivity increased. Also, both the variation in volume and conductivity decreased with the increase of pressure.

The initial volume of all samples was 4.9cm^3 . To compact the biochar from 4.9cm^3 close to 1.0cm^3 required 30-120MPa, 10-70MPa, and 20MPa for the red oak, willow, and yellow-poplar biochar, respectively (Figure 4.12). Results showed that the difference between various feedstocks was more likely related to the initial density of the biochar. In the electrical conductivity test of biochar under compression, higher pressure was required for higher density biochar to reach the final set volume. Probst and Grivei (2002) found that the difference of volume variation of carbon black with the pressure is essentially due to the structure and the resistance to mechanical stress of the samples. Similarly, the difference found within the same feedstock was likely caused by the structural changes of biochar impacted by HTTs. The BET results help to explain the difference in electrical conductivity found with increasing pressure. Specifically, the higher HTT produced biochar with larger surface areas would result in improved contact among particles. Additionally, the porous structure could be a factor in the magnitude of the change in volume produced by compression. Sanchez-Gonzalez et al. (2005) studied the change in volume of carbon black under compaction. They reported that compacted volume was not highly influenced by surface area of the carbon black material. These findings are similar to the results on the biochar produced in this research. Specifically, the biochar with higher surface area (e.g., 1000°C required a similar pressure to compact it to the same volume as lower temperature produced biochar (Figure 4.12). Given these results, the porous structure of carbon materials may be more influential in relation to the pressure required during compaction.

The conductivity under pressure varied among different feedstocks (Figure 4.13). Additionally, the volume of samples varied inversely to the applied pressure and the

conductivity of biochar increased with the decrease of volume (Figure 4.14). Under a pressure range from 0 to 15MPa, the results indicated that the conductivity variation of yellow-poplar biochar was similar to the results of willow. The conductivity variation of red oak biochar, however, was higher than the other two feedstock. Similar to carbon black, the carbon source had a strong effect on the conductivity under compression (Sanchez-Gonzalez et al. 2005, Probst and Grivei 2002, Marinho et al. 2012). For each individual feedstock, the results in this study showed the biochar obtained at higher HTT had higher conductivity under the same pressure. The conductivity of 1000°C biochar was the highest, followed by 900°C, 800°C, and 700°C biochar, respectively. This result corresponded to the results of proximate and ultimate analyses where the increase of HTT increased the carbon content of biochar. The XRD result also indicated that the ash of biochar used in this study was likely non-conductive. Therefore, the carbon content may be one of the most important factors influencing the electrical conductivity of biochar.

(a) Red oak

(b) Yellow-poplar

(c) Willow

Figure 4.12 Pressure versus volume curves of biochar.

(a) Red oak

(b) Yellow-poplar

(c) Willow

Figure 4.13 Electrical conductivity behavior of biochar versus pressure.

(a) Red oak

(b) Yellow-poplar

(c) Willow

Figure 4.14 Electrical conductivity of biochar versus volume.

4.3.6.2 Conductivity versus density

Figures 4.15 and 4.16 show the conductivity of biochar samples versus density. Overall, the electrical conductivity of all samples increased with the increase of their density. At the lower density, contact between particles are relatively weak and likely resulted in difficulty when forming effective conductive paths. However, as the density increased, densification increased due to the rearrangement of particles and the reduction in the distance between particles. Bernard Marinho et al. (2012) also reported a similar phenomenon in carbon particles. Given these results, it appears that as density increases, electrons likely pass easier between the particles.

Furthermore, the HTT is a significant factor in influencing the conductivity. Biochar obtained at the 1000°C HTT had the highest conductivity and variation, and biochar obtained at the 700°C HTT had the lowest conductivity and variation. Also, with the increase of HTT from 700°C to 1000°C, the conductivity increased at various rates for each feedstock (Figure 4.16). Additionally, at 1000°C HTT, when the density was above 0.32g/cm³, the conductivity variation in red oak biochar was the highest, followed by yellow-poplar and willow biochar, respectively. However, when the density below 0.32g/cm³ the conductivity variation of red oak biochar was lower than other two feedstock biochar. The results are likely due to the porous structure of the different feedstock. Red oak biochar had larger size pores than yellow poplar and willow biochar, and the conductivity of red oak biochar was lower at a low applied pressure.

Figure 4.15 Electrical conductivity behavior of biochar as a function of density (all results comparison).

(a) Red oak

(b) Yellow-poplar

(c) Willow

Figure 4.16 Electrical conductivity behavior of biochar as a function of density (shown by different feedstock).

The results of this study indicated that the electrical conductivity of biochar likely depended on its physicochemical properties. The main impact factors were likely carbon content and carbon structure. Lehmann and Joseph (2009) indicated that the structure of carbon highly influences the conductivity of biochar. In this study, the biochar obtained from higher HTT had a higher carbon content, a more ordered carbon structure, and exhibited higher conductivity. Another factor that likely impacted conductivity was the porous structure of biochar. The porous structure of carbon materials is likely related to the change in volume under compression. The biochar obtained from different feedstock and produced at different HTTs exhibited dissimilar porous structures. Additionally, ash content likely had a small role in influencing the biochar conductivity, as the ash of biochar used in this study was likely non-conductive. Specifically, the willow biochar exhibited the highest ash content (4.0% to 4.7%), followed by the yellow-poplar (1.5% to 1.8%) and the red oak (0.3% to 0.9%), respectively. Given these results, the lower conductivity of the willow was likely due in part to the high ash content, as non-conductive ash would have blocked some of the conductive paths. Based on the results of this research, the developed biochar appear to be promising materials for electrical sensing and conducting devices.

4.4 CONCLUSIONS

The conductivity of wood-derived carbon (i.e., biochar) was markedly influenced by the applied pressure, feedstock, and pyrolysis temperature. The applied pressure increased the conductivity of biochar by increasing the contact among particles. Due to the various densities and structures of the biochars obtained from different feedstock and varying HTTs, the influence of pressure on conductivity was different for each feedstock type. For the same feedstock, the conductivity of biochar obtained at 1000°C was the highest, followed by 900°C, 800°C, and 700°C, respectively. The results of proximate analysis shown that the fixed carbon content of red oak, yellow-poplar, and willow biochar were 89.70%-93.66%, 86.83%-90.40%, and 81.71%-85.31% respectively. Generally, biochar with carbon content had higher conductivity. FTIR analysis indicated the functional groups of red oak and yellow-poplar biochar were diminished by carbonization. From the X-ray diffraction

analysis, two broad diffraction peaks were detected for all carbonized biochar at 2θ was 23° and 43° . In addition, the results of Raman spectroscopy revealed that the carbon structure of carbonized biochar changed with different feedstock types and HTT. The research on the electrical conductivity and physiochemical properties of biochar is very critical for the further utilization of biochar as filler in ECPC materials. The results of this study provided valuable data for future research and were the basis for selection of materials in Chapter 5.

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5. THE EFFECT OF BIOCHAR FEEDSTOCK AND PARTICLE SIZE ON THE ELECTRICAL CONDUCTIVITY AND PIEZORESISTIVE BEHAVIOR OF POLYVINYL ALCOHOL/BIOCHAR COMPOSITE FILMS

ABSTRACT

Piezoresistive composites were fabricated using wood-derived biochar as a conductive filler and polyvinyl alcohol (PVA) as a polymer matrix. To investigate the effect of feedstock and particle size distribution of the conductive filler, biochar was prepared from red oak, yellow-poplar, and willow feedstock at 1000°C HTT with two particle size distributions. Results indicated that the percolation threshold of the composites was between 16wt% and 18wt%. The impact of particle size on conductivity and piezoresistive behavior depended on the feedstock. Additionally, the applied temperature increased the conductivity of all specimens in different degree, specifically at low biochar content 6wt% and 8wt%. These results indicated that the electrical conductivity and piezoresistive behavior of PVA/biochar composite films strongly depended on the feedstock, particle size, and temperature.

5.1 INTRODUCTION

The electrical conductivity of electrical conductive composites (ECPCs) occurs by dispersing a conductive filler into a non-conducting polymer matrix. A critical amount of filler is necessary to build up a continuous conductive network in this matrix. The electrical conductivity of ECPCs is a function of the amount of conductor and its particle size, shape, and distribution in the matrix. Therefore, as the loading level of the filler increases, particles come closer together and small agglomerates begin to increase in size. These conducting particles, or small agglomerates, touch other agglomerates or particles and form a conductive network (Figure 5.1), which leads to a decrease of the resistivity of the composite films. The conductivity reaches a critical value at which the conductivity levels off with increased filler concentration. This critical filler concentration needed for network formation is defined as the percolation threshold of this composite (Roldughin and Vysotskii 2000). Li et al. (1999) reported the effect of carbon black (CB) content on the electrical conductivity of Polyurethane/CB composites. When the addition of CB was less than 10wt% the conductivity (σ) was extremely low. As the CB content increased, there was an exponential increase of the conductivity until the percolation threshold of 20wt% was reached.

Figure 5.1 Three dimensional conductive paths in composite without pressure (Hussain et al. 2001).

A relatively low percolation threshold is important to effectively avoid reduction of the mechanical properties of the composite (e.g. viscosity and storage modulus) and for reducing cost (Hwang et al. 2011, Dang et al. 2008). The percolation threshold of ECPCs can be influenced by many factors including: filler particle shape, size and distribution; the type of polymer matrix; and the degree of interaction of filler within the matrix (Roldughin and Vysotskii 2000). For instance, Gubbels et al. (1994) indicated that CB with optimized conductivity, size distribution, and porosity decreased the percolation threshold of CB particle filled polymers. Chen et al. (2007) reported that the high aspect ratio of graphite nanosheets reduced the percolation threshold of silicone rubber/graphite nanosheet composites. Also, Hwang et al. (2011) found that a homogeneous dispersion of poly(3-hexylthiophene) wrapped multi-walled carbon nanotubes in a polydimethylsiloxane polymer matrix resulted in a lower percolation threshold.

Additionally, when external pressure is applied on ECPCs, especially those containing elastic type polymers, the applied force may deform the composites, and result in the conductive particles coming into contact with each other to form conductive pathways. When the applied pressure is then released, the polymer matrix tends to recover and the conducting paths are discontinued (Figure 5.2). The phenomenon where ECPC conductivity depends on an applied pressure is called the piezoresistive effect (Hwang and Jang 2011).

Figure 5.2 Formation of conductive paths in composite by pressure (Hussain et al. 2001).

The piezoresistive effect of ECPCs can be influenced by many factors, in particular, conductor concentration, mechanical and thermal properties of the polymer matrix, range of pressure, and temperature. Wang et al. (2009) reported carbon black content had significant influence on the piezoresistivity of carbon black (CB) filled silicone rubber (SR) composites. They found that under applied pressure from 0 to 1MPa, the mass ratio of CB to SR influenced the resistance of SR/CB composites. Also, the mechanical properties of the polymer are important factors in the sensitivity and reliability of piezoresistive pressure sensors. Wang and Ding (2010) compared CB filled polymers and found that under applied pressures from 0 to 3MPa, the piezoresistivity of SR was significantly higher than that of high density polyethylene (HDP), because of the better elastic behavior of SR. Another critical factor is the range of applied pressure. Most piezoresistive pressure sensor materials can only sense changes in electrical resistance within a specific range of pressure, and may present different regular patterns. For example, Wang et al. (2007) found the electrical conductivity of SR/CB composites increased under pressure in the range from 0MPa to 0.37MPa. In contrast, the electrical conductivity decreased under pressure in the range from 0.37MPa to 0.7MPa. Furthermore, the impacts of temperature on conductivity and piezoresistive behaviors should be avoided for piezoresistive pressure sensors. However, this effect is very difficult to eliminate as most flexible polymers are influenced by temperatures, with the exception of a few thermal-proof polymers. However, it is possible to determine a relatively stable temperature and/or pressure range for a variety of polymers. Knite et al. (2004) reported that the piezoresistivity of carbon black filled polyisoprene nanocomposite sensors was relatively stable from 20°C to 70°C, under an applied pressure from 0 to 0.3MPa.

Research in Chapter 4 investigated the electrical conductivity of biochar obtained from different feedstock and treated at different pyrolysis temperature. The biochar obtained in 1000°C HTT had the best electrical conductivity for each individual feedstock (red oak, yellow-poplar, and willow). Building on these results developed in Chapter 4, the purpose of the study in this chapter is to evaluate the influence of feedstock, particle content, size and distribution of biochar particles, and temperature on the electrical conductivity and

piezoresistive behavior of PVA/biochar composite films. Additionally, the research provided data for optimizing the biochar filler for potential electrical applications.

5.2 MATERIALS AND METHODS

5.2.1 Materials

Biochar was prepared from red oak (*Quercus rubra*), yellow-poplar (*Liriodendron tulipifera*), and willow SV1 (*Salix × dasyclados*). Willow ‘SV1’ is a high yield, disease resistant, and moderately pest resistant shrub willow that was grown on marginal cropland. The raw particles were first prepared by grinding chips using a Pulverisette mill outfitted with a 1mm mesh sieve. These wood particles were carbonized in a three-heating-zone furnace at a heating rate of 5°C/min to 1000°C for 1 hour. During heating a constant flow of nitrogen was passed through the furnace.

To reduce the particle size, 10g of biochar particles were placed in a liter jar. Steel balls (6.34mm in diameter) and 100ml of distilled water were added to the jar and the jar was sealed. The jar was rotated at 70 rpm for a period of 72 hours using a ball mill (US Stoneware, Model 753RM). The produced slurry was then separated using Grade 4 filter paper (Whatman), and then oven dried to a solid phase at 103°C for 12 hours and collected as the Size I (99 to 228 μ m) particles used in this research. After going through the Grade 4 filter paper, the remaining liquid phase was separated using Grade 3 filter paper (Whatman), then oven dried to a solid phase at 103°C for 12 hours and collected as the Size II (35 to 60 μ m) particles used in this research.

PVA solution at 10wt% by weight was made from PVA crystals (Acros Organics, MFCD-00081922). Distilled water (360 ml) was heated to approximately 85°C, and then 40 g of PVA crystals were added to the hot water and stirred with a magnetic stirring device. The mixture was then heated and stirred for 2-4 h at 85°C until the solution became clear. Once the material cooled to room temperature, it was stored in a laboratory refrigerator (4°C) before the composite preparation.

5.2.2 Particle Sizes Analysis

The mean particle size and distribution of biochar were measured by laser diffraction (Mastersizer 2000, Malvern).

5.2.3 Composites Preparation

Different loading levels of biochar were used in the study including 0wt%, 6wt%, 8wt%, 10wt%, 12wt%, 14wt%, 16wt%, 18wt%, and 20wt%. The prepared PVA 10wt% solution and biochar particles were mixed manually until there was an even black color distribution. The solution was then dispersed by ultrasonic treatment (Sonics & Materials, 20 kHz, Model VCX 750) for 1 min at 50% power. The mixtures were degassed in a desiccator under a vacuum (Welch, 60 Hz, Model 2546B-01) and evaporated at room temperature (approximately 25°C and a relative humidity of approximately 30%) until the films were formed. The films were dried in an oven (Thermo Fisher Scientific, Model 6524) at 55°C for 4-6 h. Upon cooling, the films were placed in sealed bags until testing.

5.2.4 Electrical Conductivity Measurement

The conductivity of the films was measured by placing them between two clamps of a dynamic mechanical analysis (DMA) instrument (TA Instruments, Q800) with the holding force between the two clamps set at 99.5kPa. The electrical response was recorded with a NI USB-6210 16-bit DAQ system, using a 5Vdc power source. The absolute accuracy of the 16-bit DAQ system is $\pm 0.003V$. The circuit was depicted in chapter 3 figure 3.1c. According to this circuit, $5V = R \times I + V_0$ and $I = \frac{5V}{R+R_{ref}}$, the resistance of sample (R) was calculated using equation 5.1:

$$R = \frac{5V \times R_{ref}}{V_0} - R_{ref} \quad (5.1)$$

where:

R_{ref} = resistance of the reference resistor (15k Ω)

V_0 = output voltage of the sample (V)

The 5V represents the input voltage of this circuit.

The test was performed at room temperature, and the conductivity (σ) of composites was calculated using equation 5.2:

$$\sigma = \frac{1}{R} \times \frac{l}{A} \quad (5.2)$$

where:

l = film thickness (cm)

A = area under loading (cm²)

R = resistance of the sample (Ω)

Three replicated films were prepared for each treatment (biochar content $\times$ particle size), with each sample being 8mm in diameter and approximately 0.50 ± 0.01 mm in thickness. The final reported results were the average of the three films.

5.2.5 Piezoresistive Test and Analysis

The prepared film samples were cut into samples with a diameter of 8mm. Tests were performed by setting a film sample between two clamps of a dynamic mechanical analysis (DMA) instrument (TA Instruments, Q800) with the holding force between two clamps elevated from 0 to 358kPa at the rate of 1kPa/second. The electrical response was recorded with a NI USB-6210 16-bit DAQ system, using a +5Vdc power source. The circuit was depicted in chapter 3 figure 3.1c. According to this circuit, $5V = R \times I + V_0$ and $I = \frac{5V}{R + R_{ref}}$, the resistance of sample (R) was calculated using equation 5.1:

$$R = \frac{5V \times R_{ref}}{V_0} - R_{ref} \quad (5.1)$$

where:

R_{ref} = resistance of the reference resistor (15k Ω)

V_0 = output voltage of the sample (V)

The 5V represents the input voltage of this circuit.

Three replicated films were prepared for each treatment (biochar content $\times$ particle size), with each sample being 8mm in diameter and approximately 0.50 ± 0.01 mm in thickness. The final exported results are the average of the three films. For testing the effect of temperature, the piezoresistive test was performed via DMA temperature control accessory at different temperature -20°C , -5°C , 10°C , 25°C , 40°C , 55°C , and 70°C , respectively.

5.3 RESULTS AND DISCUSSION

5.3.1 The Effect of Biochar Feedstock on Conductivity

Figure 5.3 shows the voltage output (V_0) and electrical conductivity of the three types of PVA/biochar composites at biochar particles content range from 0wt% to 20wt%. The biochar used for this research were Size I (99 to $228\mu\text{m}$). The PVA/biochar composites became conductive at 6wt% of added biochar particles. Conductivity then slowly increased to 10wt%, followed by sharp increase of conductivity to about 16wt%. After 16wt%, the conductivity started decreasing. The decrease at high biochar particle content was likely caused by the features of the biochar particles and possibly the presence of the non-conductive ash in the biochar as found from the XRD analysis (Chapter 4). The percolation behavior of the PVA/biochar composites is shown in Figure 5.3(b). Results indicate that the percolation threshold of the PVA/biochar composites is between 16wt% and 18wt%. The biochar films exhibited the highest conductivity at 16%wt% (near the percolation threshold) that ranged from 2.1×10^{-4} to 2.4×10^{-4} S/cm. Past research reported that polymers enhanced by CNTs exhibited the highest conductivity 10^{-3} S/cm and above when considering the most popular carbon-based fillers including carbon nanotubes (CNTs), graphite sheets, and carbon black (CB). For example, Zhang et al. (2009) reported that PVA/multi-walled CNTs exhibited a conductivity of approximately 10^{-3} S/cm at 5wt%. In relation to graphite, polymers enhanced by graphite sheets exhibited a conductivity of 10^{-4}

S/cm and above (Du et al. 2004, Zheng et al. 2003, Chen et al. 2001). For carbon black, polypropylene enhanced by carbon black exhibited a conductivity of 10^{-6} S/cm at 10wt% loading (Chodak et al. 1999). Therefore, compared to other carbon-based polymer composites the conductivity of biochar filled polymer composite is in a similar range. Additionally, since the electrical conductivity of PVA/biochar films were measured under a relatively low pressure (99.5kPa), the conductivity of films would increase significantly with an increase in applied pressure.

Figure 5.3 (a) Voltage output of PVA/biochar composites at different biochar content, (b) electrical conductivity of PVA/biochar composites at different biochar content (room temperature).

5.3.2 The Effect of Feedstock on Piezoresistive Behavior

Figures 5.4-5.6 show the piezoresistive behavior of three types of PVA/biochar composites at biochar particles content ranging from 6wt% to 20wt%. Since the PVA/biochar composites became conductive at 6wt% of added biochar particles, results for particle loading below 6wt% were omitted. The biochars used for this research were Size I (99 to 228 μm). For all PVA/biochar composites, as the biochar particles content increased, the sensitivity of piezoresistive behavior increased, but the pressure range of piezoresistive behavior decreased above 10wt%. These results help explain the piezoresistive behavior of various PVA/biochar composites at different biochar contents. The biochar particles that had higher conductivity likely formed conductive networks more readily at a relative low biochar content. In other words, the high conductivity of biochar particles reduced the percolation threshold of the composites. The results indicate that when the applied pressure range was from 0 to 358kPa, the optimized PVA/biochar films that could be used as room temperature piezoresistive pressure sensors were the PVA/biochar films with 6wt% biochar content, since their curves of V_0 versus pressure were linear or close to linear.

Figure 5.4 Piezoresistive behavior of PVA/red oak biochar films at different biochar content (room temperature).

Figure 5.5 Piezoresistive behavior of PVA/yellow-poplar biochar films at different biochar content (room temperature).

Figure 5.6 Piezoresistive behavior of PVA/willow biochar films at different biochar content (room temperature).

5.3.3 The Effect of Particle Size on Conductivity and Piezoresistive Behavior

Figures 5.7-5.9 show the particle size distribution and the average particle size of the biochar particles used in the research on the effect of particle size on the conductivity and piezoresistive behavior of PVA/biochar composites. For the biochar obtained from each wood feedstock was separated into two groups by Size I (larger) and Size II (smaller). The average diameters for Size I and Size II red oak biochar particles were $151.6\mu m$ and $49.1\mu m$, respectively. The average diameters for Size I and Size II yellow-poplar char particles were $228.2\mu m$ and $35.1\mu m$, respectively. The average diameters for Size I and Size II willow char particles were $99.4\mu m$ and $60\mu m$, respectively. Particle Size I has a larger average diameter and broader distribution than particle Size II. The difference in particle size among different feedstock was most likely caused by the various carbon content and carbon structure of biochars obtained from different feedstocks.

Figure 5.7 Particle size distribution of red oak biochar for Size I (a) and Size II (b) particles.

Figure 5.8 Particle size distribution of yellow-poplar biochar for Size I (a) and Size II (b) particles.

Figure 5.9 Particle size distribution of willow biochar for Size I (a) and Size II (b) particles.

Figure 5.10 shows that particle size influenced the conductivity of PVA/biochar films. For red oak, the smaller particle size II increased the electrical conductivity of PVA/red oak biochar films (Figure 5.10a). The smaller particle size likely increased the aspect ratio of particles, and reduced the percolation threshold of PVA/red oak biochar films slightly. However, the smaller particle size decreased the electrical conductivity of PVA/yellow-poplar biochar and PVA/willow biochar films to different extents (Figure 5.10b and c). The reduction may relate to the ash content, and structure of biochar particles obtained from different feedstock. Since the particle size was reduced, the ash could block some of the connections among biochar particles, which would result in a decrease in conductivity of PVA/biochar films. Additionally, since the conductivity of biochar depends on the limited stacked graphene structure, milling particles to a smaller size likely damaged the carbon structure of biochar. In turn, these damaged carbon structures would have influenced the conductivity of the biochar particles and therefore the films containing these particles.

(a) PVA/red oak biochar films

(b) PVA/yellow-poplar biochar films

(c) PVA/willow biochar films

Figure 5.10 Voltage output and conductivity of PVA/biochar films at different biochar particle size (room temperature).

Figure 5.11 shows the piezoresistive behavior of PVA/biochar composites with different biochar particle size. For PVA/red oak biochar films, the reduced particle size increased the piezoresistive behavior of films containing 6wt% biochar, and decreased that of films containing 8wt% biochar. There was no significant change due to differences in particle size found in the PVA/red oak biochar films containing 10 and 12wt% (Figure 5.11a). At a given weight %, there would be a higher number of individual particles when using smaller size particles, and would result in a better likelihood of forming more conductive paths.

However, for PVA/yellow-poplar and PVA/willow biochar films (Figure 5.11b and c), the reduced particle size decreased the piezoresistive behavior of films containing 6wt% and 8wt% biochar content, and increased the pressure range of piezoresistive behavior exhibited by the films containing 10 and 12wt% biochar. The difference among the films containing red oak, yellow-poplar, and willow biochar is likely related to the conductivity of biochar obtained from different feedstock. Specifically, the red oak biochar has a higher conductivity than the other two biochars. Therefore, it was possible for the particles with reduced size to form stable networks and more conductive paths while under compression. However, the smaller particles of yellow-poplar and willow biochars appeared to not have enough conductive capability to form as efficient conductive paths, as compared to red oak derived biochar.

Furthermore, the results indicate that when the applied pressure range was from 0 to 358kPa, the optimized PVA/biochar films that could be used as room temperature piezoresistive pressure sensors are the films containing 6wt% size II red oak biochar and 6wt% size I yellow-poplar or willow biochar. Specifically, because the 6wt% films exhibited linear relationship of V_0 versus pressure throughout the entire range, these types of films would be more convenient to use in many sensor applications. Additionally, the use of only 6%wt biochar would likely make for a more economical sensor.

Figure 5.11 Piezoresistive behavior of PVA/biochar films at different biochar particle size (room temperature).

5.3.4 The Effect of Temperature on Conductivity and Piezoresistive Behavior

Figure 5.12 shows that the effect of temperature on the V_0 of PVA/biochar composites with different biochar content and particle size (I and II), respectively, under applied force at 99.5kPa. In general, the V_0 of all specimens increased in different degrees with the increase of temperature from -20°C to 70°C. The effect of temperature increased more in the films containing lower biochar content (6wt% and 8wt%) than the films containing higher biochar content (10wt% and 12wt%). This phenomenon is likely related to the initial thermal properties of the polymer matrix. When the biochar content was low, the increased temperature likely increased the number of conductive paths due to the increase in the elasticity of polymer matrix. However, when the biochar content was higher, the addition of biochar likely increased the conductive paths and enhanced the tensile modulus of films. In general, the impact of temperature on the conductivity of films containing higher biochar content was smaller than that of lower biochar content.

Figure 5.12 Voltage outputs of PVA/biochar composites at different temperature under 99.5kPa.

Table 5.1 shows the influence of temperature from -20°C to 70°C on the effective pressure range of piezoresistive behavior of the PVA/biochar composites films produced using the different biochar feedstocks and varying percentages. The effective pressure range

represents the range of applied pressure where the film exhibited a piezoresistive effect. Results indicated that all the films containing 6wt% biochar content had an effective pressure range from 0 to 358kPa. Increasing temperature appeared to result in an increase in conductive paths. As biochar content increased from 6wt% to 12wt%, increasing of temperature resulted in a more narrow effective pressure range of piezoresistive behavior for the films. This behavior was likely attributed to the formation of more conductive pathways within the biochar particles at lower temperature while under pressure. However, when the pressure reached the percolation threshold of the films, the piezoresistive behavior disappeared.

The effect of temperature also depended on the type of biochar. At 8wt% and 10wt% biochar content, the pressure range of red oak biochar filled films (0-155kPa and 0-150kPa) were narrower than that of yellow-poplar (0-270kPa and 0-184kPa) and willow (0-306kPa and 0-285kPa) biochar filled films. However, at 12wt% biochar content, the pressure range of yellow-poplar biochar filled films (0-89kPa) were narrower than that of red oak (0-146kPa) and willow (0-172kPa) biochar filled films. Additionally, the films containing 6wt% biochar content showed linear relationships at -20°C, -5°C, 10°C and 25°C, so these films may be appropriate for sensing applications at temperature from -20°C to 25°C where a linear V_0 versus pressure model is ideal. The V_0 versus pressure plots of the temperature study for all the film types are provided in the Appendix.

Generally, the results indicate that for all film types, the increased temperature accelerated the change of resistance under the applied pressures. This phenomenon is likely related to the initial thermal properties of the polymer matrix. The higher temperature increased the elasticity of polymer matrix of PVA/biochar films. The increased elasticity of polymer matrix would allow the film to more easily deformation under pressure, and assist biochar particle to particle contact and the formation of conductive pathways. Along with temperature, the piezoresistive behavior of PVA/biochar films evaluated in under changing pressure and temperature were also dependent on the biochar content, feedstock, and initial conductivity of biochar particles, as previously discussed.

Table 5.1 The effect of temperature on the range of piezoresistive behavior of PVA/biochar films at different biochar feedstocks and contents.

		Effective pressure range of piezoresistive behavior (kPa)							
		T (°C)	-20	-5	10	25	40	55	70
PVA/red oak biochar films	6wt%	0 - 358	0 - 358	0 - 358	0 - 358	0 - 358	0 - 358	0 - 358	0 - 358
	8wt%	0 - 358	0 - 358	0 - 358	0 - 318	0 - 307	0 - 234	0 - 155	
	10wt%	0 - 358	0 - 358	0 - 334	0 - 253	0 - 278	0 - 219	0 - 150	
	12wt%	0 - 328	0 - 313	0 - 299	0 - 270	0 - 180	0 - 188	0 - 146	
PVA/yellow- poplar biochar films	6wt%	0 - 358	0 - 358	0 - 358	0 - 358	0 - 358	0 - 358	0 - 358	0 - 358
	8wt%	0 - 358	0 - 358	0 - 358	0 - 348	0 - 324	0 - 275	0 - 270	
	10wt%	0 - 332	0 - 325	0 - 315	0 - 300	0 - 273	0 - 216	0 - 184	
	12wt%	0 - 289	0 - 272	0 - 261	0 - 244	0 - 182	0 - 93	0 - 89	
PVA/willow biochar films	6wt%	0 - 358	0 - 358	0 - 358	0 - 358	0 - 358	0 - 358	0 - 358	0 - 358
	8wt%	0 - 358	0 - 358	0 - 358	0 - 349	0 - 342	0 - 333	0 - 306	
	10wt%	0 - 358	0 - 358	0 - 344	0 - 338	0 - 321	0 - 302	0 - 285	
	12wt%	0 - 323	0 - 296	0 - 271	0 - 227	0 - 217	0 - 165	0 - 172	

5.4 CONCLUSIONS

The study in this chapter investigated the effect of feedstock and particle size of biochar, and temperature on the conductivity and piezoresistive behavior of PVA/biochar composite films. The percolation threshold of the PVA/biochar composite films was between 16wt% to 18wt% and the conductivity of films were between 2.1×10^{-4} to 2.4×10^{-4} S/cm. At the same biochar content, the conductivity of biochar-based films (Chapter 5) was at least 20 times higher than that of commercial biochar-based films (Chapter 3).

At room temperature, for all PVA/biochar composites, as the biochar particles content increased, the sensitivity of the piezoresistive behavior increased, but the pressure range of the piezoresistive behavior decreased above 10wt%. The films containing 6wt% biochar content, especially red oak and yellow-poplar, performed the best in terms of sensing pressure changes throughout the entire range tested of 0 to 385kPa. For all the feedstock types, when the biochar content reached a high level (above 14wt%), the piezoresistive behavior was minimized (i.e., no change in voltage output with applied pressure). In comparison to the PVA/commercial biochar films tested in Chapter 3, that did not exhibit a piezoresistive behavior at 6wt%, the biochar produced using red oak, yellow-poplar, and

willow produced at 1000°C in this study were able to perform adequately at this lower biochar content.

The particle size results showed a variety of influences on the conductivity and piezoresistive behavior of the films. In relation to electrical conductivity, smaller particle sizes increased the conductivity of the films that contained red oak biochar. In the yellow-poplar and willow biochar filled films, the smaller particle size, however, resulted in a decreased conductivity. In relation to the piezoresistive behavior, the effect of particle size depended on both the biochar content and feedstock type. At 6wt% biochar content, the smaller particle size resulted in an increased piezoresistivity for the films containing red oak biochar. However, at 6wt% biochar content, the smaller particle size resulted in a decreased piezoresistivity in the yellow-poplar and willow biochar filled PVA films.

Additionally, an increase in temperature increased the conductivity of the films, especially in films that contained 6wt% and 8wt% biochar content. The impact of temperature on the piezoresistive behavior of films depended on the biochar content and feedstock type. Higher temperatures and higher biochar content resulted in a narrower effective pressure range of piezoresistive behavior. The films containing 6wt% biochar content exhibited the most linear V_0 versus pressure curves which would represent the most efficient piezoresistive pressure sensor for use at temperatures from -20°C to 25°C.

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6. SUMMARY

The research performed in this study developed and applied wood-derived biochar as a filler material to enhance the mechanical, thermal, and electrical properties of polyvinyl alcohol (PVA) composite films. The effect of feedstock, pyrolysis temperature, and particle size of biochar on the properties of both biochar and PVA/biochar composites has been investigated. Based on the results of tests and analysis, the following conclusions were drawn:

(1) The addition of commercial biochar increased the tensile modulus and storage modulus above the T_g but resulted in a reduced tensile strength. The results of the thermal testing indicated that the addition of biochar improved the thermal degradation and decomposition (T_d) of the PVA/biochar composites but lowered the T_g and T_m . These experimental results indicate that wood-derived carbon material has potential for use as an alternative to traditional carbon-based fillers to improve the mechanical and thermal properties of polymer composites. Specifically, the research laid the foundation for future research on the electrical properties of films with biochar as an alternative to conventional carbon-based fillers in electrical applications. Furthermore, the research on the improvement in feedstock, particle size, and carbon percentage would assist in the development of biochar as potential filler for more applications.

(2) The mean conductivity of PVA/commercial biochar with 6wt% and 10wt% biochar composites was determined to be 0.2×10^{-6} S/cm and 1.8×10^{-6} S/cm, respectively and resulted in bio-carbon reinforced composites that have similar electrical conductivity as most CNT and graphene-reinforced PVA composites. For the piezoresistive behavior, increasing pressure (0 - 358kPa) gradually decreased the resistance of the PVA/biochar composite films with 8wt%, 10wt%, and 12wt% biochar content by 92%, 98%, and 99%, respectively. Results indicated that the increase of biochar content from 8wt% to 12wt% significantly improved the conductivity and piezoresistive effect of PVA/biochar films. Moreover, the effect of thickness was important and complicated, since many factors including biochar size, content and spatial distribution, and electric and mechanical properties of PVA/biochar films likely influenced the results. Additionally, the piezoresistive

behaviors of the PVA/biochar films can be influenced by temperature, but in this study, the films were relative stable at certain temperature ranges. In conclusion, the piezoresistive behaviors of PVA/biochar composite films were found to be rather repeatable and stable, and provide the foundation for further investigation related to the influence of the electrical conductivity of biochar obtained from different feedstock and particle size on the piezoresistive property of polymer materials filled with biochar and carbonized wood materials.

(3) The conductivity of wood-derived carbons was markedly influenced by the applied pressure, feedstock, and pyrolysis temperature. The applied pressure increased the conductivity of biochars by increasing the contact among particles. Due to the various density and structure of the biochar obtained from different feedstock and pyrolysis temperature, the influence of pressure on conductivity was different. Within each feedstock types, the conductivity of biochar obtained at 1000°C was the highest, followed by 900°C, 800°C, and 700°C, respectively. The results of proximate analysis showed that the fixed carbon content of red oak, yellow-poplar, and willow biochar was 89.70%-93.66%, 86.83%-90.40%, and 81.71%-85.31% respectively. Generally, biochar with carbon content had higher conductivity. FTIR analysis indicated the functional groups of red oak and yellow-poplar biochar were diminished by carbonization. X-ray diffraction analysis shown two broad diffraction peaks were detected for all carbonized biochars at 2θ were 23° and 43°. In addition, the results of Raman spectroscopy revealed that the carbon structure of carbonized biochar changed with different feedstock types and HTT. The research on the electrical conductivity and physiochemical properties of biochar is very critical for the further utilization of biochar as filler in ECPC materials. Therefore, the results of this study will provide valuable data for future research.

(4) The effect of feedstock and particle size of biochar, and temperature on the conductivity and piezoresistive behavior of PVA/biochar composite films were investigated. The percolation threshold of the PVA/biochar composite films was between 16wt% to 18wt% and the conductivity of films were between 2.1×10^{-4} to 2.4×10^{-4} S/cm. At the same biochar content, the conductivity of biochar-based films (Chapter 5) was at least 20

times higher than that of commercial biochar-based films (Chapter 3). At room temperature, for all PVA/biochar composites, as the biochar particles content increased, the sensitivity of the piezoresistive behavior increased, but the pressure range of the piezoresistive behavior decreased above 10wt%. The films containing 6wt% biochar content, especially red oak and yellow-poplar, performed the best in terms of sensing pressure changes throughout the entire range tested of 0 to 385kPa. For all the feedstock types, when the biochar content reached a high level (above 14%), the piezoresistive behavior was minimized (i.e., no change in voltage output with applied pressure). In comparison to the PVA/commercial biochar films tested in Chapter 3, that did not exhibit a piezoresistive behavior at 6wt%, the biochar produced using red oak, yellow-poplar, and willow produced at 1000 °C in this study were able to perform adequately at this lower biochar content.

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Based on the findings of this research, there are opportunities to increase the use of wood-derived biochar for electrical applications. The research on mechanical and thermal

properties demonstrated that biochar has potential to be used as filler for composites. The research on electrical conductivity and piezoresistive behaviors exhibited that PVA/biochar composite films are promising materials for piezoresistive sensors, for their repeatable and stable capabilities. Finally, the research on feedstock type, particle size distribution, and temperature assisted in the development of biochar as potential filler and has the potential to assist in the development of carbon filler materials from wood with properties that more closely resemble those of carbon nanotubes and graphene fillers.

APPENDIX – Piezoresistive Behavior of PVA/biochar Films at Different Temperatures

Figure A1 Voltage output vs. pressure relationship of 6wt% PVA/red oak films.

(a) Size I

(b) Size II

Figure A2 Voltage output vs. pressure relationship of 8wt% PVA/red oak films.

Figure A3 Voltage output vs. pressure relationship of 10wt% PVA/red oak films.

Figure A4 Voltage output vs. pressure relationship of 12wt% PVA/red oak films.

(a) Size I

(b) Size II

Figure A5 Voltage output vs. pressure relationship of 6wt% PVA/yellow-poplar films.

Figure A6 Voltage output vs. pressure relationship of 8wt% PVA/yellow-poplar films.

Figure A7 Voltage output vs. pressure relationship of 10wt% PVA/yellow-poplar films.

Figure A8 Voltage output vs. pressure relationship of 12wt% PVA/yellow-poplar films.

Figure A9 Voltage output vs. pressure relationship of 6wt% PVA/willow films.

Figure A10 Voltage output vs. pressure relationship of 8wt% PVA/willow films.

Figure A11 Voltage output vs. pressure relationship of 10wt% PVA/willow films.

Figure A12 Voltage output vs. pressure relationship of 12wt% PVA/willow films.