

BIOCHAR AS A RENEWABLE CARBON ADDITIVE FOR BIODEGRADABLE
PLASTICS

by

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TABLE OF CONTENTS

1. INTRODUCTION	1
2. BACKGROUND.....	4
Bioplastics	4
Biochar	15
3. THEORY	29
4. IMPROVEMENTS IN METHODS FOR MEASURING THE VOLUME CONDUCTIVITY OF ELECTRICALLY CONDUCTIVE CARBON POW- DERS	38
Contribution of Authors and Co-Authors	38
Manuscript Information	39
Abstract	40
Introduction	40
Theory.....	41
Guard ring theory	41
Effective media theory	43
Methods.....	44
Materials	44
Test fixture assembly	45
Conductivity of powders	47
Data analysis and curve fitting.....	48
Changes in particle structure with compression	49
Results and Discussion	49
Characterization of copper and cellulose powders	49
Characterization of carbon powders.....	53
Conclusions	57
5. PHYSICAL AND CHEMICAL MECHANISMS THAT INFLUENCE THE ELECTRICAL CONDUCTIVITY OF LIGNIN-DERIVED BIOCHAR	58
Contribution of Authors and Co-Authors	58
Manuscript Information	59
Abstract	60
Introduction	60
Methods and Materials	63
Materials	63
Biochar production.....	63

TABLE OF CONTENTS – CONTINUED

Volume conductivity and impedance spectra	65
Characterization of biochar chemical structure	65
Thermogravimetric infrared spectroscopy	65
Elemental composition	66
Attuned total reflectance Fourier transform infrared spectroscopy	67
Raman spectroscopy.....	67
Characterization of biochar physical structure	67
Field emission scanning electron microscopy	67
Particle size analysis	68
Gas sorption for BET analysis	68
Statistical methods.....	68
Results and Discussion	69
Biochar processing behavior	69
Biochar electrical conductivity	72
Biochar chemical characterization.....	75
Biochar physical structure.....	82
Relationship between chemical and structural properties of biochar and electrical conductivity.....	85
Conclusions	89
 6. PRODUCING MORE GRAPHITIC LIGNIN-DERIVED CARBONS: IM- PACTS OF LIGNIN PROPERTIES ON CARBON STRUCTURE AND ELECTRICAL CONDUCTIVITY	 91
Contribution of Authors and Co-Authors	91
Manuscript Information	92
Abstract	93
Introduction	93
Materials and Methods	96
Lignin sourcing	96
Biochar production.....	98
Catalyzed biochar production.....	99
Lignin and biochar characterization.....	99
Data analysis	101
Results and Discussion	101
Lignin characterization	101
Lignin thermal transitions and biochar morphology	104
Biochar characterization	108
Iron catalyzed pyrolysis and inorganic interactions	114
Conclusions	117

TABLE OF CONTENTS – CONTINUED

7. BIOCHAR FROM FOOD WASTE AS A SUSTAINABLE REPLACEMENT FOR CARBON BLACK IN UPCYCLED OR COMPOSTABLE COMPOSITES	119
Contribution of Authors and Co-Authors	119
Manuscript Information	120
Abstract	121
Introduction	121
Materials and Methods	124
Materials	124
Biochar production.....	124
Characterization of biochar	125
Composite fabrication.....	126
Composite characterization	127
Results and Discussion	130
Biochar characterization	130
Composite characterization	134
Conclusions	147
8. BIOCHAR-FILLED BIOPLASTICS: A NEW CLASS OF BIOCOMPOSITES FOR ELECTRICAL APPLICATIONS AND BEYOND	149
Contribution of Authors and Co-Authors	149
Manuscript Information	150
Abstract	151
Introduction	151
Results & Discussion.....	153
Impact of biochar on PHBV and PLA	154
Application of biochar-PHBV/PLA composites to produce electrically conductive materials	162
Conclusions	164
Methods and Materials	164
Materials	164
Biochar production.....	165
Characterization of biochar impact on PHBV and PLA	165
Composite production and electrical conductivity	166
9. REDUCING THE ENVIRONMENTAL IMPACTS OF PLASTICS WHILE INCREASING STRENGTH: BIOCHAR FILLERS IN BIODEGRADABLE, RECYCLED, AND FOSSIL-FUEL DERIVED PLASTICS	168

TABLE OF CONTENTS – CONTINUED

Contribution of Authors and Co-Authors	168
Manuscript Information	169
Abstract	170
Introduction	170
Methods.....	173
Experimental methods.....	173
Composite production	173
Composite testing	174
Environmental impact assessment methods	174
Results.....	177
Experimental results.....	177
Life cycle assessment results.....	180
Discussion	182
Conclusions	187
 10. BIOCHAR AS A RENEWABLE SUBSTITUTE FOR CARBON BLACK IN LITHIUM-ION BATTERY ELECTRODES	 189
Contribution of Authors and Co-Authors	189
Manuscript Information	190
Abstract	191
Introduction	191
Experiemental methods.....	194
Methods	194
Biochar synthesis.....	194
Materials characterization	195
Electrode and cell fabrication	196
Electrochemical characterization.....	197
Results & Discussion.....	198
Biochar characterization	198
Electrochemical characterization.....	200
Conductive additive in LIB anodes	202
Conductive additive in LIB cathodes	203
Environmental impact assessment.....	204
Discussion.....	206
Conclusions	207
 11. CONCLUSIONS	 208
REFERENCES CITED.....	214

TABLE OF CONTENTS – CONTINUED

APPENDICES	249
APPENDIX A : Code for analysis of Raman spectra of carbon materials	250
APPENDIX B : Supplemental information to: Improvements in methods for measuring the volume conductivity of electrically conductive carbon powders.....	253
APPENDIX C : Supplemental information to: Physical and chemical mechanisms that influence the electrical conductivity of lignin-derived biochar	268
Supplemental Methods	269
Biochar digestion.....	269
Statistical methods.....	270
Supplemental Results.....	271
Experimental Results.....	271
Statistical Results	271
APPENDIX D : Supplemental information to: Biochar from food waste as a sustainable replacement for carbon black in upcycled and compostable composites.....	282
Supplemental Methods.....	283
Supplemental Results.....	284
APPENDIX E : Extended data to: Biochar-filled bioplastics: a new class of biocomposites for electrical applications and beyond.....	290
Review of thermal degradation of PLA and PHBV with biochar.....	291
APPENDIX F : Supplemental data in support of: Reducing the environmental impacts of plastics while increasing strength: biochar fillers in biodegradable, recycled, and fossil-fuel derived plastics	293
Introduction	294
Supplemental Methods.....	294
Supplemental Results.....	294
APPENDIX G : Supporting Information to: Biochar as a Renew- able Substitute for Carbon Black in Lithium-Ion Battery Electrodes	300
Environmental Impact Assessment Methods	301
Further Material Characterization	302
Further Active Material Electrochemical Characterization	302
Further Anode Additive Characterization.....	302
Cathode Additive Characterization	306

LIST OF TABLES

Table	Page
2.1 A review of the change in thermal degradation of PLA with the addition of biochar	26
4.1 Density and electrical conductivity values for powders	52
4.2 Fit grain electrical conductivity and percolation threshold for powders.....	52
5.1 Biochar production variables and abbreviations.....	64
5.2 Specific comparisons of interest for electrical conductivity of biochars.....	75
5.3 Elemental analysis and ICP-OES results for all biochars.....	77
5.4 Gas sorption surface area measurements for all biochars	82
6.1 Summary of lignin isolation methods and molecular weights. Listed temperatures are maximum processing temperatures.	97
6.2 Paramters for isolation of Alkali lignins.	97
6.3 Calculate XRD and Raman values and peak electrical conductivity for all biochar.	113
7.1 Differential scanning calorimetry results for composites of HDPE and PLA with food-waste-derived biochar	139
10.1 Cell compositions (by weight) in this study.	197
C.1 A review of electrical conductivity of biochar in past literature.	269
C.2 Nitric acid dilution for ICP-OES measurements of biochar.....	270
C.3 Raman average peak locations and I_{DG} ratio for all biochars.....	271
D.1 Average glass transition temperatures from DMA loss modulus curves of PLA.	288
E.1 A review of the thermo-mechanical degradation of PLA with the addition of biochar.....	291
E.2 Summary of biochar physical and chemical characterization.....	292
F.1 DSC values for rHDPE with 0%, 20%, and 40% biochar addition	295

LIST OF FIGURES

Figure	Page
2.1 Mechanical properties of bioplastics.....	5
2.2 PLA and PHAs molecular structure	6
2.3 Overview of biocomposite properties	11
2.4 Localization of filler materials in a polymer blend	13
2.5 Schematic of a tube furnace for lab scale biochar production.....	17
2.6 Review of biochar carbon content.....	18
2.7 Review of biochar electrical conductivity	23
3.1 Electrical conductivity and simplified microstructure of biochar	33
4.1 Schematic describing surface and volume current on the guard electrode method	42
4.2 Schematic of the guard electrode method with dimensions	46
4.3 Equivalent circuit used to fit high compression impedance spectra.....	49
4.4 AC and DC electrical behavior of high and low electrical conductivity materials with the two piston and guard electrode methods.	50
4.5 DC electrical conductivity of carbon powders with two piston and guard electrode methods	53
4.6 AC behavior of a variety of carbon powders with two piston and guard electrode methods	54
4.7 FESEM micrographs of compressed carbon black	55
5.1 Review of biochar electrical conductivity	62
5.2 Biochar yields by biomass and temperature	70
5.3 TGA-IR data for pyrolysis of biochar feedstocks	71
5.4 Biochar electrical conductivity	73
5.5 Biochar impedance spectra	76
5.6 FTIR spectra for biochars from all feedstocks	78

LIST OF FIGURES – CONTINUED

Figure	Page
5.7 Raman spectra for biochar from all feedstocks	80
5.8 FESEM micrographs of biochar from all feedstocks	83
5.9 Effects plots for impact of biochar properties on electrical conductivity	87
6.1 FTIR spectra and XRD patterns for all lignins	103
6.2 DSC curves of all nine lignins, presented endothermic up.....	105
6.3 SEM micrographs of biochars produced from all lignins	107
6.4 Pyrolysis yield and TGA curves for each lignin	108
6.5 Elemental composition of lignin and biochars.....	110
6.6 Electrical conductivity of all biochars as a function of packing fraction.	111
6.7 Characterization of biochar graphitic structure with (a) Raman spectroscopy and (b) XRD.	112
6.8 EDS maps for catalyzed lignin-derived biochar	114
6.9 Electrical conductivity and graphitization of catalyzed biochar.....	115
6.10 Relationship between graphitic crystallite in-plane size (L_a) and electrical conductivity.	117
7.1 Physical and chemical characterization of food-waste-derived biochar	131
7.2 Electrical and chemical characterization of food-waste- derived biochar	132
7.3 SEM micrographs of food-waste-derived biochar.....	132
7.4 Thermal responses of composites of HDPE and PLA with food-waste-derived biochar.....	137
7.5 SEM micrographs of composites of HDPE and PLA with food-waste-derived-biochar.....	138
7.6 Dynamic mechanical reponse of composites of HDPE and PLA with food-waste-derived biochar	140

LIST OF FIGURES – CONTINUED

Figure	Page
7.7 Impact testing of composites of HDPE and PLA with food-waste-derived-biochar	143
7.8 Impact of food-waste-derived biochar on PLA composting rates	145
8.1 Thermal behavior of PHBV with the addition of various biochars	155
8.2 Thermal behavior of PLA with the addition of various biochars	157
8.3 Electrical conductivity of composites of an 80:20 PHBV:PLA blend with biochar or carbon black	162
9.1 System boundary of biochar composites LCA.....	176
9.2 Thermal characterization of rHDPE and biochar composites.....	178
9.3 Tensile testing of rHDPE and biochar composites.....	179
9.4 Dynamic mechanical testing for rHDPE and biochar composites	180
9.5 Environmental impact assessment results for composites of PLA, PHB, rHDPE, and HDPE with biochar	182
9.6 Environmental impacts by processing step for biochar composites	183
10.1 Materials characterization of biochar and carbon blacks.....	199
10.2 Comparison of biochar and artificial graphite as an active material in lithium ion batteries.....	201
10.3 Comparison of biochar and super P as a conductive additive in the anode of lithium ion batteries.....	202
B.1 Photographs of the guard electrode conductivity setup	254
B.2 CAD models of the 3D printed parts for the guard electrode conductivity setup.....	255
B.3 Nyquist plots of the impedance spectrum for copper powder	256
B.4 Nyquist plots of the impedance spectrum for cellulose powder.....	257
B.5 Nyquist plots of the impedance spectrum for graphite	258
B.6 Nyquist plots of the impedance spectrum for HL1100 biochar	259

LIST OF FIGURES – CONTINUED

Figure	Page
B.7 Nyquist plots of the impedance spectrum for VXC72R carbon black	260
B.8 Nyquist plots of the impedance spectrum for VXCM22 carbon black	261
B.9 Time dependent variation of conductivity of copper powder using the guard-electrode method.....	262
B.10 Time dependent variation of conductivity of copper powder using the two-piston method	263
B.11 Time dependent variation of conductivity of graphite powder using the guard-electrode method	264
B.12 Time dependent variation of conductivity of graphite powder using the two-piston method	265
B.13 Time dependent variation of conductivity of graphite powder using the guard-electrode method	266
B.14 Time dependent variation of conductivity of graphite powder using the two-piston method	267
C.1 Full 3D representations of TGA-IR data for all biochar feedstocks.....	272
C.2 Nyquist plot for WS900, WS1100 and CELL900 biochars	273
C.3 Full spectra and non-baseline corrected FTIR curves for all biochar	274
C.4 Raman spectra and curve fitting for three replicates each of AL900 and AL1100 biochars	275
C.5 Raman spectra and curve fitting for three replicates each of DAL900 and DAL1100 biochars	276
C.6 Raman spectra and curve fitting for three replicates each of HL900 and HL1100 biochars	277
C.7 Raman spectra and curve fitting for three replicates each of WS900, WS1100, and CELL900 biochars	278
C.8 Pore size distribution from gas adsorption measurements for all biochars	279

LIST OF FIGURES – CONTINUED

Figure	Page
C.9 Gas adsorption isotherms for all biochars.....	280
C.10 Particle size distribution for all biochars	281
D.1 Photograph of the four-point electrical conductivity method setup	283
D.2 Photographs of the setup for PLA and FW900 biochar composting experiments.....	284
D.3 FTIR spectra of bio-oil produced during pyrolysis of FW900.....	285
D.4 EDS maps for FW900 biochar.....	285
D.5 Supplemental DSC curves for PLA and HDPE with FW900	286
D.6 TIR spectra for PLA and HDPE for 0% to 100% biochar addition.	286
D.7 All collected storage, loss and $\tan(\delta)$ curves for PLA and HDPE with FW900 biochar composites.	287
D.8 Optical microscope images of PLA samples with 2.5%, 5%, 10% and 20% FW900 biochar	288
D.9 Composted PLA samples with and without FW900 biochar	288
D.10 FESEM micrographs for (a) neat PLA and (b) neat HDPE.	289
D.11 Notch geometry of a Charpy impact sample shown in a neat PLA sample.....	289
E.1 Change in sodium sulfate content with washing as measured with (a) XRD and (b) EDS.	292
F.1 Photographs of HDPE tensile samples with 0%, 20% or 40% biochar addition.....	294
F.2 rHDPE viscosity data with 0%, 20%, and 40% biochar	295
F.3 Replicate DMA curves of composites of rHDPE with biochar.....	296
F.4 Supplemental environmental impact assessment results for PLA, PHB, rHDPE, and HDPE for 0%, 20%, and 40% biochar addition.....	297

LIST OF FIGURES – CONTINUED

Figure	Page
F.5 Supplemental environmental impacts by constituent and processing step.....	298
F.6 EDX spectra for Pacific Biochar, with the elements that are detected, labeled.	299
G.1 System boundaries for the environmental impact assessment.....	301
G.2 Further materials characterization of Super P, Vulcan XC-72, and biochar	303
G.3 Replicate electrochemical characterization of electrodes containing 90% biochar	304
G.4 Replicate electrochemical characterization of electrodes containing 90% biochar	305
G.5 Replicate electrochemical characterization of electrodes containing biochar or Super P as the conductive additive	306
G.6 Replicate EIS spectra of electrodes.....	307
G.7 Electrochemical characterization of NMC811 cathodes.....	307
G.8 EIS spectra of a NMC cathode with Super P as the conductive additive	308

ABSTRACT

Biochar - a carbon material produced from pyrolysis of biomass - is a promising alternative to petroleum-derived filler materials in biobased and biodegradable plastics. In this application, biochar can replace materials such as carbon black, with a material that is compatible with end-of-life degradation of bioplastics, while reducing costs and improving material properties. Specifically, high electrical conductivity biochar has the potential to be applied to create highly electrically conductive and biodegradable biochar-bioplastic composite materials. Herein, two critical gaps to development of biochar-bioplastic composites are addressed: the high variation in biochar electrical conductivity and poor thermal interactions between bioplastics and biochar that reduce the bioplastics molecular weight and mechanical properties. To this end, biochars are produced from a variety of feedstocks and their chemical structure and electrical conductivity are extensively characterized. The relationship between feedstock chemical properties, biochar chemical properties, and biochar electrical conductivity is examined. Feedstock oxygen and inorganic content are found to play a critical role in developing highly electrically conductive biochar. The impact of these biochars on the thermal behavior of bioplastics is then examined in detail, and multiple hypotheses for the reduction in thermal behavior that have been proposed in past studies are tested. Biochar moisture content is found to have a limited impact on polymer thermal degradation, while alkali and alkaline earth metals present in biochar reduce the thermal degradation temperature of common bioplastics. A simple washing method was developed to remove these metals and improve the thermal stability of biochar-bioplastic composites. Finally, the environmental benefits of biochar-plastic composites are examined with life cycle assessment methodology, and the developed biochar is examined as a conductive additive in lithium-ion batteries. This work addresses two critical issues that limited the potential of biochar to reduce environmental impacts of rapidly growing classes of materials, as well as demonstrating its applicability in critical applications of petroleum-derived materials. Biochar-bioplastic composites show a unique combination of high electrical conductivity and biodegradability, with strong potential for development of applications in diverse industries from agriculture to biomedical applications.

INTRODUCTION

Developing renewable alternatives to materials traditionally derived from fossil fuels is crucial for reducing our society’s reliance on non-renewable feedstocks and materials. Primary among these materials are plastics, with 367 million metric tons of plastic produced globally in 2020 [1]. In addition to the plastics themselves, many commonly used plastic additives, such as carbon black, are also fossil-fuel-derived [2]. The production of petroleum-derived plastics and additives are significant sources of greenhouse gas emissions. For example, the production of 1 kg of high-density polyethylene (HDPE) results in emissions of 2.8 kg of CO₂ equivalent, while production of 1 kg of carbon black results in 3.3 kg of CO₂ equivalent [2, 3]. Further, improperly disposed of plastic pollution results in significant environmental damage [4], and regulators in both the United States and internationally have called for methods to reduce plastic pollution [5, 6].

Replacement of ubiquitous plastic materials with bio-based and biodegradable plastic is one promising method to help mitigate their environmental impacts across a broad set of applications, from packaging to high-end electronics. Promising alternatives to petroleum-derived plastics include bio-based plastics, such as polylactic acid (PLA), poly-3-hydroxybutyrate-co-3-hydroxyvalerate (PHBV), and thermoplastic starches (TPS). These bioplastics are already well-established commercially and their application is expected more than double in the coming decade [7]. However, this growth will be accompanied by a required increase in land use for the growth of biomass-based feedstocks for these bioplastics, a significant factor in the high environmental impacts of bio-based plastic production [8]. This impact can be mitigated by adding waste-derived biomass filler materials (e.g., agricultural waste such as wheat stems or industrial waste such as lignin) to these plastics

to reduce the use of virgin materials and modify the material properties of plastic. However, widespread application of these fillers is limited by their variation based on feedstock, high moisture content, and poor interactions between the filler material and the plastic typical for typical waste-derived filler materials such as agricultural waste [9, 10].

Biochar is one such waste-derived filler that has been examined as a promising additive in both petroleum-derived and bio-based plastics [11]. Biochar is a carbonaceous material produced by the pyrolysis of biomass [12]. Interest in biochar has rapidly grown in the past decade as a method to sequester carbon, a beneficial soil amendment, a material used in environmental reclamation, and a replacement or additive for broad sets of materials, including gypsum, concrete, and plastic [11, 12, 13, 14, 15]. As an additive to plastics, biochar can be broadly applied to reduce material environmental impacts while providing a wide range of material property benefits, including increased strength, reduced cost, black pigmentation, and increased thermal and electrical conductivity [11]. Relative to raw biomass, biochar improves performance as a filler in plastics as it allows for the use of broader sets of feedstocks [11], has improved interactions with the plastic [16], reduces moisture adsorption [17], and increases thermal stability [11, 18]. Further, biochar can be produced with high electrical conductivity [19]. Therefore, it can be applied as an electrically conductive filler material in plastics to produce anti-static materials, sensors, and 3D printed electrical parts. In these plastic applications, it also can be used to replace commonly used petroleum-derived filler materials, such as carbon black [11, 20].

Broadly, this work aims to develop biochar as a renewable alternative to electrically conductive carbon black, specifically, in composites with biodegradable plastics. To this end, three specific objectives are considered: (1) optimizing biochar electrical conductivity and identifying pyrolytic mechanisms that result in high electrical conductivity, (2) improving biochar interactions with biodegradable plastics, and (3) demonstrating the applicability of biochar in common applications of carbon black and the potential of biochar to reduce the

environmental impacts of plastics.

In the first objective, an improved method for measuring the electrical conductivity of carbon powders is developed (Ch. 4). This method is applied to measure the electrical conductivity of biochar. The mechanisms that contribute to producing highly electrically conductive biochars are examined in detail for lignin-derived biochars, and promising feedstocks for further development are proposed (Ch. 5 and 6). Next, the deleterious thermal interactions of biochar and PLA are characterized, and the properties of biochar-HDPE and biochar-PLA composites are directly compared (Ch. 7). The mechanisms behind the reductions in thermal degradation temperatures of PLA and PHBV with biochar addition are examined, multiple past hypotheses for the cause of this issue are tested, and methods are developed to mitigate these negative interactions (Ch. 8). The potential of biochar to reduce environmental impacts of petroleum-derived, recycled, and bio-based plastics is then modeled with a life cycle assessment methodology (Ch. 9). Finally, the potential of highly electrically conductive biochar to replace carbon black in lithium-ion batteries is examined (Ch. 10). Combined, this work addresses critical thermal degradation issues that have previously prevented biochar and biodegradable plastics from replacing petroleum-derived materials across various applications and demonstrates the potential reductions in environmental impacts and material property benefits of this replacement.

BACKGROUND

This chapter introduces the chemical properties and structure-property relationships of common bioplastics (herein used to describe plastics that are both biobased and biodegradable). First, these polymers' typical biodegradation and thermal degradation mechanisms are presented, and their environmental impacts are discussed and compared to petroleum-derived plastics. Next, the role that polymer blends can play in tuning the properties of these bioplastics is discussed, along with the thermodynamic interactions that influence the structure and performance of polymer blends. Finally, biochar's material properties, production, and applications are introduced, and a comprehensive literature review of biochar in electrochemical and electrical applications and polymer composites is presented. Combined, this chapter provides the context in which the following chapters build the application of biochar in bioplastic composites and electrochemical storage.

Bioplastics

The application of bioplastics has grown rapidly in the past 20 years, driven by both consumer demand and regulation aimed at reducing plastic pollution [10, 21]. Two of the most commercially successful bioplastics are polylactic acid (PLA) and polyhydroxyalkanoates (PHAs) [21]. Combined, these materials make up 45% of global bioplastics production [22]. PLA and PHAs have comparable mechanical properties to many common petroleum-derived plastics, such as polypropylene (PP), polyethylene terephthalate (PET), high-density polyethylene (HDPE), and polystyrene (PS), and as such, can replace petroleum-derived materials across a variety of applications (Figure 2.1a) [21, 23].

PLA is most commonly produced from sugar or starch feedstocks via fermentation to produce lactic acid. Lactic acid is then converted to its dimer lactide via oligomerization and cyclization [21] and polymerized to form PLA via ring-opening polymerization [28]. The

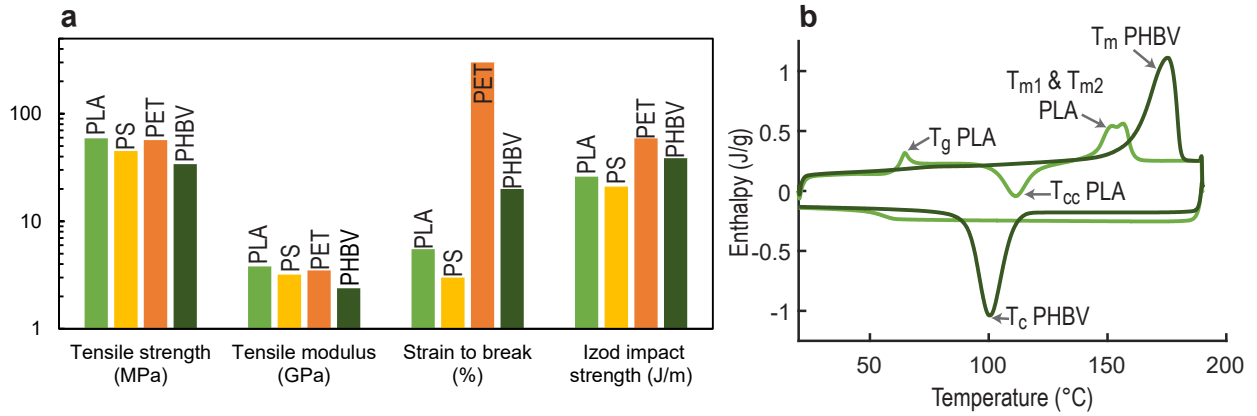


Figure 2.1: (a) Tensile strength, tensile modulus, strain-to-break, and notched Izod impact strength for PLA, PS, PET, and PHBV. Data adapted from [24, 25, 26, 27]. (b) Differential scanning calorimetry (DSC) curves for PLA and PHBV showing prominent thermal transitions: melt (T_m , T_{m1} , T_{m2}), glass transition (T_g), cold crystallization (T_{cc}), and crystallization (T_c) presented endothermic up. Data from Ch. 7 and 8.

resulting polymer is an aliphatic polyester and is typically a copolymer of two isomers: L-PLA and D-PLA (Figure 2.2). The ratio of these isomers impacts the polymer crystallinity and thermal transitions, with increased crystallinity, glass transition temperature, and melt temperature resulting from higher compositions of L-PLA monomers [29]. Typical average molecular weights for commercial PLAs are around 100,000 Da [30].

PLA can be produced with a range of thermal and mechanical properties, depending on the ratio of L to D isomers, molecular weight, and processing conditions used. Typical values of ultimate tensile strengths (σ_{TS}) for PLA range from 21 to 60 MPa, while typical Young's modulus (E) values vary from 0.35 to 3.5 GPa [31]. Common industrial PLAs (e.g., Natureworks 2003D) typically have strength and modulus values in the upper portion of this range ($\sigma_{TS} = 53$ MPa and $E = 3.5$ GPa) [32]. The glass transition temperature can vary from 45 to 60 °C, while the melt temperature can vary from 150 to 162 °C [31]. Lower melt and glass transition temperatures are typically associated with reduced molecular weight, or increased D-PLA content [33], while the mechanical properties are most strongly influenced by the degree of crystallinity. Broadly, the mechanical properties of PLA are comparable to

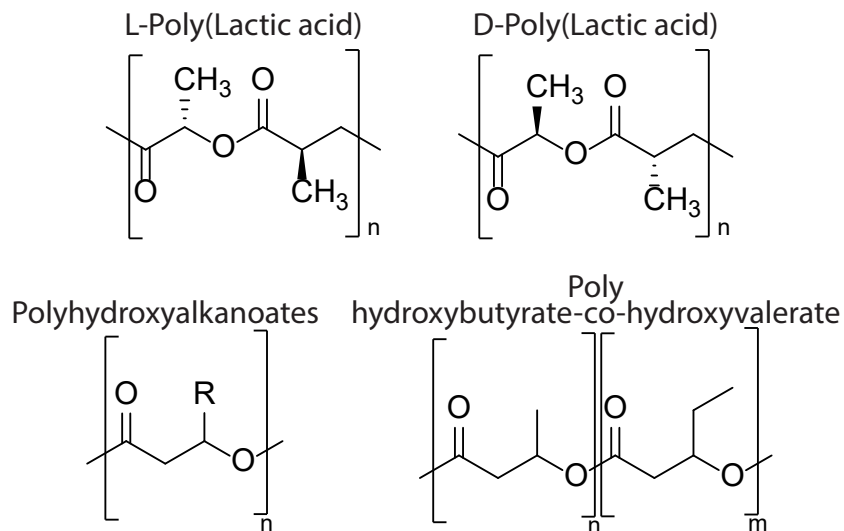


Figure 2.2: (Top) D- and L-poly(lactic acid) stereochemistry. (Bottom) General molecular structure of PHAs and molecular structure of PHBV copolymers.

those of common petroleum-derived polymers PET and PS (Figure 2.1a) [24].

PLA shows more complex crystallization and melt behavior than other polymers - with the possibility of two-stage melt transitions observed during melt and an endothermic cold crystallization transition during heating rather than a crystallization transition during cooling (Figure 2.1b). Important limitations of PLA include its low heat distortion temperature (~ 55 °C) and increased gas and water permeability relative to PET [34]. However, PLA outperforms other common bioplastics in water permeability [35]. Currently, PLA makes up around 40% of global bioplastic production, driven partly by its low cost (1.14 \$/kg) relative to other biodegradable plastics and price competitiveness with petroleum-derived plastics [36, 37]. Despite the drawbacks of low heat deflection temperature and high gas permeability, the low cost and strong mechanical properties of PLA make it an attractive alternative to petroleum-derived polymers in food packaging applications [38, 39].

PHAs represent a family of polymers and copolymers synthesized via fermentation of sugars or lipids by bacteria resulting in a linear polyester [10, 40]. In this process, PHA-

producing bacteria are deprived of key nutrients in the presence of excess carbon, stimulating the production of PHAs *in vivo* via acetyl-coenzyme-A, which is then enzymatically converted to typical PHAs at yields as high as 90% of the dry cell mass [41, 42]. The PHAs are then separated from the bacteria by centrifuging, cell lysis, filtration, and solvent purification [43]. PHAs have the general structure shown in Figure 2.2, where R is the functional group that varies by type of PHA based on the bacterial species and carbon feedstock used to produce the polymer [44]. Primary among commercialized PHAs are polyhydroxybutyrate (PHB) and its copolymer poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), in which hydroxybutyrate and hydroxyvalerate monomers have methyl and ethyl function groups respectively (Figure 2.2).

Adding the hydroxyvalerate copolymer to PHB provides several benefits, including increased thermal stability and improved mechanical properties [21]. The properties of PHBV can be modified by varying the ratio of the hydroxybutyrate and hydroxyvalerate copolymers. Typically, increased hydroxyvalerate content results in reduced melt temperature, glass transition temperature, and crystallinity [45]. As a result, the mechanical properties of the resulting copolymer can be tuned to the expected application - with higher hydroxyvalerate content resulting in increased impact strength, ductility, and biodegradation rate but decreased tensile strength [45, 46]. The application of PHBV is currently limited by its high cost, poor toughness, and a small window for thermal processing [36]. Unlike PLA, PHBV is not price-competitive with common petroleum-derived plastics at 10.93 \$/kg [47], severely limiting its commercial application. This high price is primarily due to the high energy requirements for PHBV production [10]. The small temperature window for thermal processing of PHB and PHBV is due to their relatively high melt temperature (175 °C for PHB and $\sim$ 160 °C for PHBV) and low thermal decomposition temperature ($\sim$ 200 °C) [48]. The thermal decomposition temperature of PHBV increases relative to PHB at low percentages of hydroxyvalerate (<10%), but decreases at higher percentages

[48]. Therefore, commercial injection molding grades of PHBV (e.g., Tianan ENMAT Y1000) have approximately 5-7 mol. % hydroxyvalerate monomers, maximizing the range between melt and decomposition temperatures [49].

While both PLA and PHBV are biodegradable, the conditions required for their biodegradation differ. Typically, PLA degrades at slower rates than other bioplastics [21]. In PLA, biodegradation typically begins with hydrolysis via chain scission at ester bonds in the polymer backbone, resulting in many low molecular weight lactic acid oligomers [50]. These short lactic acid oligomers can then be absorbed and metabolized by several microbes present in compost [51]. Under environmental conditions (e.g., in soil or a landfill), PLA degradation occurs slowly, with over six months required for degradation [52]. In contrast, under industrial composting conditions, PLA degrades in as little as 30 days [52, 53]. This shift in behavior is attributed to the temperature of industrial composting facilities being higher than the glass transition temperature of PLA, increasing the water absorption rate of PLA and therefore the hydrolysis rate. Further, increased levels of PLA-degrading organisms are present in compost than in soil [52].

In contrast to PLA, PHBV degrades readily under environmental conditions, as the microorganisms that produce PHB-depolymerase enzymes are more readily present in the environment. As such, PHBV will fully degrade in as little as one month in soil [54]. Both PLA and PHBV biodegradation are heavily influenced by polymer structure, including molecular weight, crystallinity, isomer and copolymer ratios, and surface energy [46, 55]. Typically, increasing crystallinity and hydrophobicity decrease biodegradation rates, while increasing hydroxyvalerate content in PHBV and D-PLA content in PLA increase biodegradation rates. In both PLA and PHBV, adding filler materials can impact biodegradation rates [56, 57], both by influencing polymer properties such as crystallinity and by modifying composite bulk properties such as moisture absorption.

A critical drawback to both PLA and PHBV is the limited temperature range between

melt and thermal degradation temperatures. For PLA, this range is typically 170-270 °C, while for PHBV, this range is typically 160-200 °C. For both polymers, a reduction in molecular weight is seen at lower temperatures than the onset of mass loss [58, 59]. This limited range constrains the temperatures used for melt processing methods such as extrusion, injection molding, and hot pressing. In PLA, this thermal degradation primarily occurs via chain scission of the ester bond, resulting in the reformation of lactide monomers [58]. Similarly, in PHBV, thermal degradation occurs via chain scission of the ester bond; however, this reaction forms an intermediate six-member ester ring that thermally degrades to crotonic acid [60, 61]. In both polymers, the rate of thermal degradation is increased by the presence of oxygen, water, or metal-containing compounds [58, 60]. This thermal degradation is of particular concern when selecting filler materials. Biomass fillers that have been extensively studied to modify the properties of biodegradable plastics are often high in moisture. Therefore their inclusion can reduce the properties of PLA or PHBV [62] and careful filler selection and drying are required to ensure thermal compatibility with PLA or PHBV.

Bioplastics are typically presented as “eco-friendly” alternatives to petroleum-derived plastics. However, the shifts in environmental impact between bioplastics and petroleum-derived plastics vary depending on the environmental impact category considered. Typically, production of PLA results in lower greenhouse gas emissions and fossil fuel consumption than production of petroleum-derived plastics [63, 64, 65, 66, 67]. This decrease is attributed to the lack of fossil fuel feedstock, and low energy requirements for production [21]. However, the end-of-life of the material meaningfully impacts the life cycle emissions. As PLA recycling is not widely available, it may be landfilled, incinerated, or composted in scenarios where petroleum-derived plastics would be recycled. In this case, the overall lifecycle emissions for PLA are greater than those for petroleum-derived plastics [63]. In contrast, PHB produced from sugars shows higher greenhouse gas emissions than either PLA or petroleum-derived

plastics [66, 67]. These high emissions are attributed to the high energy requirements for PHBV production [66]. However, this impact can be reduced by using waste-derived feedstocks, such as methane emissions from landfills as the feedstock for PHB production, rather than sugars that are currently commercially used [66, 67].

To fully categorize the environmental impacts of bioplastics, environmental impact categories beyond those typically considered in a life cycle assessment must be examined. For example, both PLA and PHA may result in lower plastic pollution than petroleum-derived plastics, as they degrade over time [68]. However, limited studies to date suggest that prior to biodegradation PLA and PHAs result in similar ecotoxicity impacts in the marine environment to petroleum-derived plastics [68]. Further, production of both PLA and PHAs currently requires increased land use relative to petroleum-derived plastics [69, 70, 71]. This increased land use can result in land-use changes to sugar or corn-producing agricultural land, resulting in decreased soil carbon content and loss of ecosystem diversity [71]. When considering these impacts, some studies find bioplastics to result in higher greenhouse gas emissions than petroleum-derived plastics [71]. These land-use changes can be mitigated using waste-derived feedstocks for bioplastic production and efficient use of feedstocks, polymer production processes, and crop cultivation coproducts. Overall, bioplastics have the potential to provide several environmental benefits, including reduced reliance on fossil fuels, the potential for reduced plastic pollution, and reduced greenhouse gas emissions from the production of PLA. However, as their use increases, it is essential to consider efficient feedstock production or waste-derived feedstocks and develop effective bioplastic recycling systems to prevent adverse environmental impacts associated with bioplastic production.

An important limitation of bioplastics is their limited range of material properties relative to petroleum-derived plastics. This limitation can be partially mitigated by using biocomposites - composite materials that combine bioplastics with natural materials as a fiber or filler. Common fiber or filler materials include bamboo, cotton, jute, flax, or hemp

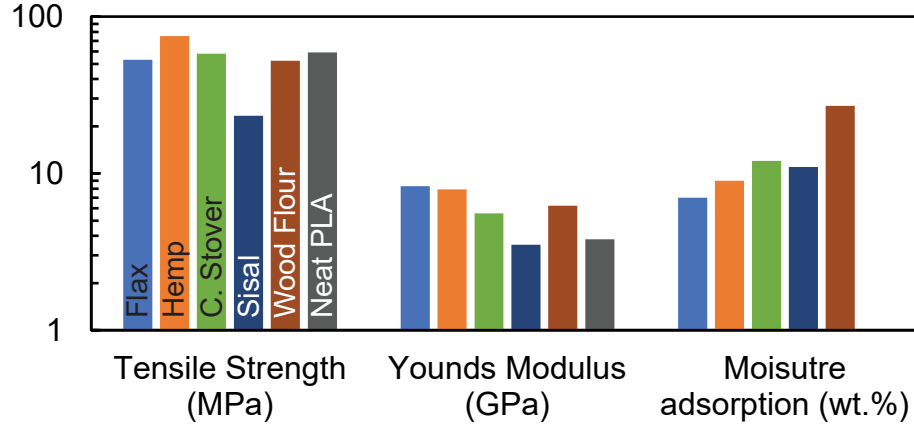


Figure 2.3: Tensile strength and Young's modulus composites of PLA with 30% flax, hemp, corn stover, sisal, and wood flour natural fibers and moisture adsorption percentages of those fibers at equilibrium at approximately 65% RH. Data adapted from [75, 76, 77, 78, 79, 80, 81, 82].

fibers, wheat stems, wood, cellulose, or lignin [10, 72, 73, 74]. These materials provide several benefits over traditional fiber or filler reinforcements (Figure 2.3). Natural fibers typically have a lower density ($1.3\text{-}1.6\text{ g/cm}^3$) than glass or carbon fiber reinforcements ($1.7\text{-}2.5\text{ g/cm}^3$), lower cost (30-130% of glass fiber cost), and the ability to biodegrade along with a bioplastic at the end of the materials useful life [10, 73, 74]. While natural materials have lower strength and modulus values than glass or carbon fibers, their addition can still improve the strength and stiffness of plastics (Figure 2.3), allowing for the use of bioplastics in a broader range of applications [10, 75]. The properties of each fiber vary depending on the ratio of cellulose, hemicellulose, and lignin present in the fiber. For example, fibers with high crystalline cellulose content will be higher in strength than a fiber high in lignin content but also adsorb more moisture [10].

Biocomposites present several drawbacks compared to traditional composites. During material processing, the low thermal degradation temperature of biomass limits the temperature range used during melt processing of the plastic. Further, the high moisture

content of biomass can contribute to hydrolysis of PLA or PHBV during processing, reducing their molecular weight and mechanical properties [10]. Water adsorption into the natural materials can result in swelling during use, causing poor dimensional stability and reduced mechanical properties. The addition of natural fibers can decrease the fire and bacterial resistance of the material - limiting biocomposite application in critical areas such as building materials and food packaging [75]. Further, a poor interface between the fiber and polymer can reduce mechanical properties. Poor interfaces in biocomposites are often caused by a mismatch between the surface energy of hydrophobic polymers and hydrophilic natural materials [9].

Similarly to biocomposites, blends of two or more polymers can be used to tune the properties of bioplastics to a desired application [83]. Polymer blends are broadly categorized as immiscible when the polymers do not mix and exist as two distinct phases or miscible when the polymers do mix. Of particular interest for this work are immiscible blends of PLA and PHBV. The miscibility of polymers is dependent on their surface energies and molecular weights, with lower molecular weight PHBV and PLA blends tending to be more miscible than higher molecular weight blends [39, 84]. In addition, the impact of polymer blends on material properties, such as thermal transitions, differs between miscible and immiscible blends. For example, in miscible blends the glass transition temperatures of the two constituent polymers will combine into a single glass transition that can be predicted by the rule-of-mixtures [84]. In contrast, immiscible polymer blends will present two individual, slightly shifted glass transitions for each defined phase, with the shift being towards the glass transition temperature of the other blended polymer and the magnitude of the shift depending on the blend ratio [84, 85].

For immiscible blends, the morphology of these phases can be varied by changing the blend ratio of the individual constituent polymers. Depending on blend ratios and the viscosity of the individual polymers, the morphology of these phases can be predicted. At

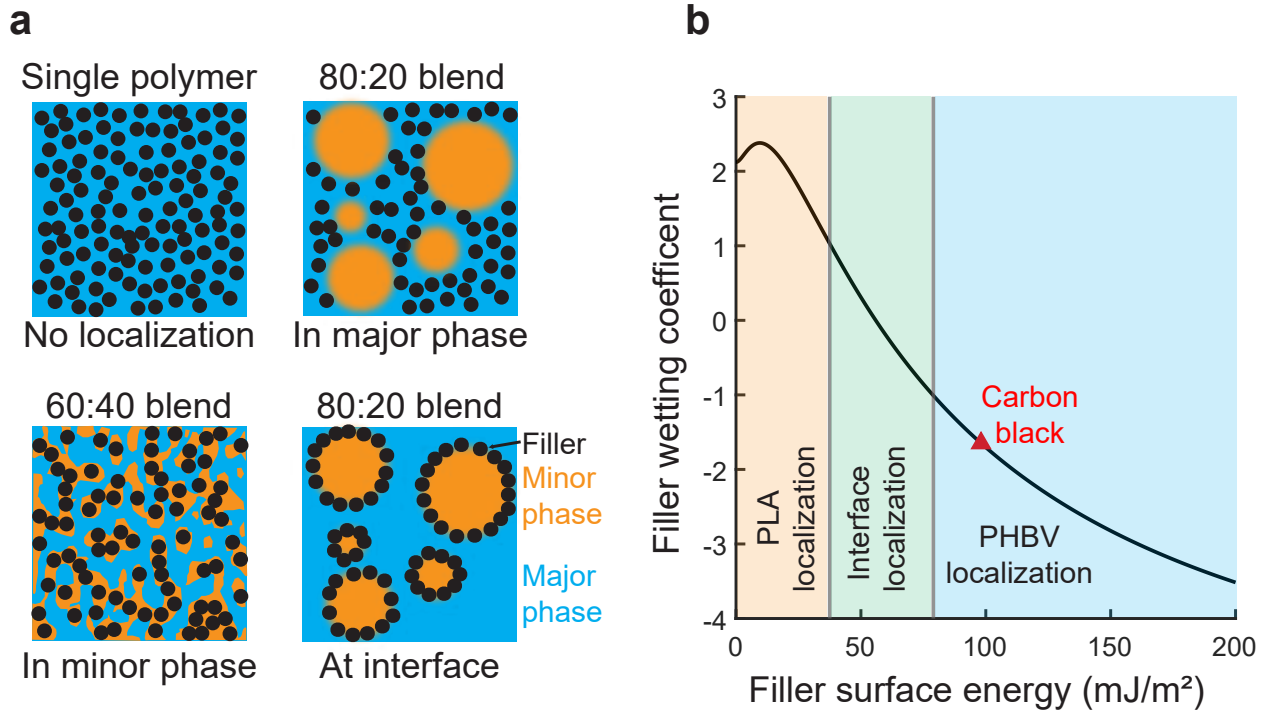


Figure 2.4: Localization of filler materials in a polymer blend. (a) Example morphologies of fillers in an unblended polymer, 80:20 blend with localization in the major phase, 60:40 blend with localization in the minor phase, and 80:20 blend with localization at the interface. (b) Filler localization as a function of filler surface energy for a PHBV/PLA polymer blend as calculated with the Owens-Wendt Theory. Example carbon black surface energy is shown [90].

nearly equal blend ratios, immiscible polymer blends will have two continuous phases. At uneven ratios, the higher blend ratio polymer will form a major phase and the second lower blend ratio minor phase will form “islands” within this major phase [84, 86]. Immiscible ternary blends can produce more complex morphologies, such as shell layers around the minor phase [87, 88]. Immiscible blends of PLA and PHBV result in tensile and flexural strength and modulus values that closely follow the rule-of-mixtures prediction [26]. However, the strain to failure of PLA/PHBV blends is greatly improved over either neat polymer [26, 89]. Further, the heat deflection temperature is improved over neat PLA, partially mitigating this critical limitation of PLA at a lower cost than the use of pure PHBV [26].

Importantly for the work presented in this dissertation, fillers added to polymer blends selectively localize to either polymer phase or at the interface between the phases, depending on surface energy interactions of the polymers and filler (Figure 2.4). First, the morphology of the polymer blend can be predicted by the Owens-Wendt Theory [91] combined with the Harmonic Mean Theory [92]. The Owens-Wendt Theory states that:

$$\gamma_{ij} = \gamma_i + \gamma_j - \frac{4\gamma_i^d\gamma_j^d}{\gamma_i^d + \gamma_j^d} - \frac{4\gamma_i^p\gamma_j^p}{\gamma_i^p + \gamma_j^p} \quad (2.1)$$

where i and j are the two polymers, γ_i and γ_j represent the surface energy of each polymer, γ_{ij} represents the surface energy of the blend and p and d indicate the polar or dispersive components of that surface energy. Based on these values, the spreading coefficient of the polymer blend λ_{ij} can then be calculated:

$$\lambda_{ij} = \gamma_j - \gamma_i - \gamma_{ij} \quad (2.2)$$

If λ_{ij} is positive, the blend is immiscible, while if it is negative, the blend is miscible. Next, the localization of the filler in the blend can be calculated:

$$\omega_{ij} = \frac{\lambda_{i,F}\lambda_{j,F}}{\lambda_i} \quad (2.3)$$

Where $\lambda_{i,F}$ and $\lambda_{j,F}$ represent the interfacial tension between the filler and polymer i and j , respectively, and ω_{ij} is the wetting coefficient of the filler in the polymer blend. If ω_{ij} is greater than 1, the filler will localize in polymer j , if it is less than -1, it will localize in polymer i and if it is between 1 and -1, it will localize at the interface between the polymer blends (Figure 2.4).

This relationship can be used to modify the electrical conductivity of the resulting polymer material for electrically conductive filler materials in polymer blends. This

localization can allow electrical percolation to occur at lower filler loadings than in a bulk material, allowing for higher electrical conductivity in the resulting composite material [92]. Depending on where the filler material localizes in the polymer blend, the percolation threshold of the resulting polymer can be meaningfully reduced - allowing for materials with a broader range of properties to be produced [92]. This localization is further impacted by extrusion, and injection molding conditions allowing for further selective tuning of the electrical conductivity and mechanical properties of a filler-polymer blend composite [93].

Biochar

Biochars are a broad set of materials produced by biomass pyrolysis via heating in a low oxygen environment. This pyrolysis reaction converts biomass to a porous carbon material that is stable in the environment, with a diverse set of material properties depending on biomass feedstock. These properties can be tuned based on pyrolysis temperature, temperature ramp rate, dwell time, catalysts or activation processes used, and particle size. In addition to biochar, this reaction produces heat, biogas (H_2 , CH_4 , and CO), and bio-oils (a complex mixture of acids, ketones, alcohols, and aromatic compounds) that can be directly combusted for energy or refined and applied as chemical feedstocks [12, 94]. Biochars have been most widely examined and commercialized as a method to sequester carbon and as a beneficial soil amendment [12]. Biochars and similar materials are sometimes referred to in the literature as biocarbon, activated carbon, carbonized biomass, non-graphitizing carbons, and biomass chars or charcoals. In this dissertation, the term biochar is used to highlight the benefits of this material in bioplastics during biodegradation - however, the application of similar materials as fillers in petroleum-derived plastics are more typically referred to as biocarbon [11, 95].

The term biochar gained popularity in the literature in the 2000s to specifically describe pyrolyzed biomass developed for combined carbon sequestration and soil amendment

applications. However, the use of similar materials as a soil amendment was practiced at least as early as 500 BCE by indigenous cultures in the Amazon to improve crop yields [96]. In soil amendment applications, the stable carbon structure of biochar allows its addition to the soil to improve soil carbon content. In addition, biochar's highly adsorptive porous structure improves soil moisture content, retention of nutrients, and the health of soil microbial communities [12]. Biochars derived from waste feedstocks (e.g., agricultural waste, forestry waste, industrial biomass waste such as lignin, or residential waste such as food or yard waste) are of particular interest for carbon sequestration, as they avoid the emissions associated with the primary production of biomass [97, 98]. Beyond carbon sequestration, biochar has been explored in several applications, including water filtration, mine reclamation, and as a filler or additive in cementitious or polymeric materials [11, 94]. In these applications, biochar can replace conventional materials with reduced environmental impacts.

Biochar is produced at a commercial scale with many pyrolysis technologies, including drum pyrolyzers, fluidized bed reactors, screw pyrolyzers, and top-lit updraft gasifiers [12]. At the laboratory scale, biochar is typically produced in a tube furnace under a flow of inert gas, such as nitrogen (Figure 2.5) [11, 99]. Preliminary testing during method development for the work presented in this dissertation found that pyrolysis products are capable of devitrifying typical quartz tube furnace tubes at temperatures above 900 °C [92]. Therefore alumina tubes are preferred for the production of high-pyrolysis-temperature biochar. Production of biochar in a tube furnace allows for the tuning of atmosphere, maximum pyrolysis temperature, heating rate, and residence time, and production of several grams of biochar at a time.

The properties of biochar are significantly impacted by pyrolysis temperature, heating rate, and feedstock. Pyrolysis processes are broadly categorized by heating rate into slow pyrolysis (1-10 °C min⁻¹) and fast pyrolysis (>100 °C min⁻¹); fast pyrolysis favors the

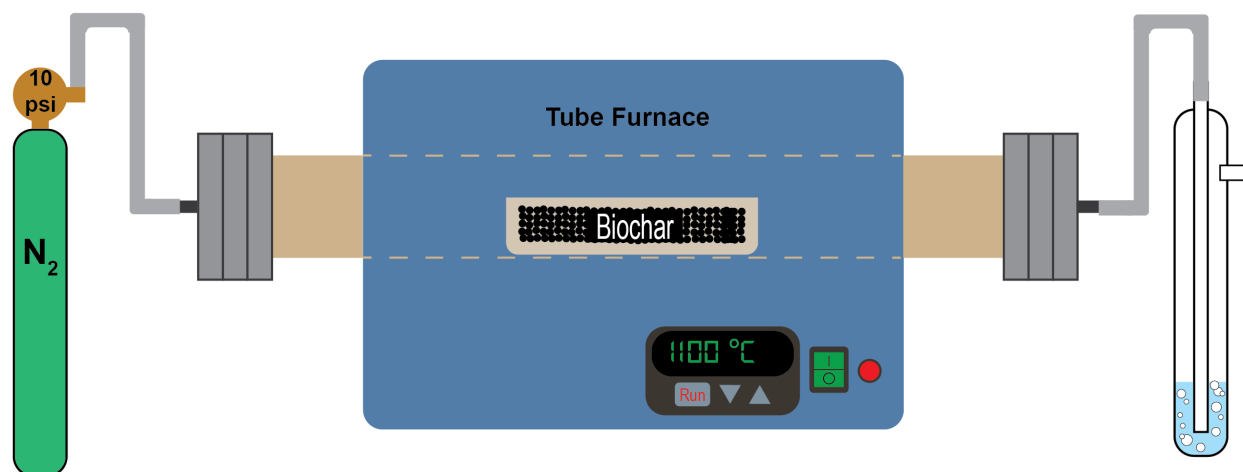


Figure 2.5: Schematic of the experimental setup typically used for producing biochar at the laboratory scale [99], and used to produce all non-commercial biochars in this dissertation.

production of biogas and oil [100] while slow pyrolysis favors the production of biochar, with biochar yields varying from as low as 8% for fast pyrolysis to as high as 60% for slow pyrolysis [12, 100, 101]. In addition to lower yields, higher heating rates can “lock-in” defects in the biochar carbon structure, causing deformations in the graphitic structure that persist even at high pyrolysis temperatures [102]. Therefore, lower heating rates are preferred for producing highly graphitic biochar.

Typically, with increasing pyrolysis temperature carbon content, graphitization, and surface area of biochar will increase, while oxygen and hydrogen content, biochar yield, and presence of functional groups decrease (Figure 2.6) [12, 103, 104, 105, 106, 107, 108]. Due to this loss of functional groups and oxygen content, as pyrolysis temperatures increase, biochar becomes more hydrophobic [109] and graphitic regions within the biochar grow and become more ordered [12, 19, 102]. At low pyrolysis temperatures, the initial chemical composition of the biomass feedstock plays a significant role in the structure of the biochar. In particular, the ratio of cellulose to lignin in the initial biomass determines how quickly biochar graphitizes [19, 110]. As a result, feedstocks with higher lignin content (i.e., hardwood or nut shells)

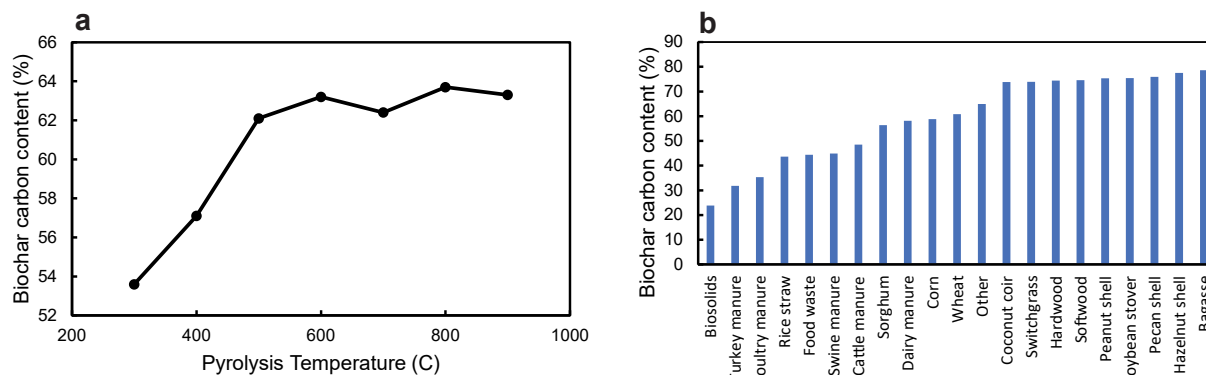


Figure 2.6: Change in biochar carbon content as a function of (a) pyrolysis temperature and (b) feedstock. Data adapted from [12] and is an average of 80 studies.

produce biochars with higher carbon content (Figure 2.6) [12]. In addition, heteroatoms and metals present in the feedstock can impact pyrolysis reactions by catalyzing or inhibiting the formation of graphitic structures in biochar [102, 111, 112, 113].

The chemical and physical properties of biochar can be modified with several pre- and post-pyrolysis methods. Ball milling procedures have been applied to reduce biochar particle size, resulting in particle sizes on the scale of 100 nm to 10 μ m while increasing biochar surface area [114, 115]. Washing procedures have been applied at a commercial scale to remove inorganics from biochar and improve porosity [116]. Post-pyrolysis or mid-pyrolysis activation processes can use various chemical or physical processes, including microwave radiation, carbon dioxide, superheated steam, or inorganic compounds such as KOH, with the primary goal of increasing biochar surface area or modifying functional groups [117, 118]. Further, in several studies, catalysts such as iron have been applied during pyrolysis to increase biochar graphitization [119, 120, 121, 122]. These catalysts have been well established to shift biomass from a non-graphitizing to graphitizing feedstock [102], and can be removed after pyrolysis via treatment with acids [119]. However, in some cases, the catalyst may interact with inorganics inherent in the feedstock, reducing the effectiveness of the catalyst [119]. Understanding the interactions between inherent inorganics and catalysts

remains a crucial gap in utilizing these catalysts across a wide variety of biomass.

The energy requirements and environmental impacts of biochar and biofuel co-products during pyrolysis are of crucial concern for applying biochar as a sustainable alternative to carbon black. Most work to date quantifying biochar environmental impacts has focused on lower pyrolysis temperature (300-700 °C) biochar for applications such as soil amendment, carbon sequestration, or mine waste remediation [97, 98]. In these applications, the production of biochar has the potential to sequester large quantities of carbon (as much as 3.9 kg CO₂ eq. per kg feedstock) [97]. The environmental impacts of higher pyrolysis temperature (>900 °C) biochars have been less studied. However, the greenhouse gas emissions of these materials can be predicted by examining pyrolysis energy requirements, biochar carbon content, and biochar yields. Pyrolysis energy requirements show a linear relationship with pyrolysis temperature between 400 and 600 °C, with a high dependence on feedstock [123]. At higher temperatures (e.g., 1100 °C), pyrolysis remains net energy positive, with non-biochar product higher heating values of around 395 kJ per mol feedstock [124]. This finding shows that high-temperature biochar has the potential to be produced with limited energy inputs, allowing for similar carbon sequestration to what has been well established for lower temperature biochars - reduced only by the lower biochar yields at higher temperatures.

Lignin is a particularly promising feedstock for biochar for mechanical and electrochemical applications. As a primary constituent of plant biomass, lignin is the second most abundant naturally occurring polymer after cellulose and has an aromatic carbon polymer structure [125]. Further, lignin is an abundant co-product from pulp paper making and cellulosic bioethanol processes, with 50-100 million tons of lignin isolated annually [125, 126]. This production is expected to increase in the coming years as cellulosic biorefineries continue to grow to meet increased demand for biofuels [127]. Lignin polymers are typically comprised of three primary monomers: coniferyl alcohol, sinapyl alcohol, and p-coumaryl alcohol, with

varying linkages between these monomers, resulting in a highly complex molecular structure [128]. This structure varies between 40 and 60 wt.% carbon content, with most of the remainder present as oxygen [129, 130]. Different isolation methods and biomass feedstocks can result in different chemical structures of the lignin by starting with varying biomass lignin structures, fractionating different molecular weights, or introducing inorganic or organic contaminants. The resulting lignins are typically broadly categorized by the method used to extract them (e.g., Kraft lignin, Organosolv lignin, or hydrolysis lignin). These lignins vary in oxygen content, inorganic content and species, molecular weight, and content of lignin monomers and linkages. The high carbon content, aromatic structure, and thermal stability of lignin relative to other biomass components make it an attractive feedstock for biochar for material science applications. However, its conversion requires higher pyrolysis temperatures than other biomass feedstocks to carbonize [131].

A large majority (>98%) of the lignin isolated as byproducts of the papermaking or biofuel processes is currently combusted for energy [125]. Various methods have been examined to upcycle this important waste stream, including the development of lignin-derived plastics, adhesives, and carbon materials [119, 132, 133, 134, 135, 136]. Development of methods to use this lignin in higher-value applications is currently limited by economic factors giving rise to the phrase “You can make anything from lignin except money” [137]. However, carbon materials are considered some of the highest value potential applications to upcycle lignin [138]. The single-step pyrolysis process, limited energy requirements, and high value of carbon materials make pyrolysis of lignin a strong contender for an economically viable method to reuse this waste stream.

Of particular interest to this dissertation is the use of biochar in electrical applications. At high pyrolysis temperatures, biochar can be produced with a graphitic structure, resulting in comparable electrical conductivity to petroleum-derived carbon materials (this chemical structure and the pyrolysis reactions contributing to it are more broadly discussed in Ch. 3).

Further, the potential for developing highly porous biochar, such as with activation processes, allows for the development of highly capacitive materials [139]. As such, biochar has been extensively studied for application in a broad set of electrochemical applications, including supercapacitors, active materials in battery electrodes, fuel cells, and electrochemical sensors [20, 140].

The electrical conductivity of biochars varies widely by feedstock, pyrolysis temperature, and processing conditions (Figure 2.7). Comparison of electrical conductivity between studies is challenging, as the measurement method used greatly impacts the resulting electrical conductivity value [141, 142]. As a result, wide variations in electrical conductivity are reported for both petroleum-derived carbon powders, and biochars in the literature [141, 142, 143]. As pyrolysis temperature increases between 300 °C and 1200 °C, biochar electrical conductivity increases with a plateau in electrical conductivity following percolation of graphite crystallites at around 1000-1200 °C [19, 102]. Typically, lignin-derived biochars produced at high pyrolysis temperatures (>900 °C) show slightly higher average electrical conductivity (average of 13.1 S/cm for a review of 32 biochars) than from whole biomass feedstocks (average of 12.1 S/cm for a review of 20 biochars) (Figure 2.7)[19, 99, 103, 107, 111, 113, 114, 141, 143, 144, 145, 146, 147, 148, 149, 150, 151, 152, 153, 154, 155, 156, 157, 158, 159]. This high electrical conductivity has been attributed to lignins high aromatic carbon content, resulting in higher carbon biochar than cellulose or whole biomass [160]. However, cellulose graphitizes at lower temperatures, resulting in higher electrical conductivity at low pyrolysis temperatures, but low biochar yields at high pyrolysis temperatures [146]. Further, different studies have proposed different mechanisms for this high electrical conductivity, with differences in inorganic content [111, 114], oxygen content [114], surface area [114], density [152], carbon content [153] and the size of the graphitic crystallites [19, 113] all having been proposed to influence biochar electrical conductivity.

In addition to bulk electrical conductivity, past studies have found the graphitic carbon

structure and pyrolysis co-products to vary depending on the feedstock, including between different types of lignin [131, 132]. This variation is accompanied by a subset of studies that find some lignin-derived biochars to have low electrical conductivity (<0.1 S/cm), even at pyrolysis temperatures greater than 1000°C [114, 145, 150]. Understanding the actual differences in electrical conductivity between these materials and high electrical conductivity biochars is complicated by the high variation in electrical conductivity between different studies, with different methods of measuring the same material resulting in as much as two orders of magnitude differences in electrical conductivity [114, 141]. Further, past studies have identified high variation in graphitic structure between biochars produced from different types of lignin [119] and a less graphitic carbon structure than petroleum-derived materials [132] as crucial factors that limit the use of lignin-derived carbon materials. A critical gap in the development of lignin-derived biochars is understanding the pyrolysis mechanisms that contribute to the wide variation in biochar electrical conductivity and graphitization that has been observed in past work.

Biochar has been explored as a replacement for petroleum-derived carbons across various electrochemical applications, including as a catalyst for hydrolysis, sensing applications, and energy storage applications such as fuel cells, battery electrodes, and super capacitors. Many studies have found similar performance in these applications with biochar as petroleum-derived materials [20, 140, 162]. Research examining biochar in electrochemical applications has expanded rapidly in recent years, with over one-third of total articles being published in 2021 alone [20]. Biochar’s high adsorption potential and electrical conductivity make it a strong alternative to petroleum-derived materials in sensing applications. Biochar has been examined in a wide variety of sensing applications, including sensing heavy metal ions in wastewater [163], organic contaminants [164], ammonia gas [165], and viruses [166] and as a replacement for petroleum-derived materials in electrical sensing applications [167]. In these applications, the high porosity and functional groups present in biochar allow

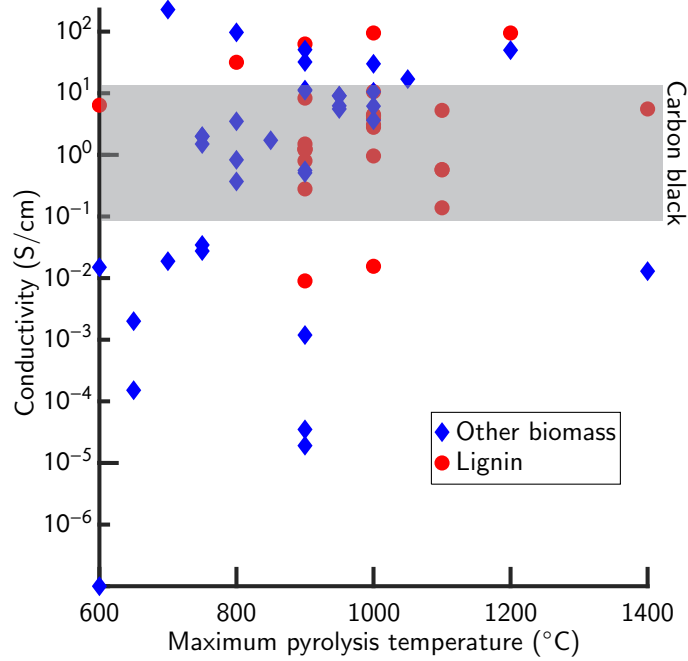


Figure 2.7: A review of literature electrical conductivity values for biochar produced from lignin and other biomass [19, 99, 103, 107, 111, 113, 114, 143, 144, 145, 146, 147, 148, 149, 150, 151, 152, 153, 154, 155, 156, 157, 158, 159]. The grey box shows a range of typical carbon black conductivities, independent of processing temperature [141, 161]. Additional information on these biochar conductivity data is shown in Table C.1. Reproduced from Ch. 5.

adsorption of the sensed element, and the high electrical conductivity of biochar allows for the measurement of the change in electrochemical response after adsorption. Similarly, biochar has shown strong performance in electrochemical storage applications, comparable to petroleum-derived carbon materials. In supercapacitors, biochar has shown a specific capacity ranging from 80-615 F/g with high cycling stability [20, 168, 169], driven by its high surface area and oxygen-containing functional groups. In batteries, biochar has been examined as the active material in both the cathode and anode across various battery chemistries [20]. Most commonly, biochar has been examined in the anode of lithium- or sodium-ion batteries as a replacement for graphite or hard carbon. In lithium-ion batteries, biochar shows higher specific capacity than graphite due to increased adsorption of lithium

ions [119, 170, 171]. However, biochar shows a higher portion of this specific capacity in the sloped region of the lithiation curve, behavior typical of hard carbon active materials [119, 170]. This performance varies depending on biochar surface area, graphitic structure, and electrical conductivity [119, 171, 172]. In sodium-ion batteries, biochar has shown increased capacity and performance than graphite, which is attributed to the larger distance between graphene layers in biochar than in graphite and the larger size of sodium ions relative to lithium [173].

Biochar has been extensively studied to improve the mechanical properties of plastics. As a filler material in plastics, biochar provides several benefits, including reduced density and cost relative to other common filler materials [11]. In common petroleum-derived plastics, including HDPE, PP, and PET, the addition of biochar has been found to increase tensile strength and stiffness, but results in a more brittle material, reducing impact strength and strain-to-failure [17, 174, 175, 176]. Two factors are primarily responsible for these shifts in mechanical behavior. First, biochar's higher hardness and modulus than common polymers increase strength and stiffness. Second, the highly porous structure of the biochar interlocks with the polymer chains [16]. Further, several studies have found biochar with small particle sizes ($<10\text{ }\mu\text{m}$) to have a nucleating effect on polymer crystallite formation, resulting in increased crystallinity [175, 176].

Conversion of biomass to biochar provides several benefits for biocomposites and addresses many of the primary issues with biomass biocomposites. The high thermal degradation temperature of biochar eliminates many concerns with biomass degradation during melt processing of biocomposites, particularly for high melt temperature polymers such as PET or nylon [11, 18]. Biochar composites show lower moisture adsorption than biomass composites [17, 56], improving the dimensional stability of the composite in high moisture environments. Additionally, pyrolysis typically converts biomass from a hydrophilic material to hydrophobic material, with the degree of hydrophobicity governed by the surface

area, pore radius, and functional groups [177]. However, at higher pyrolysis temperatures, biochar tends to become less hydrophobic as aliphatic functional groups react off [177]. As a result, past nano-indentation studies have found a stronger interface between polymers and biochar than polymers and biomass [16].

Biochar shows strong potential to reduce the environmental impacts of plastic. Past life cycle assessment (LCA) studies of biochar composites have found that biochar reduces the global warming potential of biochar-PP composites in automotive panel applications by 25%, relative to talc-PP composites [178, 179]. This decrease in global warming potential is accompanied by a decrease in other environmental impact categories and is attributed primarily to reductions in the weight of the final part. These studies identify biomass growth as a primary contributor to the environmental impacts of biochar composites. Importantly, these impacts can be mitigated by using waste-derived feedstocks. However, these LCA studies of biochar composites are limited in scope, examining only PP-biochar composites in specific applications compared to conventional filler materials. Broader studies comparing the application of biochar across biobased, recycled, and petroleum-derived plastics are needed to understand how biochar may be applied to reduce environmental impacts across the plastics industry as a whole.

The well-established benefits of biochar as soil and compost amendment make it a promising filler material in biodegradable plastics, as it can act as a soil amendment and continue to sequester carbon when the plastic biodegrades. In addition, past studies have found that biochar improves the biodegradation rate of PLA under composting conditions [56]. This increase is attributed to increased moisture absorption of the material with the addition of biochar relative to neat PLA. Further, the addition of PHBV containing toxic nanoparticles to soil containing biochar has been shown to mitigate the negative environmental impacts of the nanoparticles while improving biodegradable plastic degradation rates [180]. Combined, these studies provide evidence for the positive benefits of

biochar during the biodegradation of PHBV and PLA. However, these studies are limited in scope, and more research on the extent, impact, and effect of biochar properties on bioplastic biodegradation is needed.

Table 2.1: A review of the change in thermal degradation of PLA with the addition of biochar. T_{BioC} represents the highest treatment temperature of the biochar, d_{bioc} is the average particle diameter, W_{BioC} is the weight percentage of the biochar in the composite, ΔT_{deg} is the change in the onset temperature of thermal degradation relative to neat PLA, and $\Delta \chi_p$ is the change in crystallinity relative to neat PLA. The highest is examined for studies with multiple weight percentages of biochar added. N/R refers to values that were not reported by the referenced study. Table reproduced from Appendix E.

BioC Feedstock	T_{BioC}	d_{BioC}	W_{BioC}	ΔT_{deg}	$\Delta \chi_p$
	°C	μm	wt. %	°C	% Cryst.
Switchgrass[17]	500	< 600	20	Decrease	N/R
Miscanthus [181]	650	20-75	10	-22	+3
Miscanthus [181]	650	0.9	10	-43	+1.7
Miscanthus [182]	700	20-75	10	N/R	-1/+2
Bamboo [56]	N/R	10	7.50	- 16.3	-35.6
Bamboo [183]	N/R	9.52	≤ 40	-22.5	+20.97
Bamboo [184]	N/R	5.42	≤ 12.5	N/R	-26.9
Bamboo [185]	600	N/R	≤ 40	Decrease	+14.8
Bamboo [186, 187]	800	75-300	$\leq 35\%$	-72	-8.63
Chicken feathers [188]	600	N/R	20	-40.4	NR
Coffee grounds [189]	700	10	≤ 7.5	-46.7	+2.6

Despite strong performance in petroleum-derived plastics, past studies have found the addition of biochar to PLA and PHBV to result in poor thermal stability (Table 2.1) [17, 56, 92, 181, 182, 183, 184, 185, 186, 187, 188, 189, 190, 191, 192]. This results in a reduction

in the onset of thermal degradation in PLA between 5 and 72 °C, a loss in melt viscosity, and a meaningful reduction in mechanical properties. As a result, the material is extremely challenging to melt process and has mechanical strength that is too low for many common applications. The mechanisms behind this loss in thermal stability with the addition of biochar are debated. The current prevailing hypothesis was originally proposed by Snowden et al. and hypothesizes that oxygen and moisture trapped in the porous structure of the biochar act to prematurely hydrolyze or oxidize the ester bonds in PLA during heating [181, 182, 191]. Some studies have hypothesized that the graphitic biochar acts as a lubricant to increase mobility between polymer chains in PLA [56, 183]. Other studies propose that during extrusion, biochar acts to locally heat the PLA, resulting in thermal degradation local to the biochar [17]. Finally, some studies have proposed that inorganics present in biochar act to catalyze the thermal degradation of PLA and PHBV [193]. To date, no study has systematically examined the mechanisms responsible for this reduced thermal degradation, and mitigating this issue remains a critical gap in the development of biochar as a filler material in bioplastics.

The high electrical conductivity of biochar and its strong performance in polymer composites make it a promising alternative to petroleum-derived carbon materials across many applications. In addition, biochar has proven soil and compost amendment properties and improves the biodegradation rate of biodegradable plastics, making it compatible with the end-of-life of these materials. The sequestration of carbon in the biochar can reduce the environmental impact of these materials. Combined, these properties make biochar a promising option for developing carbon-negative, biodegradable, and electrically conductive composite materials. However, critical gaps in understanding the interactions between biochar and PLA or PHBV limit the applicability of biochar in these important bioplastics. Despite extensive study and numerous proposed hypotheses, no studies have systematically examined the mechanisms responsible for this performance loss. Further, the pyrolysis

mechanisms contributing to high electrical conductivity in biochar are poorly understood. Further, an improved understanding of the mechanisms contributing to highly electrically conductive biochar is needed to select feedstock sources for biochar production for this important and growing application.

THEORY

Biochar structure is greatly affected by feedstock, material processing, and pyrolysis conditions [194]. As a result of these factors, significant variation is seen in biochar's chemical structure and resulting material properties. This variation has been well established for low-pyrolysis-temperature biochar for agricultural applications, with established regulatory guidelines for optimal material properties [195, 196]. However, these variations are more poorly understood for biochar in electrical and electrochemical applications, as reviewed in Ch. 2. Herein, the chemical structure of biochar and the pyrolysis reactions of biochar are discussed for lignocellulosic biomass used to produce biochar at temperatures up to 1100 °C. In addition, the mechanisms by which this structure contributes to high biochar electrical conductivity are presented.

A cohesive model for the chemical structure of biomass-derived carbons was first proposed by Franklin in 1951 [197]. Franklin categorizes precursors for graphitic carbon as graphitizing or non-graphitizing. Graphitizing carbons show well-ordered, aligned crystalline graphite structures, with layer diameters between 18 and 65 Å and 4 to 33 layers per parallel-group, depending on feedstock and maximum treatment temperature. In contrast, non-graphitizing carbons were found to have a disordered crystalline structure, with non-aligned stacks of 2-8 parallel graphene layers, similar in diameter to those of graphitizing carbons. In non-graphitizing carbons, only small increases in the number of parallel graphene layers are observed with increasing temperature. Whether a feedstock forms graphitizing or non-graphitizing carbon is primarily governed by the hydrogen and oxygen content of the feedstock - with high hydrogen content favoring graphitization, while high oxygen content favors non-graphitization. Thus, pyrolysis of typical biomass feedstocks results in non-graphitizing carbons. Franklin attributes the limited stacking and disordered crystallite structure of non-graphitizing carbons to crosslinks between graphitic crystallites at relatively

low treatment temperatures ($<400\text{ }^{\circ}\text{C}$), resulting in the structure of the carbon “setting”. In contrast, in graphitizing feedstocks, this crosslinking is disrupted by the reaction of hydrogen with carbon at these temperatures, allowing small graphitic crystallites formed at low temperatures to combine into larger stacks at higher temperatures. Non-graphitizing carbons do not form ordered graphite structures even at high treatment temperatures, sufficient to break down this crosslinking ($2000\text{--}3000\text{ }^{\circ}\text{C}$), as these crystallites are not well ordered enough to effectively stack into larger graphite crystals. Non-graphitizing carbons are harder (giving rise to the term “hard carbon”) and more porous than graphitizing carbons due to their crosslinking and gaps between their disordered graphitic crystallites. While subsequent studies have expanded understanding of the structure of non-graphitizing carbons, Franklin’s model forms the basis for the current understanding of the chemical structure of these materials.

At temperatures below $1000\text{ }^{\circ}\text{C}$, not all biomass components are completely pyrolyzed resulting in a mixture of amorphous and graphitized carbon. Between 400 and $1100\text{ }^{\circ}\text{C}$, the carbon structure of biochar is most significantly impacted by pyrolysis temperature. Below this temperature, the structure is primarily influenced by the structure of the biomass precursor; at higher temperatures, only small changes in structure are observed with increased pyrolysis temperature [102]. In lignocellulosic biomass, pyrolysis reactions can broadly be categorized by the primary constituent of biomass that decomposes at each temperature. At low temperatures ($<150\text{ }^{\circ}\text{C}$), any water in the material evaporates, causing an initial mass loss. Next between 150 and $400\text{ }^{\circ}\text{C}$, biomass functional groups react to form CO and CO_2 , but the carbon structure retains the largely amorphous structure of biomass, and the electrical behavior is largely capacitive due to the presence of polar functional groups [146]. As pyrolysis temperatures approach $400\text{ }^{\circ}\text{C}$, the majority of hemicellulose and cellulose react in a single pyrolysis step, resulting in mass losses of approximately 80% and 90% for hemicellulose and cellulose, respectively. In contrast, thermal degradation of lignin

components of biomass begins at approximately the same temperature as hemicellulose but occurs slowly, with high mass residues ($>30\%$) at $1000\text{ }^{\circ}\text{C}$ [131]. As the pyrolysis temperature rises above $400\text{ }^{\circ}\text{C}$, low molecular weight graphene structures begin to form and increase in size. At these temperatures, nearly all carbon is sp^2 -bonded [102]. Between 400 and $600\text{ }^{\circ}\text{C}$, an intermediate, low molecular weight, amorphous carbon phase forms [146, 198]. The presence of this phase separates small graphitic structures, limiting electrical conductivity. Limited mass loss is observed in this temperature range, with primary products of CO and CO_2 attributed to reaction of persistent hemicellulose and lignin $-\text{OH}$, $\text{C}-\text{O}$, and $\text{C}=\text{O}$ containing functional groups and CH_4 attributed to reaction of $\text{O}-\text{CH}_3$ functional groups on lignin [131, 198].

At $1000\text{ }^{\circ}\text{C}$, the electrical conductivity of the bulk material is approximately six orders of magnitude higher than it was at $600\text{ }^{\circ}\text{C}$, and limited increases in electrical conductivity are observed with higher temperature treatment. The material is approximately 90 wt.% carbon in inorganic-free materials, with the remainder present primarily as oxygen [146]. The structure of this carbon is primarily be 2-3 layer stacks of 1-3 nm diameter graphene sheets [102]. These graphene layers are connected in a "graphene triad structure" by distorted-graphitic structures, which can have significant curvature preventing the formation of truly graphitic stacks, or long-range order [102]. These structures are randomly oriented within the broader material, resulting in the high porosity of these materials [170]. This material has no long-range crystalline order and therefore is considered neither amorphous nor crystalline [102].

During the rapid growth of graphene structures in biochar between 600 and $1000\text{ }^{\circ}\text{C}$, several persistent defects can form, resulting in displacements and distortions in the graphene structure [102]. For example, oxygen functional groups can be trapped in the graphene structure, 5- or 7-member carbon rings can form, resulting in curvature in the carbon structure, and "fjords" can form in the graphene structure [102]. These displacements and

distortions act as a stable cross-link to connect ordered graphene regions and cause the lack of long-range order in the resulting material. At low temperatures, these defects can react to form CO, CO₂, or H₂O. However, these defects often persist at high pyrolysis temperatures as a result of being trapped between non-reactive graphitic structures.

A quasi-percolation model can describe the increasing electrical conductivity in non-graphitizing carbons with increasing pyrolysis temperature. In this model, the carbon structure is described as two distinct phases: a non-conductive amorphous carbon phase and a conductive graphitic phase. As pyrolysis temperature increases, the graphitic phase grows until growth is limited by contact with other graphitic crystallites, or defects in the graphene structure prevent further growth [199]. As the graphitic regions grow, decreased distance and increased contacts between electrically conductive regions contribute to a rapid rise in electrical conductivity. This conductivity shows similar electrical percolation behavior to that observed in packed electrically conductive powders [200] or polymer composites [201]. This model can be broadly categorized into five regions, which roughly correlate with the mass loss behavior discussed above (Figure 3.1) [19, 146]. At temperatures below 400 °C, the predominant phase is amorphous carbon, and electrical behavior is highly resistive (10^{-8} S/cm). The limited conductivity occurs due to dipole polarization of hydroxyl and carboxyl functional groups. As treatment temperature increases in this region, electrical conductivity decreases as these functional groups decompose. Between 400 and 500 °C, electrical conductivity increases as graphitic structures begin to form. Electrical conductivity in this region is still low (10^{-6} S/cm), and the microstructure is dominated by amorphous carbon. Between 500 and 600 °C, while contact has not been made between graphitic sheets, graphitic structures have grown to sufficient size to allow for electron hopping, and the electrical percolation threshold has been reached. Above 600 °C, contact begins to be made between some graphitic structures, and electrical conductivity begins to increase rapidly, rising from approximately 10^{-5} S/cm at 600 °C, to 10^1 S/cm at 1000 °C. Finally, above 1000

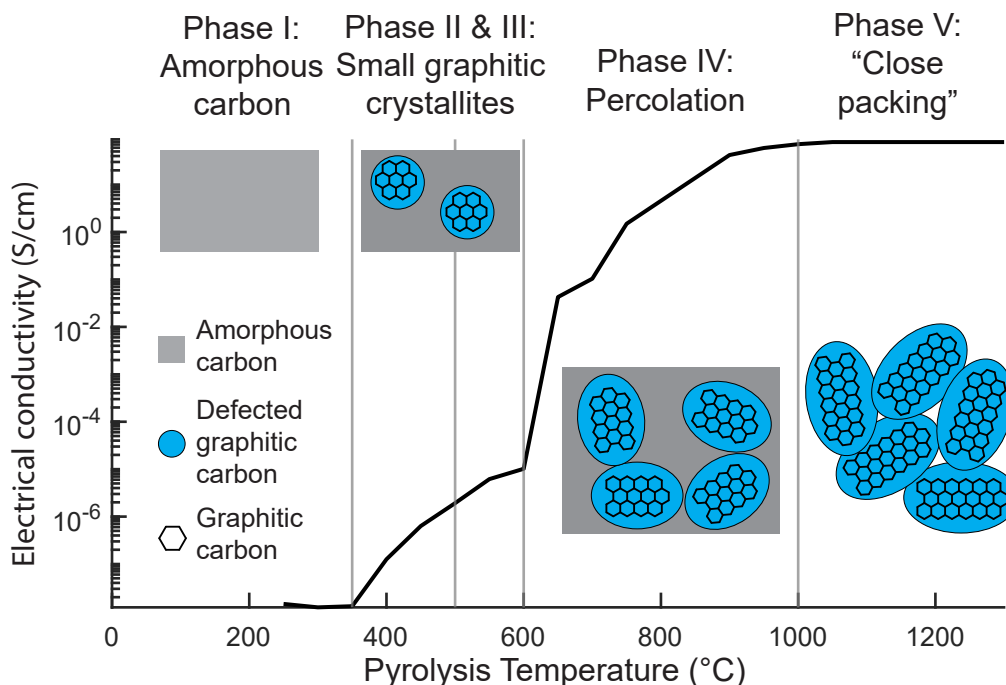


Figure 3.1: Electrical conductivity and simplified microstructure of biochar as a function of pyrolysis temperature. Data and model adapted from [19, 146].

°C, complete contact is made, mimicking close packing of electrically conductive powders in a packed powder system. Above this point, no further increase in electrical conductivity is observed. While all feedstocks follow the above described electrical behavior, the exact electrical conductivity values vary by feedstock and study, resulting in the previously discussed high variation in electrical conductivity (Figure 2.7).

The models and chemical structures discussed above for forming electrically conductive carbon structures from biomass pyrolysis assume that the precursors are free of inorganic compounds [102]. However, for many common biomass feedstocks, this assumption is not true [12]. Particularly for lignin feedstocks, kraft and alkali isolation procedures may result in high sodium sulfate content [202]. The impact of these inorganics on pyrolysis of biomass is poorly understood, with some studies proposing that sodium sulfate catalyzes the formation of electrically conductive structures, while others propose that it inhibits it [111, 112, 113].

Further, some inorganic catalysts, such as iron and nickel, can be used to shift biomass from a non-graphitizing to a graphitizing feedstock [102, 119]. In this case of an iron catalyst, three mechanisms are hypothesized to result in improvements in graphitization. These mechanisms act at temperatures above the melt temperature of iron through liquid iron-solid carbon interactions [119]. Graphitic crystallites may nucleate in the melt phase of iron, crystallite growth during the formation of iron carbide, and crystallite growth during cooling as the carbon becomes non-soluble in iron. The biocarbon resulting from treatment with these catalysts has larger graphene stacks than in uncatalyzed biocarbon and shows a structure more similar to graphite [119]. Understanding the role of inorganics in biomass during pyrolysis and their interaction with external catalysts remains a crucial gap in identifying appropriate biomass sources for highly electrically conductive, biobased carbon materials.

Raman spectroscopy, X-ray diffraction (XRD), and Fourier-transform infrared (FTIR) spectroscopy are primary tools to characterize carbon materials. In this work, these techniques are applied in Ch. 5, 6, 7, and 10 to characterize biochars. Both Raman and FTIR spectroscopy are vibrational spectroscopy techniques, measuring the vibrational energy response of chemical bonds present in the material [203]. FTIR applies an infrared wavelength electromagnetic signal and measures the absorption of this signal as a function of wavelength, which results from transitions between vibrational levels in the molecule that are associated with specific bonds. Raman spectroscopy applies an electromagnetic signal at ultraviolet, visible, or near-IR wavelengths and measures the shift in the response caused by the electronic polarization of the bond. Typically, FTIR is preferable to examine asymmetric, polar groups, while Raman spectroscopy is preferable for symmetric, non-polar structures.

As a result of these differences in measurement methods, Raman and FTIR spectroscopy show largely different responses for biochars, with FTIR being preferable to examine the presence of polar functional groups and inorganic species present and Raman examining the graphitic structure. Analysis of biochar by FTIR is limited by their black, refractory

optical properties, which can result in nearly complete adsorption of the IR signal [204]. This adsorption is especially prominent in high-temperature biochars, where IR-inactive graphitic structures are the predominant structural feature. To partially mitigate this issue, reflective FTIR techniques (i.e., attuned total reflectance (ATR)) can be applied to limit the penetration of the IR signal into the sample, decreasing adsorption [204]. FTIR spectra of biochar typically decrease in overall intensity with increasing pyrolysis temperature as biomass functional groups react, with minimal response seen at pyrolysis temperatures of 1000 °C [19]. At high pyrolysis temperatures, a large baseline shift is observed in the ATR-FTIR spectrum of biochars, which is attributed to increased penetration depth at high wavenumbers [204]. FTIR spectrum of biochars can also identify inorganic compounds, such as silica (Si–O), carbonate ($-\text{CO}_3$), and sulfate ($-\text{SO}_4$) groups commonly present in biochars [185, 203, 204, 205].

In contrast to FTIR, Raman spectra of biochar are dominated by responses related to graphitic carbon - namely the D ($\sim 1350 \text{ cm}^{-1}$) and G ($\sim 1582 \text{ cm}^{-1}$) bands [206]. The G band results from relative motion sp^2 bonded carbon structures, like those that are predominately present in graphitic carbon, while the D band results from the breathing mode of carbon rings, which increases with disorder around sp^2 bonded carbons, including defects and displacements in the graphitic structure (i.e., oxygen, or 5- or 7- member carbon rings) and edges of the graphitic structure with hydrogen present [19, 206]. A spectral deconvolution model for analyzing the carbon structure of disordered carbons based on their D and G responses has been developed by Ferrari and Roberts [206]. This method combines a Lorentzian fit for the D peak, a Breit-Wigner-Fano (BWF) fit for the G peak, and a linear baseline to determine D and G peak positions, intensities, and widths at half-height [206, 207]. A full description of this fit is given by McGlamery et al. [207], and a MATLAB code to deconvolute Raman spectra of disordered carbons is given in Appendix A. These spectral features are tied to several structural differences in disordered carbons. The size of

graphitic crystallites (L_a) present in these materials is inversely proportional to the intensity ratio of the deconvoluted D and G bands (I_{dg}), as shown in Equation 3.1 [206, 208].

$$L_a = (2.4 \times 10^{-10})\lambda^4 \times I_{DG}^{-1} \quad (3.1)$$

where λ is the wavelength of the laser used. Similarly, the width of the G-peak is related to bond-angle disorder in graphitic rings, which may be caused by the curvature of the graphitic sheet or strain due to displacements in the larger graphitic structure [102, 206]. A shift in the location of the G peak to lower Raman shifts has been associated with increasing amorphous carbon content [206].

XRD measures diffraction of a source in the X-ray wavelength range to infer the crystalline structure of a material. The angle (θ) of the X-ray source and detector are varied, varying the incidence angle of the X-ray with the crystalline structure. At particular angles, the response to the x-ray results in constructive interference, amplifying the original signal. This response is unique to a particular crystalline structure. XRD lineshape can characterize both the number of stacks in a graphitic crystallite (002 reflection, typically present at $2\theta = 26.7^\circ$ for graphite) and the average plane size of layers of a graphitic crystallite (100 and 10 l reflections, typically present at $2\theta = 42$ and 44° for graphite). The distance between layers in a graphitic crystallite, d , can be calculated from the 002 peak position via Bragg's law, as displayed in Equation 3.2. Similarly, the size of the graphitic crystallite in the stacking direction (L_c) and in-plane direction (L_a) can be calculated based on the peak width at half-maximum via the Scherrer equation of the 002 and 100 peaks, respectively (Equation 3.3) [207].

$$d = \frac{1.54\text{\AA}}{2 \sin \theta} \quad (3.2)$$

$$L = \frac{0.9\lambda}{W \cos \theta} \quad (3.3)$$

Where λ is the X-ray wavelength and W is the width at half peak height in radians. Additionally, XRD responses of crystalline inorganic compounds (including sodium sulfate in lignin-derived biochars) can aid in identifying inorganic compounds present in biochar [204].

Despite seventy years of research since Franklin first proposed a model for the structure of non-graphitizing carbons, critical gaps remain surrounding the carbon structure and electrical conductivity of biomass-derived carbons. Primary of these is the cause of the significant variation in electrical conductivity observed between different feedstocks and studies for similar pyrolysis temperatures and the role that inorganic compounds present in biomass play during pyrolysis. In this dissertation, the electrical conductivity of biochar is examined in high-temperature regions (900 and 1100 °C), above which no increase in electrical conductivity is expected with increased pyrolysis temperature. A broad range of feedstocks are examined to identify key characteristics that contribute to high electrical conductivity.

IMPROVEMENTS IN METHODS FOR MEASURING THE VOLUME
CONDUCTIVITY OF ELECTRICALLY CONDUCTIVE CARBON POWDERS

Contribution of Authors and Co-Authors

Manuscript in Chapter 4.

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Contributions: Conceptualization, Resources, Writing - review & editing

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Abstract

Electrically conductive carbon powders are commonly used as filler materials in polymers to create electrically semi-conductive composite materials for use in battery electrodes and anti-static applications. Current methods for characterizing the conductivity of these powders use two pistons to compress the powders. Two-piston methods are known to underestimate conductivity. This study develops a guard-electrode method based on ASTM D257 to better characterize the bulk conductivity and impedance spectra of electrically conductive powders. The conductivity and impedance spectra of a highly conductive powder (copper powder) and a low conductivity powder (cellulose) were used to bound the conductivity of carbon black, graphite, and biochar. Powders were measured through a full range of compression with both the two-piston and the guard-electrode method. In all cases, measurements using the guard-electrode method have higher conductivity and lower impedance than the same powders measured using the two-piston method. The grain conductivity of the particles is obtained through fitting the relationship of conductivity versus packing fraction using the GEM equation. The guard-electrode method is shown to be more similar to established conductivity values as measured via a four-probe technique for copper and graphite than the two-piston method.

Introduction

Carbon powders, such as carbon black, graphite, and biochar, are known to have high electrical conductivity [153, 209, 210]. When these powders are used as filler materials in polymers, the resulting composite material can be used for applications including electromagnetic shielding, anti-static materials, and in fuel cell electrodes [211, 212]. It is important to be able to characterize the electrical conductivity and behavior of these powders to aid in the development of new carbon powders and in selecting carbon powders

for a desired application.

A common method for characterizing bulk electrical conductivity of powders is to compress the powders or pellets made from the powders between two pistons [200, 213]. This method measures conductivity as a function of applied pressure and allows for the conductivity of different powders to be compared. The results of this method are affected by the geometry of the setup, the size and shape of the particles, and the packing density of the powders in the piston. Contact resistance between the powder and the electrode on the piston may cause errors in the measurement [142]. Different experimental setups may then yield different results, preventing an accurate comparison of work done in different studies [142]. In addition, this method does not account for leakage current, which leads to underestimating the conductivity of the powders [214, 215]. Different studies have used a wide variety of methods to apply pressure and compress the powders [142, 210, 213, 216]. Pressure application methods are less repeatable than displacement measurement methods, as applying pressure assumes a constant pressure distribution throughout the powder. This assumption is highly dependent on method of pressure application, test geometry and lack of friction [142]. Displacement is a direct measurement of the state of the powder, and therefore lends itself to easier reproducibility of measurements.

This study looks to address these issues by developing and demonstrating a method of measuring the electrical conductivity of powders which is based on displacement rather than pressure, accounts for leakage current, and is comprised of common or 3D printable parts to allow for easy replication of results.

Theory

Guard ring theory

ASTM D257 describes a method for measuring the DC resistivity of flat solids [217]. This method uses two pistons and a guard electrode to measure either volume resistivity or

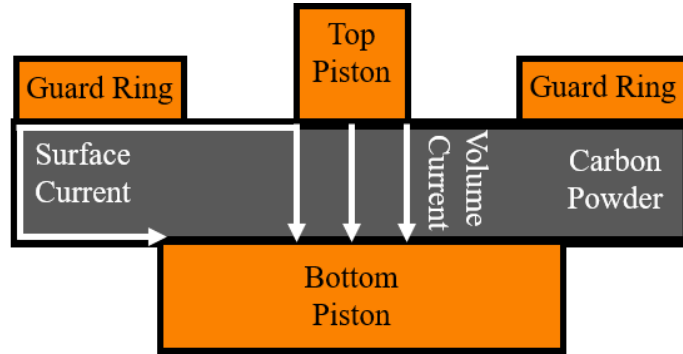


Figure 4.1: Schematic describing surface and volume current. Surface current travels over the surface of the powder, leading it to pass over the guard electrode, while volume current passes directly through the powder to the lower electrode.

surface resistivity, depending on the setup of the circuit. The guard electrode allows for the separation of volume and surface resistivities, as shown in Figure 4.1. Total resistance is assumed to be the sum of three values:

$$R_{total} = R_{surface} + R_{volume} + R_{contact} \quad (4.1)$$

where $R_{contact}$ is a combined contact resistance that accounts for the contact resistance between the electrode and the powder and the contact resistance between different particles in the powder. Therefore, it is hypothesized that a volume resistivity measurement will better approximate the bulk conductivity of a compressed powder sample than a total resistivity measurement, as is used in the traditional two-piston method, by removing the surface resistivity component [215]. In addition, as volume resistivity is the measurement commonly used to characterize conductive polymer composites [217], measurement of volume resistivity of carbon powders provides valuable information about how these powders will behave in electrically conductive composite materials.

Effective media theory

The expected conductivity behavior of a packed powder system is an S-curve with three regions of conductive behavior. At packing fractions below the percolation threshold (Φ_c), the system is dominated by the insulating phase and no conductive path exists through the powder. At packing fractions slightly above the percolation threshold, a conductive path exists through the system and conductivity increases rapidly. At high packing fractions, close packing is achieved and no further increase in conductivity is seen. In porous carbon powders at high pressures, compressive deformation occurs causing the internal pore structure of the particles to collapse. This deformation defines the behavior of the system at high pressures causing a decrease in conductivity.

Effective media theories (EMTs) can be used to describe the behavior of conductive, compressed particle systems during the transition from insulating to conductive behavior [200]. Of particular interest is the general effective media equation (GEM), as described by McLachlan (1986) [218]:

$$(1 - \Phi) \frac{\sigma_l^{1/t'} - \sigma_m^{1/t'}}{\sigma_l^{1/t'} + \frac{1-\Phi_c}{\Phi_c} \sigma_m^{1/t'}} + \Phi \frac{\sigma_h^{1/t'} - \sigma_m^{1/t'}}{\sigma_h^{1/t'} + \frac{1-\Phi_c}{\Phi_c} \sigma_m^{1/t'}} = 0 \quad (4.2)$$

where:

$\Phi \rightarrow$ Volume fraction of conductive phase

$\Phi_c \rightarrow$ Percolation threshold

$\sigma_h \rightarrow$ Conductivity of the conductive phase

$\sigma_l \rightarrow$ Conductivity of the insulating phase

$\sigma_m \rightarrow$ Conductivity of the composite of both phases

$t' \rightarrow$ A geometric exponent described in Eqn. 4.4

For a powder-air system, the conductivity of air can be approximated as $\sigma_l = 0$, causing

Eqn. 4.2 to simplify to:

$$\sigma_m = \sigma_h \left(\frac{\Phi - \Phi_c}{1 - \Phi_c} \right)^{t'} \quad (4.3)$$

The exponent, t' is defined by the geometry of the particle so that:

$$t' = \frac{2 - 3L_a}{3L_a(1 - 2L_a)} \Phi_c = \frac{1 + 3L_c}{3L_c(1 - L_c)} \Phi_c \quad (4.4)$$

and

$$\Sigma L_{a,b,c} = 1 \quad (4.5)$$

L_a , L_b , and L_c are defined based on the dimensions of the particles in each direction, with the assumption that there is low deviation in shape from particle to particle. For spherical particles, such as carbon black, $L_a = L_b = L_c = \frac{1}{3}$. A full derivation of these equations is shown in Celzard et al. (2002) [200].

As Φ and σ_m are respectively the independent and dependent variables when measuring the conductivity of compressed powders, Eqn. 4.3 can be fit to the collected data, with t' , Φ_c and σ_h as fit parameters. As t' and Φ_c can be estimated based on the particle geometry and values of σ_h have previously been measured for graphite and copper, the fit of these parameters can be compared to expected results [200, 219].

Methods

Materials

A number of carbon-based powders were investigated. Carbon black powders include: Vulcan XC72R (VXC72R CB) and Vulcan XC MAX22 (VXC MAX22 CB). Carbon blacks were provided by Cabot Corporation (Georgia, USA). Graphite (Product #1.04206) was provided by Sigma-Aldrich (Missouri, USA). Lignin-sourced biochar (HL1100) was produced

from laboratory isolated lignin, described by Singh et al. (2019) [220]. The lignin was placed in a tube furnace under a 30 mL/min flow of nitrogen. The temperature of the tube furnace was ramped at 10 °C/min to 1100 °C, held for 1 hr and ramped back down to room temperature. Copper powder (Product #266086, particle size of $< 425\ \mu\text{m}$ and purity of $>99.5\%$) was supplied by Sigma-Aldrich (Missouri, USA) and was measured as a standard material, due to its well characterized conductivity behavior. Cellulose (Fibrous, medium, product #C6288) was supplied by Sigma-Aldrich (Missouri, USA) and was measured to determine the behavior of the system close to the instruments upper resistance limit.

Test fixture assembly

A test fixture was assembled of 3D printed parts, 0.635 cm (0.25 in) diameter copper rod, 0.9525 cm (0.375 in) diameter copper rod and a 0.8738 cm (0.344 in) inner diameter, 1.905 cm (0.75 in) outer diameter copper washer. Photos of the 3D printed parts are shown in the supplemental information (Figure B.1 and B.2) and .STL files for 3D printed parts are available online [221]. 3D printed parts were printed on an Anycubic Photon SLA 3D Printer with Anycubic Colored UV Resin (Aqua Blue). All parts were held into the 3D printed fixture with Loctite adhesive. Contact surfaces were lathed then sanded flat and polished on a polishing wheel to minimize the contact resistance between the copper electrodes and the measured sample. 18 gauge wires were soldered to the copper parts, to allow for connection to instrumentation. The completed lower part of the assembly was mounted on a ThorLabs 0.5" Travel Vertical Translation Stage (Part # MVS005). The upper portion of the assembly was mounted on a polycarbonate plate, and supported 3.81 cm (1.5 in) above the minimum height of the translation stage. The lower portion of the fixture was adjusted to be centered on the upper portion of the fixture.

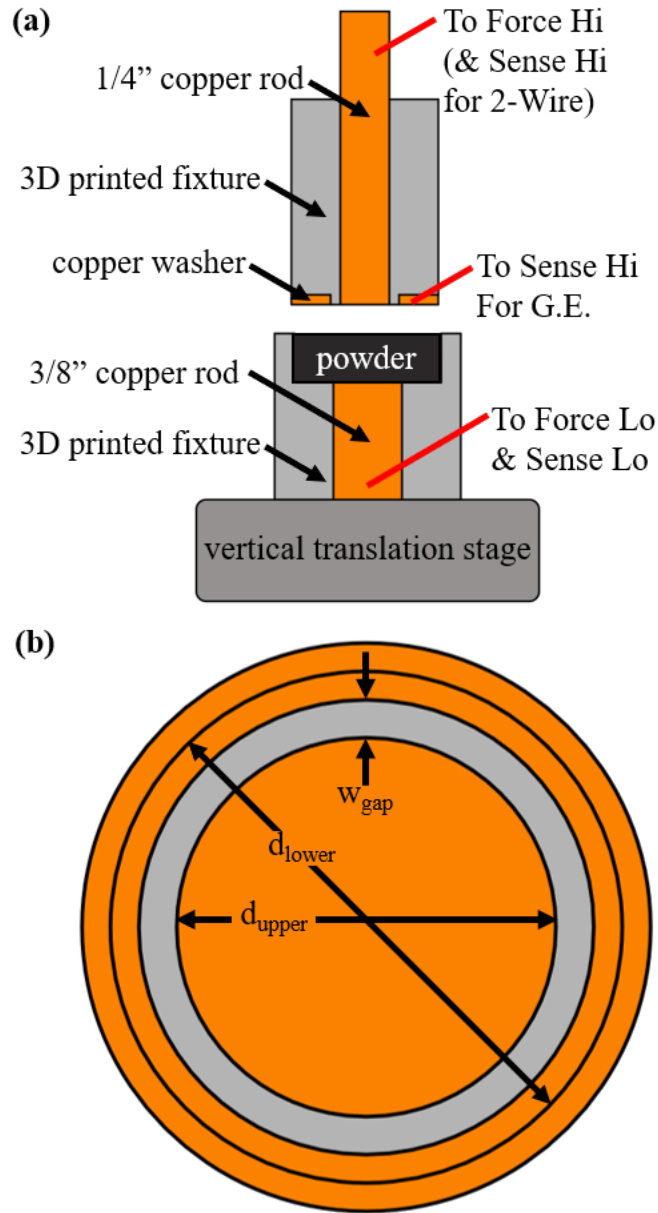


Figure 4.2: (a) Schematic of the test fixture. (b) Cross-section of the test fixture showing relevant dimensions. Additional images of the test fixture are included in the supplemental information (Figure B.1 and B.2).

Conductivity of powders

In order to compare the guard-electrode method to the established two-piston method DC conductivity measurements were taken of copper, cellulose and all carbon powders in both the guard-electrode configuration and in a two-piston configuration, as shown in Figure 4.2. All powders were compressed through a range of thicknesses; measurements were taken at every 0.0127 cm (0.005 in) of compression.

DC conductivity was measured on a Keithley 2450 Source measurement unit (SMU) in Ohmmeter mode. Powders were compressed from the point that the SMU successfully passed the lower limit of current ($0.1 \mu\text{A}$) through the sample until no more pressure could be applied. Measurements were taken every 0.0127 cm (0.005 in) of displacement. For each DC conductivity measurement, 100 readings were averaged beginning 30 seconds after the powder was compressed.

In order to explore the time dependency of this measurement and determine if a stable reading has been reached after 30 seconds, resistance measurements were recorded continuously until 30 seconds for VXC72R CB, copper and graphite samples. Time dependent conductivity and variance data is included in the supplemental information (Figure B.9-B.14).

Impedance spectra were collected with a Hioki 3533-01 LCR meter from 0.1 Hz to 200 kHz. Spectra were collected at every 0.0635 cm (0.025 in) of compression from the first point that the SMU successfully passed $0.1 \mu\text{A}$ of current through the sample, until no more pressure could be applied. Impedance spectra were also measured in both guard-electrode and two-piston configurations.

Data analysis and curve fitting

Measured resistance values were converted to conductivity using:

$$\sigma_m = \left(\frac{A_e \times R}{t} \right)^{-1} \quad (4.6)$$

where R is the measured resistance, t is the thickness and A_e is the effective area as calculated by [222]:

$$A_e = \pi \times (d_{upper} + w_{gap})^2 / 4 \quad (4.7)$$

for the guard-electrode method and

$$A_e = \pi \times (d_{upper} + d_{lower})^2 / 16 \quad (4.8)$$

for the two-piston method, where d_{upper} and d_{lower} are the upper and lower piston diameters respectively, and w_{gap} is the width of the gap between the upper piston and the copper washer as shown in Figure 4.2.

Packing fraction was calculated as the ratio of apparent density to grain density [200]:

$$\Phi = \frac{m / (t \times A)}{\rho} \quad (4.9)$$

where m is the mass of the powder, t is the thickness of the powder, A is the cross sectional area of the fixture and ρ is the bulk density of the powder.

Values for σ and Φ for both the guard-electrode method and the two-piston method are fit with Eqn. 4.3 to determine σ_h , Φ_c and t' using the MATLAB Curve Fitting Toolbox (MATLAB version R2020A, 9.8.0.1380330). All R^2 values are > 0.95 .

Impedance spectra were fit with an equivalent circuit using AfterMath software (v. 1.6.10153, Pine Research Instrumentation) in order to determine the resistance and

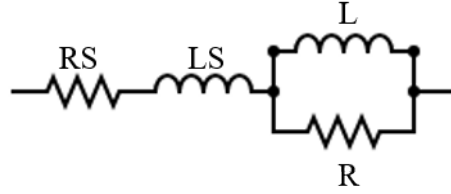


Figure 4.3: Equivalent circuit used to fit high compression impedance spectra.

inductance of the system. The simple circuit shown in Figure 4.3 was chosen as it was the simplest circuit that fit the data with a χ^2 value of < 0.1 . This circuit was used to fit high compression impedance spectra for copper powder samples. Cellulose samples and low compression measurements show capacitive behavior, which cannot be accurately fit with this equivalent circuit.

Changes in particle structure with compression

VXC72R CB particles were examined pre- and post- compression on a Field Emission Scanning Electron Microscope (FESEM) to determine if any changes in particle size or structure were seen. Carbon samples were placed on carbon sticky dots (Ted Pella, product #16084-3), sputter coated with iridium on a Emitech K-875X Sputter Coater at 30 mA for 60 seconds and examined on a Supra 55VP System 2512 at 1 kV with a SE2 detector.

Results and Discussion

Characterization of copper and cellulose powders

Copper and cellulose powders were tested in order to characterize the behavior of the test fixture for both high and low conductivity materials. Impedance measurements of copper powder showed largely resistive behavior with inductance present at high frequencies. At low compressions, some capacitance was seen. After initial contact, copper showed little change in impedance behavior with increasing pressure. The guard-electrode method measured a

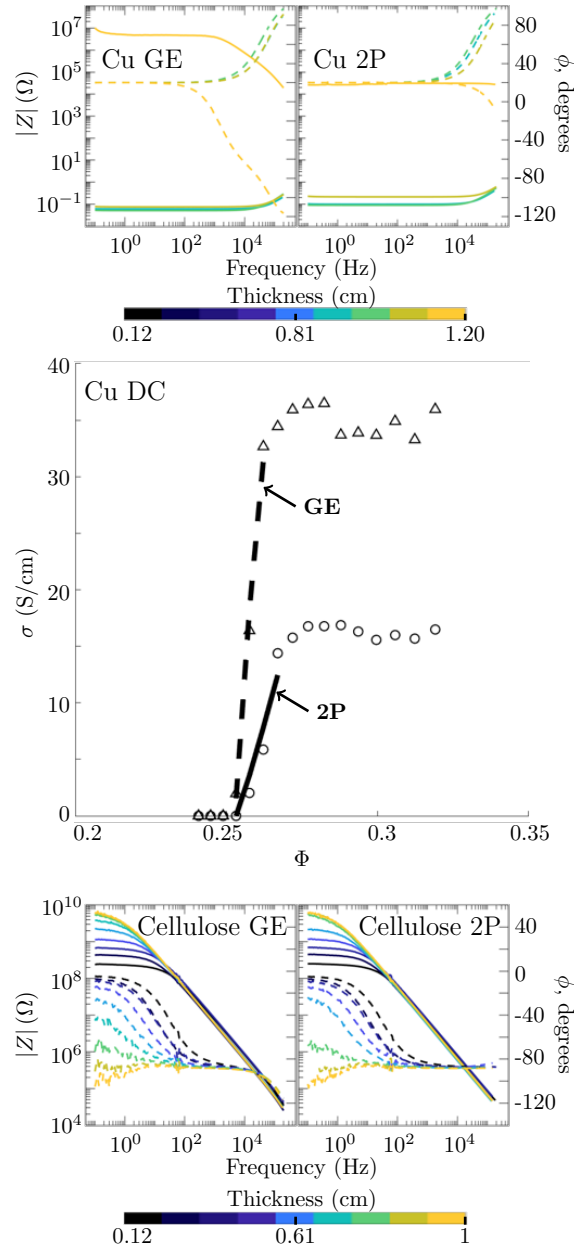


Figure 4.4: (Top) Log scale Bode plot of the AC behavior of copper for both the two-piston method and the guard-electrode method. Dashed lines are the phase angle (ϕ , right axis) and solid lines are the absolute value of impedance (left axis). (Middle) DC behavior of copper for the guard-electrode method (triangles and dashed line) and two-piston method (circles and solid line), fit with Eqn. 4.3 with the parameters shown in Table 4.2. (Bottom) Log scale bode plot of the AC behavior of cellulose for both the two-piston method and the guard-electrode method. Dashed lines are the phase angle (ϕ , right axis) and solid lines are the absolute value of impedance (left axis). Cellulose had a DC conductivity below the lower measurement limit of the SMU and therefore was not measured.

minimum impedance value on the order of $10^{-2} \Omega$, while the two-piston method found a minimum value on the order of $10^{-1} \Omega$, demonstrating the ability of the guard-electrode method to better capture the behavior of low impedance materials. As copper is expected to have largely resistive behavior at high packing fractions, the presence of inductance in copper powder indicates that the shielding of the wires used is insufficient for frequencies greater than approximately 10^3 Hz [223]. Nyquist plots of the AC behavior of copper are shown in the supplemental information (Figure B.3).

The equivalent circuit of the impedance spectrum of copper gives an average system resistance of 6.273 ± 1.240 m Ω for the guard-electrode method, and 13.524 ± 7.032 m Ω for the two-piston method. This equivalent circuit gives a system impedance of 202.612 ± 31.091 nH for the guard-electrode method and 416.214 ± 50.440 nH for the two-piston method. No trend is seen in system resistance or impedance with changes in compression.

At low frequencies, the LCR meter is capable of capturing the AC behavior of cellulose. Below 10^2 Hz, impedance decreases and the phase angle shifts from highly capacitive behavior to highly resistive behavior with increasing compression. Above 10^2 Hz, the impedance is outside of the measurement range advertised by Hioki [224], leading to the sharp boundary seen for all compressions. Nyquist plots of the AC behavior of cellulose are shown in the supplemental information (Figure B.4).

DC measurements of copper powder follow the typical S-curve behavior of conductivity with increasing packing fraction for a conductive material [201]. The guard-electrode method showed a peak conductivity of the packed powder of 36.478 S/cm, while the two-piston method was found to have a peak value of 16.869 S/cm (Fig. 4.4, center). Copper powder was found to have an unpacked density of 2.268 g/cm³ and a grain density of 8.96 g/cm³ [219] giving an expected percolation threshold of 0.2531 [200]. As copper transitioned quickly from an insulating to conductive regime, this value is assumed to be the percolation threshold rather than fitting for percolation threshold. The data shows copper to have a percolation

Table 4.1: Skeletal density (ρ), unpacked density (ρ_u), and maximum measured conductivity for the two-piston ($\sigma_{2P,max}$) and guard-electrode methods ($\sigma_{GE,max}$). Errors on unpacked density are $\pm$ one standard deviation. As a novel material without a characterized density, HL1100's density is estimated from similar biochars in the literature.

Powder	ρ g/cm ³	ρ_u g/cm ³	$\sigma_{2P,max}$ S/cm	$\sigma_{GE,max}$ S/cm
Copper	8.96 [219]	2.268	16.869	36.478
VXC72R CB	1.92 [225]	0.042 ± 0.002	3.051	10.988
VXCMA22 CB	1.90 [226]	0.188 ± 0.001	2.769	10.634
Graphite	2.26 [219]	0.239 ± 0.006	4.136	8.992
HL1100 BioC	2.00	0.2539 ± 0.0023	0.888	5.271

Table 4.2: Grain conductivities (σ_h), percolation thresholds (Φ_c) and fit exponents (t') as determined from fitting conductivity data to Eqn. 4.3 for all powders investigated for the two-piston and guard-electrode methods. Given errors are 95% confidence intervals.

Powder	Two-piston method			Guard-electrode method		
	σ_h (S/cm)	Φ_c	t'	σ_h (S/cm)	Φ_c	t'
Copper	$(3.882 \pm 1.540) * 10^4$	$0.253^\dagger$	1.983 ± 0.637	$(2.168 \pm 1.54) * 10^5$	$0.253^\dagger$	0.960 ± 2.152
VXC72R CB	57.390 ± 12.250	0.071 ± 0.017	2.525 ± 0.250	173.1 ± 51.2	0.114 ± 0.018	1.969 ± 0.278
VXCMA22 CB	8.071 ± 0.550	0.314 ± 0.001	0.683 ± 0.037	32.86 ± 2.42	0.314 ± 0.002	0.717 ± 0.041
Graphite	99.480 ± 22.610	0.199 ± 0.033	1.678 ± 0.815	494.6 ± 162.7	0.197 ± 0.013	1.803 ± 1.850
HL1100 BioC	3.542 ± 2.259	0.337 ± 0.024	1.163 ± 0.460	27.63 ± 18.19	0.338 ± 0.023	1.060 ± 0.445

[†] Copper percolation thresholds were determined as the ratio of unpacked density to grain density [200] due to the quick transition from low to high conductivity.

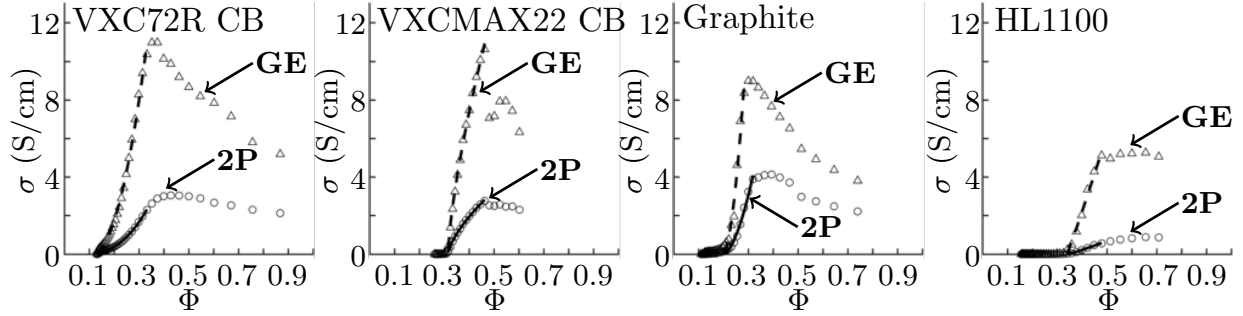


Figure 4.5: DC measurements as a function of packing fraction for each carbon powder. Triangles are the guard-electrode method and circles are the two-piston method. The curve is fit with Eqn. 4.3, with the parameters shown in Table 4.2.

threshold between 0.2489 and 0.2531 for the guard-electrode method and between 0.2531 and 0.2576 for the two-piston method, validating this assumption. When fit to the GEM equation (Eqn. 4.3), the grain conductivity of copper is found to be $\sigma_h = (2.168 \pm 1.54) \times 10^5$ S/cm for the guard-electrode method and $\sigma_h = (3.882 \pm 1.54) \times 10^4$ S/cm for the two-piston method. As bulk copper is expected to have a conductivity of 5.959×10^5 S/cm [219], both measurements undervalue the true conductivity of copper, with the guard-electrode method representing a more accurate measurement. The discrepancy between measured and established values is hypothesized to be due to contact resistance between particles in the packed powder system, leading to a conductivity that is lower than the solid material [227]. DC measurements were not taken on cellulose, as the resistance of cellulose was above the upper limit of the SMU at all compressions.

Characterization of carbon powders

All four carbon powders' DC conductivities were measured as a function of packing fraction (Φ), and fit with Eqn. 4.3. In all cases, the expected S-curve shape was seen, but with a decrease in conductivity after the peak. This decrease in conductivity is attributed to deformation of the powder with increased compression, causing a decrease in thickness with

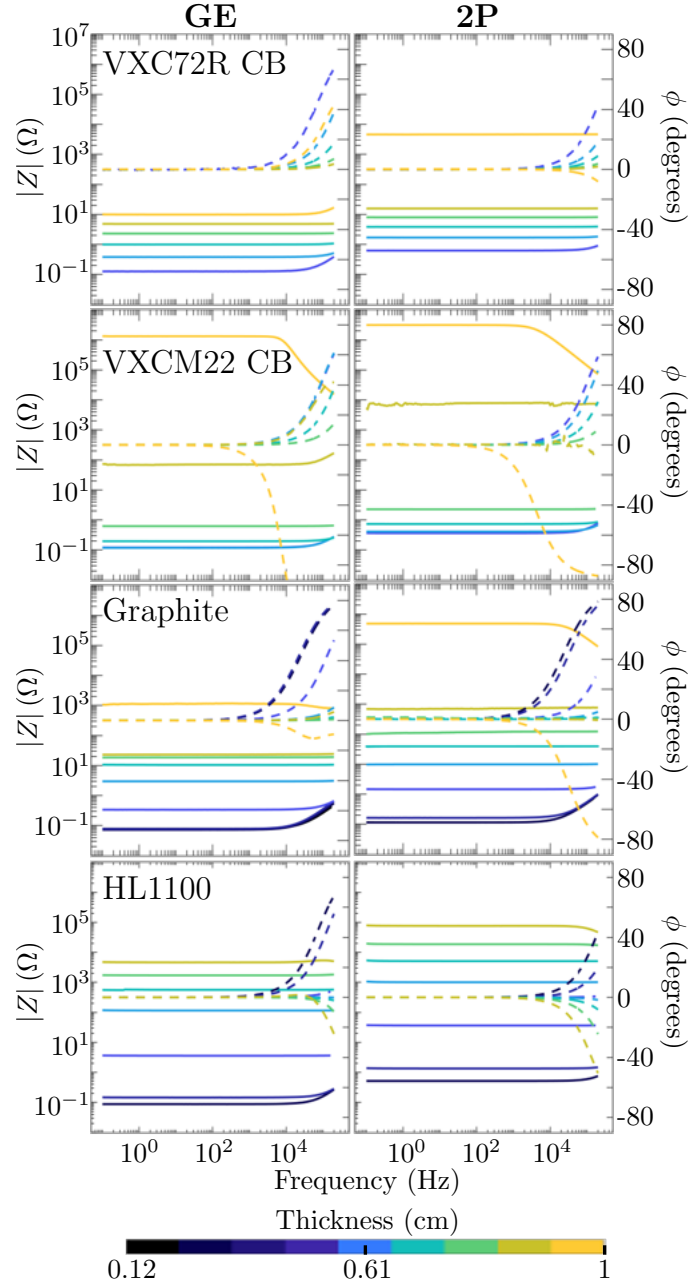


Figure 4.6: Log scale Bode plots of the AC behavior for each carbon powder. Dashed (left) lines are the guard-electrode method. Solid (right) lines are the two-piston method.

little change in resistance. Similarly, packing fractions greater than expected for close packing of the original particle geometries are attributed to collapse of the particle structure at high pressures. This deformation was confirmed by examining VXC72R CB with FESEM imaging

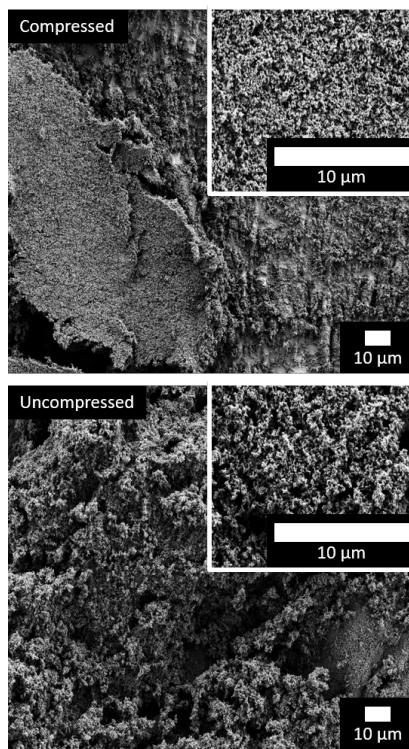


Figure 4.7: FESEM images of VXC72R CB in both compressed and uncompressed states. Main images are at 2500x magnification and insets at 25kx magnification. All scale bars are 10 μm .

(Fig. 4.7). The porosity and structure of the carbon black aggregate surface can be seen to have collapsed, leading to a smoother less porous surface and an inability to distinguish individual particles. This supports the hypothesis that changes in particle structure are responsible for the decrease in conductivity seen after peak conductivity. The presence of the expected S-curve indicates that the microscope stage used for this experiment applied sufficient pressure to capture the full insulating-to-conducting transition of these powders.

For all powders, the guard-electrode method showed a higher conductivity than the two-piston method (Table 4.1). Both VXC72R CB and graphite are well characterized in the literature, allowing for easy comparison to established values. The guard-electrode method peak measured conductivity for VXC72R CB of 10.99 S/cm is slightly higher than

the conductivity of 4.5 S/cm found in the literature at approximately the same packing fraction, while the two-piston method peak conductivity of 3.05 S/cm is slightly lower [161]. The anisotropic electrical behavior of graphite leads to a range of expected conductivities from 0.023 S/cm to 215.2 S/cm depending on the orientation of the graphite flakes [210]. The fit conductivity of graphite falls in the middle of this range for both two-piston and guard-electrode methods, indicating that there is still some disorder in the packing of the graphite flakes [200].

When fit with Eqn. 4.3, percolation thresholds and grain conductivities (Table 4.2) for the powders were found to be in good agreement with established values. Both carbon blacks can be assumed to be an aggregate of spherical particles [228], with a theoretical percolation threshold of 0.3116 [229]. The fit percolation thresholds of VXCMA22 CB (0.314 for both methods) is found to be in good agreement with the spherical value of 0.3116. VXC72R CB differs significantly from this value. Cabot describes this carbon black as having a low percolation threshold relative to other carbon blacks [226]. We hypothesize that this may be due to the low unpacked density and porosity relative to VXCMA22 CB [225, 226]. The percolation threshold of HL1100 biochar also indicates a spherical structure on average, with a percolation threshold of 0.337 for the two-piston method and 0.338 for the guard-electrode method. Graphite has a flake structure [200], and is found to have a percolation threshold of 0.199 when measured with the guard electrode method and 0.197 for the two-piston method, in good agreement with the percolation threshold for artificial graphite flakes of 0.224 found by Celzard et al. (2002) [200].

All four carbon powders measured have similar impedance behavior. Impedance decreases with compression, and little frequency dependence is seen. This behavior matches past work examining the impedance spectra of carbon black [230, 231]. In all cases, the guard-electrode method shows a lower impedance than the two-piston method. The behavior of these powders is largely resistive. At high compressions inductance is seen at high

frequencies. This inductance is similar in magnitude to the inductance of the copper powder, and again is attributed to the unshielded wires and connections [223]. At low compressions, some capacitive behavior is seen. Nyquist plots for the carbon powders are included in the supplemental information (Figure B.5-B.8).

Conclusions

Measurements of conductivity using the guard-electrode method are shown to be in better agreement with established values for VXC72R CB, graphite and copper than the two-piston method. The experimental setup used is shown to be capable of characterizing the full insulating-to-conducting S-curve that is typically seen in conductive powders as they are compressed, and to be able to capture impedance spectrum of these materials across a wide range of thickness values. High frequency AC measurements are limited in this particular setup, due to challenges with the lack of shielding on electrodes and cables. This design could be modified with shielding for high frequency applications. This method has overcome the challenges of measuring the conductivity of carbon powders, allowing for more accurate and repeatable conductivity and impedance spectra measurements of these important electrically conductive materials.

Supporting Information to this Chapter is presented in Appendix B.

PHYSICAL AND CHEMICAL MECHANISMS THAT INFLUENCE THE ELECTRICAL
CONDUCTIVITY OF LIGNIN-DERIVED BIOCHAR

Contribution of Authors and Co-Authors

Manuscript in Chapter 5

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Contributions: Conceptualization, Methodology, Investigation, Formal analysis,
Writing - original draft, Visualization

Author: Rachel Ulrich

Contributions: Software, Formal analysis, Writing - original draft

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Contributions: Methodology, Investigation, Formal analysis, Writing - review &
editing

Author: Cecily Ryan

Contributions: Conceptualization, Resources, Supervision, Writing - review & editing

Manuscript Information

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Carbon Trends

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Abstract

Lignin-derived biochar is a promising, sustainable alternative to petroleum-based carbon powders (e.g., carbon black) for polymer composite and energy storage applications. Prior studies of these biochars demonstrate that high electrical conductivity and good capacitive behavior are achievable. However, these studies also show high variability in electrical conductivity between biochars ($\sim 10^{-2}$ – 10^2 S/cm). The underlying mechanisms that lead to desirable electrical properties in these lignin-derived biochars are poorly understood. In this work, we examine the causes of the variation in conductivity of lignin-derived biochar to optimize the electrical conductivity of lignin-derived biochars. To this end, we produced biochar from three different lignins, a whole biomass source (wheat stem), and cellulose at two pyrolysis temperatures (900 °C, 1100 °C). These biochars have a similar range of conductivities (0.002 to 18.51 S/cm) to what has been reported in the literature. Results from examining the relationship between chemical and physical biochar properties and electrical conductivity indicate that decreases in oxygen content and changes in particle size are associated with increases in electrical conductivity. Importantly, high variation in electrical conductivity is seen between biochars produced from lignins isolated with similar processes, demonstrating the importance of the lignin’s properties on biochar electrical conductivity. These findings indicate how lignin composition and processing may be further selected and optimized to target specific applications of lignin-derived biochars.

Introduction

Carbon black is an amorphous graphitic carbon powder that has developed as an essential filler for thermally and electrically conductive composites [232, 233]. Carbon black’s excellent electrical conductivity, low percolation threshold, and low cost make carbon black an ubiquitous additive to create electrically conductive composite materials for polymer

composite and energy storage applications [216, 232, 234, 235, 236]. The development of replacements for carbon black from renewable feedstocks, such as biomass, could improve the sustainability of these important applications. It is critical to understand and control the synthesis parameters that increase electrical conductivity of carbon materials derived from these alternate sources in order to develop renewable alternatives to carbon black.

One promising renewable feedstock for the production of carbon filler materials is lignin. Lignin is a primary component of woody biomass, an abundant biopolymer, and a waste product of papermaking and bio-ethanol industries, with over 50 million metric tons isolated each year [237]. Due to lignin’s aromatic carbon monomer backbone, waste sourcing, and low cost it has potential as an ideal precursor for renewable alternatives to carbon black [238]. Lignin can be pyrolyzed to form biochar, a carbon-rich material most typically applied as a soil amendment [12]. Depending on processing conditions and source, lignin-derived biochar can be produced with properties similar to those of carbon black [114, 140] including small particle sizes [239], high electrical conductivity [150], and strong capacitance [156].

A review of past studies shows high variability in biochar electrical conductivity. Biochars produced at 900 °C have been found to have electrical conductivities ranging from 1.91×10^{-5} S/cm to 62.96 S/cm (Figure 5.1) [19, 99, 103, 111, 113, 114, 141, 144, 146, 147, 148, 149, 150, 151, 152, 153, 154, 155, 156, 157, 158, 159, 240, 241]. For reference, a typical range of conductivities observed for carbon black is shown as the grey region between 0.5 and 12 S/cm in Figure 5.1. Differing pyrolysis temperatures, feedstocks, preprocessing conditions, heating rates, and catalysts used may impact the electrical conductivity of biochar. When examining only lignin-derived biochars, a wide range of conductivities is still observed, with conductivities of biochar produced at 900 °C ranging from 0.009 S/cm to 62.96 S/cm. Past studies have proposed differences in metal content [111, 114], oxygen content [114], surface area [114], density [152], carbon content [153] and the size of the graphitic crystallites [19, 113] as factors influencing conductivity. However, to our knowledge, no study to date

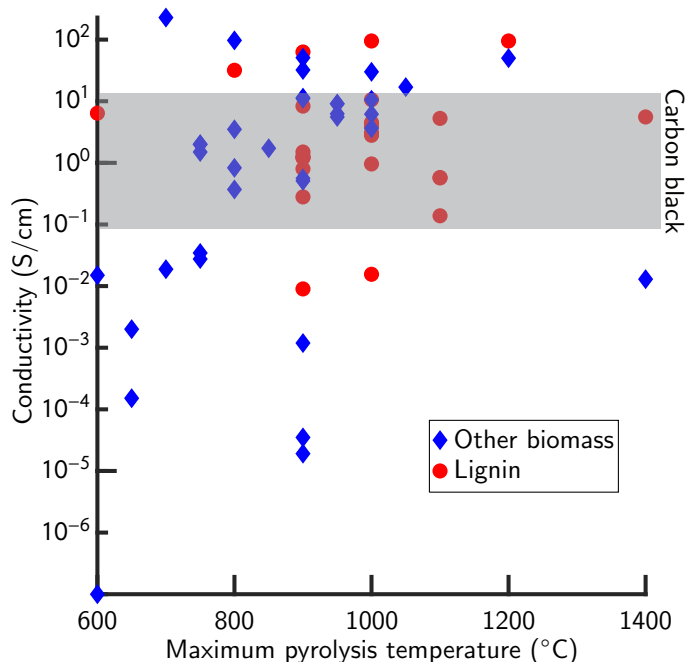


Figure 5.1: A review of literature electrical conductivity values for biochar produced from lignin and other biomass [19, 99, 103, 111, 113, 114, 141, 144, 146, 147, 148, 149, 150, 151, 152, 153, 154, 155, 156, 157, 158, 159, 240, 241]. The grey box shows a range of typical carbon black conductivities, independent of processing temperature [141, 161]. Additional information on these biochar conductivity data is shown in Table C.1.

has systematically examined the mechanisms behind the observed differences in electrical conductivity in biochar. Understanding the mechanisms that govern conductivity in biomass-derived carbon electronics, including lignin, is necessary to optimize biochar as an alternative to carbon black in electrically conductive applications.

In this study, we examine the relationship between lignin sourcing and the electrical conductivity of lignin-derived biochar. We hypothesized that lignin sourcing would have a significant impact on biochar properties, and in particular electrical conductivity. Biochar was produced from three lignins: alkaline lignin, dealkaline lignin, and a laboratory isolated lignin. To keep biochar processing consistent, biochar was produced at maximum pyrolysis temperatures of 900 °C and 1100 °C. To build a better understanding of the relationship between biochar properties and electrical conductivity, we characterized the physical and

chemical properties of the biochar and measured the electrical conductivity of each biochar. We then explored the relationship between lignin sourcing, biochar properties, and the resulting biochar’s electrical conductivity. This research identifies key directions of future work to improve the electrical conductivity of biochar and supports the development of conductive biochar as a renewable alternative to carbon black.

Methods and Materials

Materials

Three different lignins were used as biochar feedstocks to examine variations between different lignin processing conditions. Alkaline and dealkaline lignins were purchased from TCI America (product # L0082 and L0045 respectively, Portland, OR, USA). Both TCI lignins are isolated from wood via a sodium sulfite (Na_2SO_3) treatment, followed by chemical modifications, including desulfonation, oxidation, hydrolysis, and demethylation. These lignins differ in that alkaline lignin has been treated after isolation to have a pH between 8 and 10 [242]. Laboratory isolated lignin was provided by the Hodge Research Group (Montana State University, Bozeman, MT, USA). This lignin is isolated from poplar wood by an alkaline pre-extraction process followed by acidification with sulfuric acid [220].

In addition to lignins, biochar was produced from non-lignin biomass sources. Solid stem wheat stem feedstock was provided by the Montana State University Agricultural Research and Teaching Farm (Bozeman, MT, USA). Cellulose feedstock was purchased from Sigma-Aldrich (Fibrous, medium, product #C6288, St. Louis, MO, USA). All biochar feedstocks were stored in a drying oven at 105 °C until use.

Biochar production

Lignin, biomass, and cellulose feedstocks for biochar production were ball milled to reduce particle size. Ball milling was performed with zirconia media at 60 rpm (1 Hz), for 24

Table 5.1: Biochar production variables and abbreviations.

Feedstock	Pyrolysis Temperature	
	900 °C	1100 °C
Alkaline Lignin	AL900	AL1100
Dealkaline Lignin	DAL900	DAL1100
Hodge Lab Lignin	HL900	HL1100
Wheat Stem	WS900	WS1100
Cellulose	CELL900	CELL1100 [†]

[†] No biochar was produced from cellulose at 1100 °C due to low pyrolysis yields.

h for lignins and cellulose, and 72 h for wheat stems. After milling, feedstocks were stored in a drying oven at 105 °C for at least 24 h before pyrolysis.

Biochar was produced by slow pyrolysis in a Thermo Fisher Lindberg/Blue M Mini-Mite tube furnace with an alumina tube and alumina boat as described by Quosai *et al.* (2018) [99] and Arroyo *et al.* (2018, 2019) [92, 190]. Nitrogen was flowed through the tube at 100 mL/min for 10 min before heating and at 30 mL/min during heating. The furnace temperature ramp was 10 °C/min to a maximum temperature of 900 °C or 1100 °C. The maximum temperature was maintained for 1 h and then cooled to room temperature. All biochars were ball milled in a Retsch Mixer Mill 400 for 2.5 min at 30 Hz after pyrolysis to reduce clumping and then stored in a drying oven at 105 °C until use. A complete list of biochar production variables and abbreviations is shown in Table 5.1. Due to low biochar yields at 1100 °C, cellulose was only used to produce biochar at 900 °C.

Volume conductivity and impedance spectra

Volume conductivity is the primary material property of interest for electrically conductive filler materials. The volume conductivity of biochars was determined on a guard electrode compression fixture described by Kane *et al.* [141]. Volume conductivity measurements were performed on a Keithley 2450 Sourcemeter, with an applied current of 100 mA. For each biochar, 200 mg of biochar was placed in the sample holder, and resistance measurements were taken every 0.127 cm (0.05 in) of thickness from the point of the first contact until no more pressure could be applied. A settling period of 30 s was used, and measurements between 25 and 31 s were selected for use. Five measurements were taken of the same sample of each biochar, with an average of 100 resistance readings taken for each measurement.

To better characterize the electrical behavior of the biochar, electrical impedance spectra were collected with the same guard electrode compression fixture and a Hioki 3533-01 LCR meter. Impedance spectra were collected on 200 mg of biochar every 0.127 cm (0.05 in) from the point where 0.1 μA could be passed through the sample until no more pressure could be applied.

Characterization of biochar chemical structure

Thermogravimetric infrared spectroscopy Thermogravimetric analysis combined with infrared spectroscopy (TGA-IR) was performed on the biochar feedstocks to examine the pyrolysis reactions and the differences in pyrolysis rates between the different lignin feedstocks. TGA-IR was performed on a TA Instruments Q5000 IR and a Thermofisher Nicolet iS10 FTIR Spectrometer with a TGA-IR module. Samples were 20 mg and were ramped at 10 $^{\circ}\text{C}/\text{min}$ to 1100 $^{\circ}\text{C}$ under a nitrogen flow of 30 mL/min, mimicking pyrolysis conditions. The transport tube and IR gas cell were maintained at 300 $^{\circ}\text{C}$ to prevent condensation of gases. IR spectra were collected with a resolution of 8 cm^{-1} and six scans

per measurement, between 500 and 4000 cm^{-1} .

Elemental composition Energy-dispersive X-ray spectroscopy (EDX) was performed to determine the elements present in the biochar. A JEOL JSM-6100 scanning electron microscope with a RÖNTEC XFlash 1000 energy-dispersive X-ray detector was used to collect the spectra and for imaging, with an electron beam energy of 20 kV. Biochar samples were placed on carbon sticky dots (product #16084-3, Ted Pella Inc., Redding, CA, USA) and sputter coated with iridium on an Emitech K-875X sputter coater at 30 mA for 60 s.

Combustion analysis was performed to measure the C, H, N, and S elemental composition of the biochar. Combustion analysis was performed and analyzed in duplicate by Atlantic Microlab Inc. (Norcross, Georgia, USA).

Based on the results of the EDX measurements, Na, Mg, Ca, and K were selected for inductively coupled plasma optical emission spectroscopy (ICP-OES) measurements. Before measurement, samples were digested using 10 mL trace-metal grade concentrated nitric acid (Fisher Scientific, product #A509P500, Pittsburgh, PA USA) on a Mars6 iWave digester. Two heating cycles were run to 220 °C with a ramp time of 15 min, a hold time of 15 min, and under 800 psi of pressure. Diluted samples (see Table C.2 for dilutions) and cation standards were run in a matrix of 2% HNO_3 on a SpectroBlue ICP-OES in axial view mode (high sensitivity).

Oxygen content was calculated as the remaining mass not quantified by combustion or ICP-OES analysis for AL, DAL, HL, and CELL feedstocks. For WS feedstocks, a silicon peak was observed via EDX analysis. Silicon (Si) content was quantified by multiplying the ratio of the peak intensity of the Si peak to the peak intensity of the C peak by the carbon content measured by combustion analysis. This silicon content was then subtracted from the remainder after combustion and ICP-OES analysis to determine the oxygen content in WS-derived biochars.

Attuned total reflectance Fourier transform infrared spectroscopy Attuned total reflectance (ATR) Fourier transform infrared spectroscopy (FTIR) was performed to examine the functional groups of the biochar and their dependence on feedstock and pyrolysis temperature. ATR FTIR was performed using a Thermo Fisher Nicolet iS10 FTIR spectrometer with a Smart iTX ATR accessory with a diamond crystal. Spectra were collected between 600 and 4000 cm^{-1} at a resolution of 4 cm^{-1} , and with 64 scans for each biochar sample. Spectra were baseline corrected using OMNIC software (Thermo Fisher, v. 9.9.509) to account for baseline drift.

Raman spectroscopy Raman spectroscopy was performed to investigate the graphitic content of each biochar sample using a Horiba LabRam HR Evolution NIR Raman microscope. Raman spectra were acquired with a 50 $\times$ LWD objective, a stigmatic spectrometer with a grating of 1800 gr/mm, and a 532 nm 100 mW laser at 1-10% power. Raman spectra were collected between 1000 and 1800 cm^{-1} , corresponding to the region containing the G ($\sim 1580 \text{ cm}^{-1}$) and D ($\sim 1340 \text{ cm}^{-1}$) peaks [206, 243].

Deconvolution of the Raman spectra was performed to determine D and G peak intensities. Deconvolution was performed in MATLAB (Mathworks inc., R2020a, v. 9.8.0.1380330) with the Curve Fitting Toolbox (v. 3.5.11). Spectra were fit with a Lorentzian lineshape for the D peak and a Breit-Wigner-Fano (BWF) lineshape for the G peak [206, 207]. The D to G ratio I_{DG} was calculated as the intensity ratio of the D peak to the G peak in the best fit.

Characterization of biochar physical structure

Field emission scanning electron microscopy Field emission scanning electron microscopy (FESEM) was performed to examine biochar particle size and surface and pore structure. Biochar was placed on carbon sticky dots (Ted Pella, product #16084-3), sputter coated with iridium, and examined on a Supra 55VP microscope at 1 kV and a working

distance of approximately 6 mm with an SE2 detector.

Particle size analysis Biochar particle size was measured using a Malvern Mastersizer 3000 particle size analyzer. Samples were dispersed in DI water, and the results were analyzed with the assumption of non-spherical particles.

Gas sorption for BET analysis Nitrogen adsorption was measured at 77 K on all biochar samples using a Micromeritics 3-Flex sorption analyzer to determine the surface area and pore size distribution. Before testing, samples were degassed for 12 h at 150 °C under oil-free vacuum to 10^{-8} mbar. Approximately 0.3-2 g of each sample was subjected to nitrogen adsorption and desorption between $P/P_0 = 10^{-7}$ to 0.95 at 77 K. The results were fit to the Brunauer-Emmett-Teller (BET) model [244] to determine specific surface area using standard consistency criteria for microporous solids [245]. A non-local density functional theory (NLDFT) carbon slit pore model was used to determine the pore size distribution using Micromeritics Microactive software. Gas adsorption isotherms are shown in Figure C.9.

Statistical methods

Statistical analyses were conducted in the R software environment (R Core Team, version 4.0.3, 2020) [246]. Contrasts were estimated using the emmeans package [247], a linear mixed-effects model was estimated, and results visualized using the lmerTest package [248] and effects package [249], respectively. Five pseudo-replicate measurements of electrical conductivity were taken on a single sample of each biochar as described above. Since cellulose feedstock processed at 1100 °C did not yield any measurable biochar, an analysis of variance (ANOVA) was conducted on nine treatment levels of temperature and feedstock combinations (see Appendix C for additional details on the ANOVA process). As a follow-up analysis, Bonferroni-corrected comparisons of interest were explored.

The relationship between biochar chemical and physical properties and electrical conductivity was explored using a forward, step-wise p-value model selection process. The following variables were each considered for inclusion in the final model: surface area, oxygen-to-carbon (O:C) molar ratio, hydrogen-to-carbon (H:C) molar ratio, inorganic content (sum of Na, S, Mg, Ca, and K content), and average I_{DG} . Due to issues with multicollinearity, the variables carbon content and O:C molar ratio could not both be included in the model, and carbon content was removed. The response variable, maximum electrical conductivity (σ_{max}), necessitated a square-root transformation. Nested random effects were used for treatment ($i = \text{AL900, AL1100, DAL900, DAL1100, CELL900, HL900, WS900, WS1100}$), pseudo-replicates within treatment ($j = 1, 2 \dots 5$), and time observation within pseudo-replicate ($k = 1, 2 \dots 7$ for measurements at 25-31 seconds). Therefore this transformation is given as an equation for $\sqrt{\hat{\sigma}_{max,ijk}}$. A full description of this model is given in Appendix C, and the code used to generate the model is available [250].

Results and Discussion

Biochar processing behavior

Biochar pyrolysis yields differed depending on the feedstock used and the maximum treatment temperature (Figure 5.2). AL900 had the highest average yield at 50.9 wt.%, while CELL900 produced the lowest measurable yield, with an average yield of 10.0 wt.%. For all feedstocks, pyrolysis at 1100 °C yielded less biochar than pyrolysis of the same feedstock at 900 °C. Cellulose feedstocks were not examined at 1100 °C, as no measurable solid material remained after pyrolysis of cellulose at 1100 °C.

TGA-IR analyses simulating the pyrolysis process showed an initial decrease in weight between 70 °C and 110 °C in all feedstocks due to water loss (Figure 5.3). Above this temperature range, the cellulose feedstock degrades in a single step beginning at approximately 300 °C, with a maximum slope at approximately 324 °C (Figure 5.3, blue). By

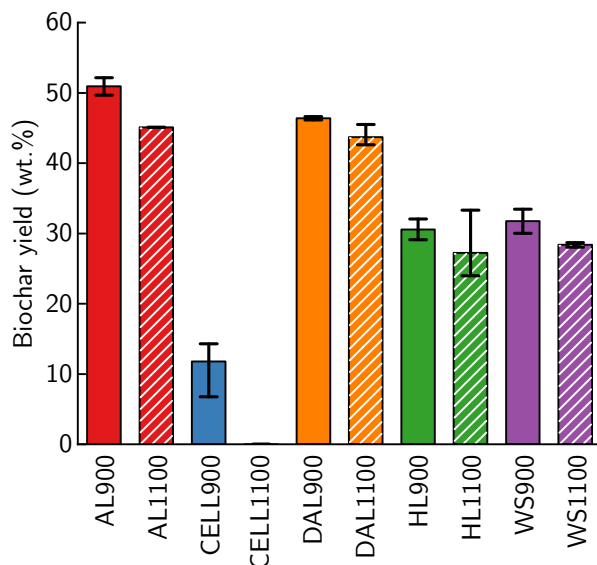


Figure 5.2: Biochar production yield by biochar type. Bars represent the mean yield of all recorded runs, and error bars indicate maximum and minimum values. No solid mass remained after pyrolysis of cellulose at 1100 °C; therefore, it was not included in the remainder of the study.

600 °C, no solid char remained in CELL samples. This decomposition has previously been attributed to the degradation of the cellulose polymer into its constituent glucose monomers, followed by degradation of these monomers to CO, CO₂, H₂, CH₄, and other short volatile hydrocarbons [131]. IR spectroscopy of the gases produced during TGA shows a single, strong peak in the Gram-Schmidt spectra at approximately 30 minutes (300 °C). The IR spectra at 30 minutes support past findings, with peaks observed at 2368 cm⁻¹ (CO₂), 1768 cm⁻¹ (C=O), 2970 cm⁻¹ (C-H) and 1242 cm⁻¹ (C-O-C) (Figure C.1) [131].

In contrast to cellulose, all lignin feedstocks show a slower degradation rate consistent with the expected behavior of the complex, aromatic carbon structure of lignin [131]. Two notable increases in slope can be seen in all lignins beginning between 180 and 220 °C and between 630 and 720 °C (Figure 5.3, top). IR measurements of the gases released during TGA show CO₂ (2368 cm⁻¹) and CO (2185 cm⁻¹) to be released continuously from approximately 200 °C to 1100 °C for pyrolysis of all lignins, while C-O-C and C=O peaks

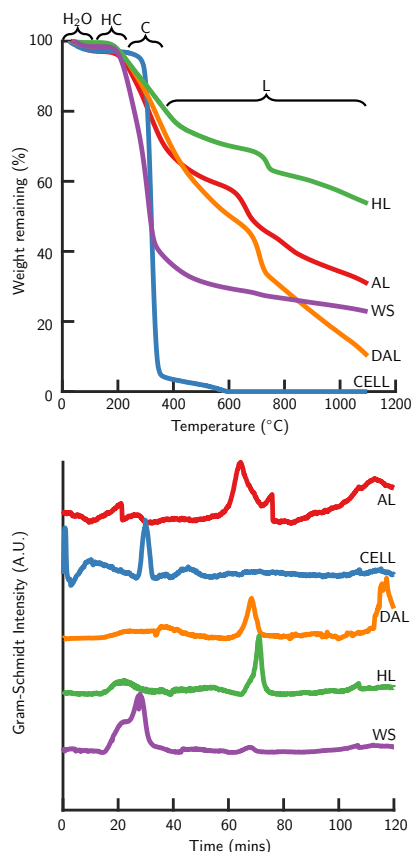


Figure 5.3: (Top) TGA of all feedstocks to 1100 °C mimicking the production conditions of the biochar. Labeled temperature ranges correspond to the region used to identify: H₂O: evaporation of water, HC: degradation of hemicellulose, C: degradation of cellulose, and L: degradation of lignin. (Bottom) Stacked Gram-Schmidt spectra displaying the intensity of the full IR spectra during the above TGA curves. Accounting for the time delay for the gas to move between the TGA and IR, the TGA weight change and the evolution of peaks in the Gram-Schmidt plot would be expected to align at a rate of 10 °C/min. Full three-dimensional representations of TGA-IR Data are available in the supplemental information.

are observed at later time points, corresponding to the increase in TGA curve slope observed at approximately 700 °C (Figure C.1). Neither TGA data nor IR measurements of gases released during TGA show meaningful differences between lignins beyond differences in weight loss.

Pyrolysis of WS involves a combination of these two mechanisms, consistent with the expected degradation of biomass comprised of cellulose, hemicellulose, and lignin. FTIR

spectra at 30 minutes of WS pyrolysis products show the release of CO_2 (2368 cm^{-1}) and CO (2185 cm^{-1}), as well as additional hydrocarbons indicated by peaks corresponding to C-H (2933 cm^{-1}), C-O-C (1242 cm^{-1}) and C=O (1768 cm^{-1}) bonds [131] (Figure C.1). Similar to CELL, TGA-IR spectra of WS show the release of C-O-C and C=O to happen together with CO_2 and CO after approximately 30 minutes. However, a second peak of C-O-C and C=O is seen at approximately 110 minutes, which may indicate that the lignin present in WS shows similar pyrolysis behavior to the isolated lignin.

TGA measurements show higher mass remaining than at the end of a biochar production run at the same temperature for most feedstocks. As TGA measurements did not include the 1 hour dwell time included in biochar production, it is hypothesized that this increased time at the highest treatment temperature is the source of most observed differences. Additionally, during the production of HL biochars, it was observed that some solid char remained in the ceramic tube after the ceramic boat was removed and that much of the solid char remaining was above the rim of the ceramic boat containing the lignin. We hypothesize that this mass loss during the production of HL biochars in the tube furnace is the cause of the observed difference between production and TGA mass loss measurements. In contrast with other biochars, TGA measurements of CELL biochar show no solid mass remaining at $900\text{ }^\circ\text{C}$, while an average of 11.78% solid mass remained during biochar production. As the pyrolysis of cellulose is more endothermic than the pyrolysis of lignins [131], this increase in residual weight may be due to uneven heat transfer into the higher mass of cellulose used during biochar production than that used during TGA.

Biochar electrical conductivity

As a replacement for carbon black in carbon-based composites for energy storage applications, the primary material property of concern is electrical conductivity. All biochars show the expected conductivity s-curve, as the powder is compressed through its percolation

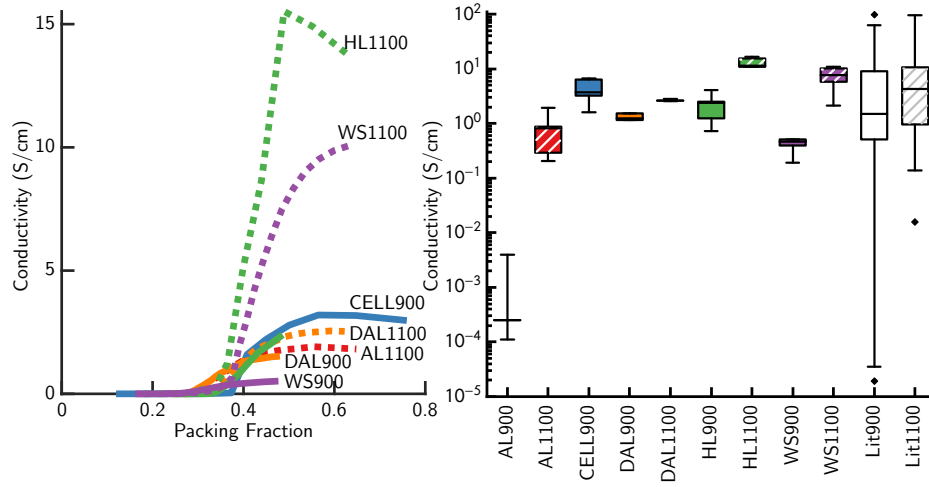


Figure 5.4: (Left) Conductivity (σ) as a function of packing fraction for the first compression of all biochars examined. AL900 showed near-zero ($\sigma < 10^{-2}$) for all compressions and cannot be seen on the plot. (Right) Box plot of conductivity for all biochars examined in this study. Lit 900 and Lit 1100 represent biochars from the literature produced between 800-1000 and 1000-1200 °C, respectively. See Table C.1 for a full summary of these biochars.

threshold and transitions from insulating to conducting electrical behavior (Figure 5.4), indicating that the full range of conductivity behavior was captured for these materials [141, 200]. Small decreases in biochar conductivity are observed in some biochars following their peak, which has previously been attributed to the deformation of biochar particles with increased pressure after close packing has been achieved [141]. The maximum electrical conductivity of biochar in this study ranged from 0.002 S/cm for AL900 to 18.5 S/cm for HL1100. This range is similar to what has been observed in past literature for lignin-derived biochar produced between 900 °C and 1100 °C, which shows conductivity varying from 0.009 S/cm (Lignotech lignin, 900 °C [114]) and 95 S/cm (16% micro fibrillated cellulose and 84% lignosulfonate, 1000 °C [19]). The range of electrical conductivity measured indicates that the variation in electrical conductivity observed in past work is not solely due to variations in pyrolysis rate, added catalysts, and electrical conductivity measurement technique between studies, as these variables have been held constant in this study. The conductivity of HL1100

measured in this study is higher than has been previously reported for this same biochar [141]. This increase is attributed to reduced contact resistance from improvements in the polishing of the electrodes [251].

An ANOVA, accounting for the random effects of sample and time observation, shows strong evidence for a difference in electrical conductivity for different biochars ($p < 0.001$). Pairwise comparisons indicate no evidence for a difference in electrical conductivity between AL1100 and DAL1100, suggesting that little difference in electrical conductivity exists between biochars produced from the two TCI lignins (AL and DAL) at 1100 °C (Table 5.2). When compared to biochar produced from laboratory isolated lignin (HL), biochar produced from both TCI lignins (AL and DAL) at 1100 °C show evidence for lower electrical conductivity (Table 5.2). This difference in electrical conductivity between lignins suggests that the post-isolation treatment of AL by TCI does not notably impact conductivity but that higher electrical conductivity can be obtained with other lignin isolation methods. Comparisons within each feedstock between pyrolysis temperatures of 900 °C and 1100 °C show almost no evidence for an increase in electrical conductivity for AL- or DAL-derived biochar with an increase in pyrolysis temperature. In contrast, WS-derived biochars show moderate evidence, and HL-derived biochars show strong evidence for an increase in electrical conductivity with an increase in pyrolysis temperature (Table 5.2). HL shows a larger estimated increase in conductivity from 900 °C to 1100 °C (+8.12 S/cm) than AL (+1.26 S/cm), DAL (+2.02 S/cm) or WS (+6.94 S/cm) feedstocks (Table 5.2). Possible mechanisms behind these differences between feedstocks are examined in more detail below.

All biochars measured in this study primarily show resistive AC electrical behavior (Figure 5.5). At the point of highest compression, biochar impedance showed little frequency dependence. AL900, the highest impedance biochar, showed some capacitive behavior at high frequencies. In all biochars, some inductive behavior is observed at high frequencies. This inductive behavior has previously been attributed to poor shielding of connections and cables

Table 5.2: Specific comparisons of interest for electrical conductivity of biochars. Two sets of comparisons are shown between different types of lignin pyrolyzed at 1100 °C (Lignin) and between each feedstock pyrolyzed at 1100 °C and 900 °C (Temp.).

	Comparison	Estimated difference [†] (S/cm)	t-statistic	p-value
Lignin	AL1100–DAL1100	-2.81 ± 6.67	-1.2	1
	AL1100–HL1100	-9.35 ± 6.67	-4	0.0021
	DAL1100–HL1100	-6.54 ± 6.67	-2.8	0.0577
Temp.	AL1100–AL900	1.26 ± 6.67	0.54	1
	DAL1100–DAL900	2.02 ± 6.67	0.86	1
	HL1100–HL900	8.12 ± 6.67	3.47	0.0095
	WS1100–WS900	6.94 ± 6.67	2.97	0.0373

[†] Estimated differences represent the difference between the first and second listed biochar, and are reported with Bonferonni-corrected 95% confidence intervals.

used in this experimental setup [141]. The AC electrical behavior observed for all biochars is consistent with results seen for biochar and carbon black in past work [141, 230].

Biochar chemical characterization

The chemical composition of all biochars was measured to explore biochar constituents' role in biochar electrical conductivity. Combustion analysis showed a high percentage of carbon for all biochars, ranging from 60.7% for WS1100 to 92.2% for CELL900. In all lignin-derived biochars, carbon content increases as pyrolysis temperature increases from 900 °C to 1100 °C. HL-derived biochar shows higher carbon content at both 900 °C and

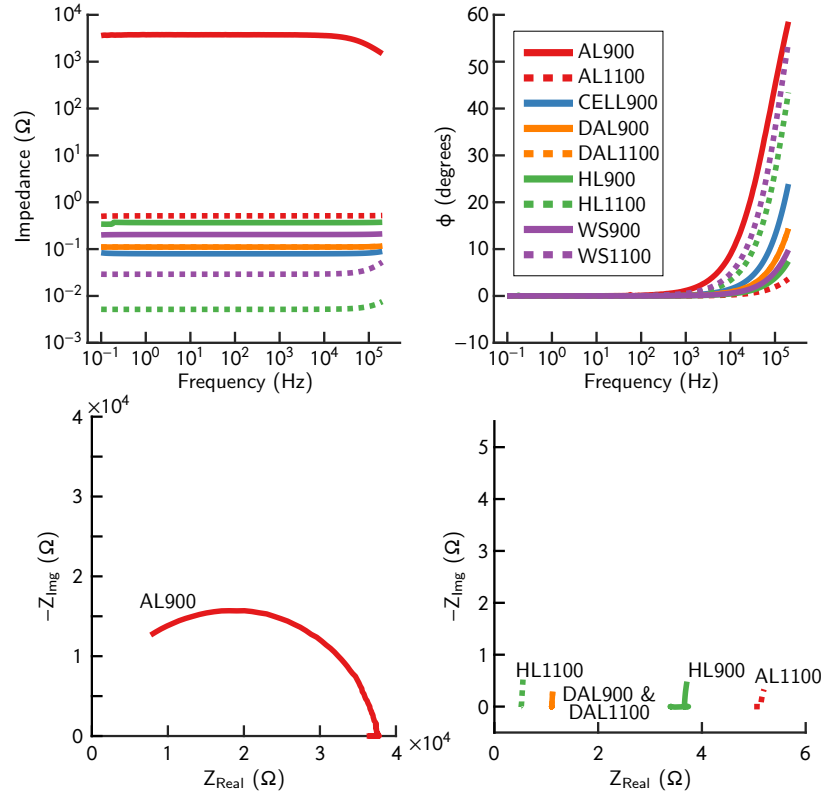


Figure 5.5: (Top) Electrical impedance spectra for each biochar from 0.1 Hz to 200 kHz at the point of maximum compression. A Bode plot of impedance is shown on the left and phase shift (ϕ) on the right. (Bottom) Nyquist plots for electrical impedance spectra for (left) AL900 and (right) AL1100, DAL900, DAL1100, HL900 and HL1100 biochars. The limited imaginary component observed in all biochars except AL900 indicates a largely resistive response, while the semi-circular Nyquist plot of AL900 indicates capacitive behavior. Nyquist plots for WS900, WS1100, and CELL900 biochars are shown in Figure C.2.

1100 °C than AL- or DAL-derived biochar, reaching a carbon content of 83.5% for HL1100. Hydrogen content was low for all biochars relative to their biomass feedstocks [131], with H:C molar ratios for lignin-derived biochars ranging from 0.13 for AL900 to 0.064 for HL1100. Similarly, O:C molar ratios decrease from 0.32 for AL900 to 0.08 for HL1100. All biochars measured in this study show higher hydrogen content at 900 °C than 1100 °C. The loss of hydrogen content with increasing pyrolysis temperature is expected to result in more graphitic biochars with higher pyrolysis temperatures.

Table 5.3: Elemental analysis and ICP-OES results for all biochar. Results for C, H, N and S are an average of two measurements.

Biochar	C [†]	IC ^{††}	H [†]	N [†]	S [†]	Na	Mg	K	Ca	O	H:C	O:C
	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	mol/mol	mol/mol
AL900	64.0	0.79	0.7	0.8	3.0	9.82	0.05	0.15	0.16	21.29	0.13	0.32
AL1100	70.6	0.92	0.6	0.7	3.0	8.07	0.08	0.15	0.20	16.17	0.10	0.21
CELL900	92.2	0.04	0.6	0.0	0.0	0.01	0.01	0.15	0.01	7.09	0.08	0.06
DAL900	65.2	0.92	0.7	0.6	4.8	10.57	0.14	0.15	0.08	17.68	0.13	0.25
DAL1100	69.4	1.04	0.4	0.5	5.5	8.91	0.14	0.15	0.09	15.00	0.07	0.17
HL900	71.5	0.18	0.7	0.7	4.0	6.79	0.01	0.15	0.05	15.88	0.12	0.18
HL1100	83.7	0.20	0.5	0.7	2.5	2.47	0.01	0.21	0.06	9.81	0.06	0.08
WS900	60.8	4.24	1.2	1.0	0.2	0.01	0.44	2.86	0.71	13.57 [‡]	0.23	0.17
WS1100	60.7	4.34	0.7	1.0	0.1	0.13	0.43	3.10	0.77	13.65 [‡]	0.13	0.17

[†] C, H, N and S values are an average of two measurements.

^{††} IC values are calculated from the Mg and Ca ICP-OES data and calculations based on the assumption that they are in the form of carbonates [252, 253].

[‡] WS oxygen content was estimated as described in the Methods.

High quantities of sulfur (S) and sodium (Na) are observed in all lignin-derived biochars. While AL- and DAL-derived biochars were observed to increase in S content with increasing pyrolysis temperature, HL-derived biochar decreased with 4.0% S at 900 °C and 2.5% S at 1100 °C. Na content decreased with rising pyrolysis temperatures for all lignin-derived biochars. Lower quantities of S and Na are observed in non-lignin sourced biochars, with 0% S observed in CELL900, 0.16% S in WS900, and 0.12% S in WS1100 (Table 5.3). Only trace amounts of Mg, K, and Ca are observed in lignin- and cellulose-derived biochars, with higher content in WS-derived biochars. EDX measurements show high quantities of Si in WS-derived biochars, which was not quantified via ICP-OES in this study but was used to estimate oxygen content in WS-derived biochars. Limited inorganic carbon (IC) is expected in these biochars, as IC is primarily present as calcium carbonate or dolomite in biochars and

low quantities of Ca and Mg are observed in all biochars measured in this study [252, 253]. For all of the lignin biochars used in this study, IC is less than 1.5% of the total carbon (TC). Due to their higher Ca and Mg content, WS-derived biochars have higher IC content at around 7% of the TC.

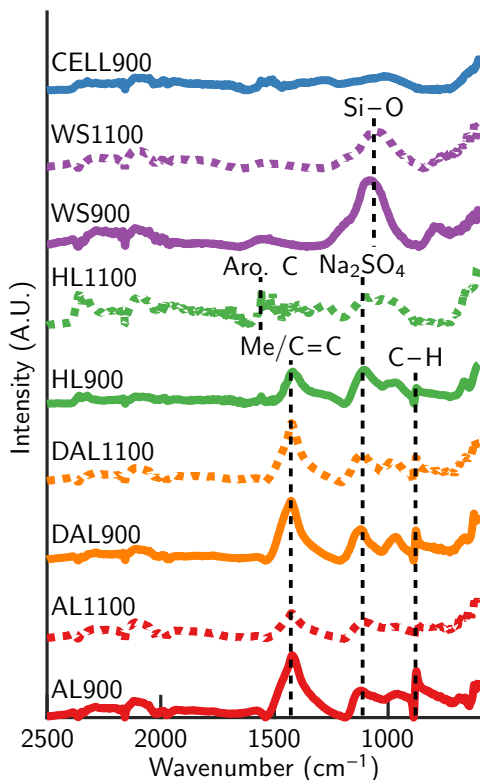


Figure 5.6: Stacked FTIR ATR spectra for all biochars with a baseline correction performed to show the peaks present, uncorrected spectra are shown in Figure C.3. Low-intensity FTIR signals with a baseline shift at low wavenumbers have previously been attributed to aromatic carbon structures [198] and have previously been observed in both lignin-derived biochars and carbon black [114]. The C=C or methoxyl group (Me) peak indicated at 1420 cm^{-1} is associated with the presence of lignin monomers and indicates that the original lignin structure has not fully degraded in AL900, AL1100, DAL900, DAL1100, and HL900. A peak at approximately 1118 cm^{-1} corresponding to Na_2SO_4 or Na_2SO_3 is seen in all lignin-derived biochars, indicating that it does not fully degrade with pyrolysis at 1100 $^{\circ}\text{C}$. No peaks were observed outside of the wavenumber range shown.

In all biochars, ATR FTIR spectra show baseline shifts that have previously been attributed to polyaromatic carbon structures [19, 102, 114, 198] (Figure 5.6). Except for

HL1100, all lignin-derived biochars showed the same primary peaks. The strong peak at approximately 1420 cm^{-1} has previously been attributed to methoxyl groups in lignin monomers [254] or C=C bonds in aromatic rings of lignin monomers [198, 255]. The magnitude of this peak decreased with increasing pyrolysis temperature, indicating a loss of the original lignin structure at higher pyrolysis temperatures. The sharp peak observed at 876 cm^{-1} identifies the presence of C-H bonds associated with aromatic carbon rings [198, 255]. This peak decreased with increasing pyrolysis temperature, a finding consistent with the decrease in H:C molar ratios observed at higher temperatures.

FTIR spectra of all lignin-based biochars indicated the presence of Na_2SO_4 and Na_2SO_3 , as shown by the peak at 1118 cm^{-1} , the weak, broad peak at 2285 cm^{-1} and the overlapping peaks at 620 and 660 cm^{-1} [185, 203, 205] (Figure ATR). Elemental analysis, ICP-OES, and EDX confirm high quantities of both Na and S. As Na_2SO_4 and Na_2SO_3 is used in the kraft lignin isolation process [204, 242], the presence of this band indicates that some Na_2SO_4 or Na_2SO_3 from the lignin isolation process remains after lignin pyrolysis. This finding is supported by past studies of lignin pyrolysis, which have indicated the formation of Na_2SO_3 crystalline regions in lignin-derived biochar [185, 256].

In contrast to AL- and DAL-derived biochars, FTIR spectra show a shift in structure in HL-derived biochars as pyrolysis temperature increases from $900\text{ }^\circ\text{C}$ to $1100\text{ }^\circ\text{C}$ (Figure 5.6, green). The strong peak associated with lignin monomers (1421 cm^{-1}) was reduced, and new peaks were seen at 1558 and 1507 cm^{-1} , which are caused by C=C stretching associated with aromatic carbon, and aromatic skeleton vibrations respectively [99, 198, 204]. This shift in the FTIR spectra indicates that a reordering of the original aromatic lignin structure has occurred between $900\text{ }^\circ\text{C}$ and $1100\text{ }^\circ\text{C}$ in HL-derived biochar. The broad Na_2SO_4 or Na_2SO_3 peak (1118 cm^{-1}) is lower in magnitude than the other lignin-derived biochars. Along with observed decreases in Na and S concentrations, the decreased magnitude of Na_2SO_4 in HL1100 indicates that some of the Na_2SO_4 seen in other lignin biochars has reacted during

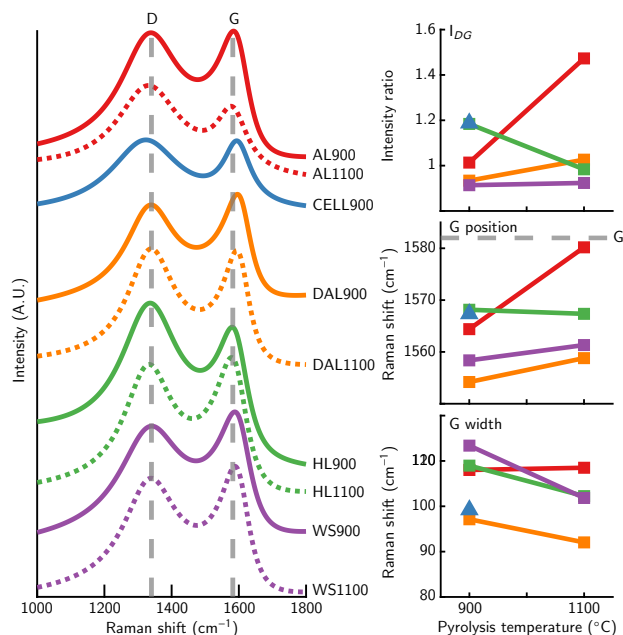


Figure 5.7: (Left) An average of the three replicate fit Raman spectra for all biochars. The representative positions of D (1340 cm^{-1}) and G peaks (1582 cm^{-1}) are shown. Fits are a combination of a Lorentzian peak (D, centered on 1340 cm^{-1}) and a BWF peak (G, centered on 1582 cm^{-1}). Additional Raman spectra replicates, as well as the curve fitting process, are shown in Figure C.4-C.7. (Right) The average difference in the ratio of D and G intensities for each biochar (top), average shift relative to the characteristic position for the G band for each biochar with the characteristic position shown by the grey dashed line (middle), and width of the G band for each biochar (bottom). The line colors for the right figures represent the same feedstocks as in the left figure. Values for D-position, G-position, and I_{DG} ratio are shown in Table C.3.

the pyrolysis of HL1100.

WS900, WS1100, and CELL900 biochars all exhibit few, low absorbance peaks, indicating a largely graphitic structure with few functional groups [19, 257]. The presence of an Si–O peak (1082 cm^{-1}) in WS900 and WS1100 differentiates the infrared spectra of WS-derived biochars from those of other feedstocks [204]. The WS-derived biochars also show a C=C aromatic out of plane bending peak at around 799 cm^{-1} [99] and few additional peaks, indicating a highly graphitic carbon structure.

Raman spectra of all biochar examined show both D and G peaks characteristic of

disordered graphitic carbon. As highly crystalline graphite exhibits very little or no intensity of the D peak, this peak indicates smaller graphitic crystallites and the presence of edge defects or oxygen functional groups on the aromatic carbon structure [19, 114]. The size of graphitic crystallites is inversely related to the ratio of the intensities of the D and G peaks (I_{DG}) [206, 208]. As increasing graphite crystallite size drives electric percolation in non-graphitizing carbons [102], decreasing I_{DG} ratio is expected to lead to an increase in electrical conductivity of the biochar. AL and DAL-derived biochars both increase in I_{DG} ratio with increasing pyrolysis temperature, while HL-derived biochars decrease (Figure 5.7, top right). As decreasing I_{DG} ratio is expected to correlate with increased electrical conductivity, the increase in I_{DG} ratio in AL and DAL as the pyrolysis temperature increases from 900 °C to 1100 °C may contribute in part to their non-significant change in electrical conductivity. In contrast, WS and HL-derived biochars show only a small change and a decrease in I_{DG} ratio respectively as pyrolysis temperature increases from 900 °C to 1100 °C, and both show a statistically significant increase in electrical conductivity.

In addition to changes in intensity, apparent shifts in Raman peak position and width can indicate changes in the graphitic structure. An apparent G peak location below 1582 cm^{-1} is seen in all biochars measured in this study. This peak shift has previously been associated with the presence of amorphous carbon, with increasing amorphous carbon content further decreasing the apparent peak location [206, 258]. Additionally, the increased width of the G peak is associated with the growing presence of bond angle disorder in sp^2 carbons [206]. Except for AL-derived biochar, all biochars measured in this study decrease in G peak width with increasing pyrolysis temperature (Figure 5.7, bottom right). Together, these results indicate that a more ordered polyaromatic carbon structure is formed at higher pyrolysis temperatures in most biochars examined in this study.

Biochars observed in this study primarily show resistive AC behavior, which has previously been associated with graphitic carbon, while capacitive behavior is related to the

presence of amorphous carbon [259]. The limited capacitive behavior observed in biochars in this study indicates that percolation has occurred between low impedance, resistive graphitic carbon regions [19, 102].

Biochar physical structure

The morphological structure of the biochars obtained in this study was examined with FESEM imaging (Figure 5.8). FESEM images show WS900 and WS1100 biochars having larger particle sizes than the lignin or cellulose sourced biochars, with the original fiber structure of these materials maintained. Higher magnification imaging shows WS-derived biochars to have a smoother surface than the lignin- or cellulose-derived biochars.

Table 5.4: Surface area and primary pore size as measured by nitrogen adsorption and average particle size as measured by particle size analysis.

Biochar	Surface area m ² /g	Primary pore size Å	Average particle size µm
AL900	27.0	32.9	13.1
AL1100	21.2	10.9	12.0
CELL900	480.2	8.4	4.9
DAL900	11.5	26.2	14.0
DAL1100	10.7	10.9	15.0
HL900	18.0	10.9	19.1
HL1100	109.1	7.9	5.5
WS900	86.8	11.0	62.0
WS1100	75.9	11.0	130

Particle size measurements supported the FESEM findings; WS-derived biochars exhibited a larger particle size than most lignin-derived biochars (Table 5.4). HL1100 and

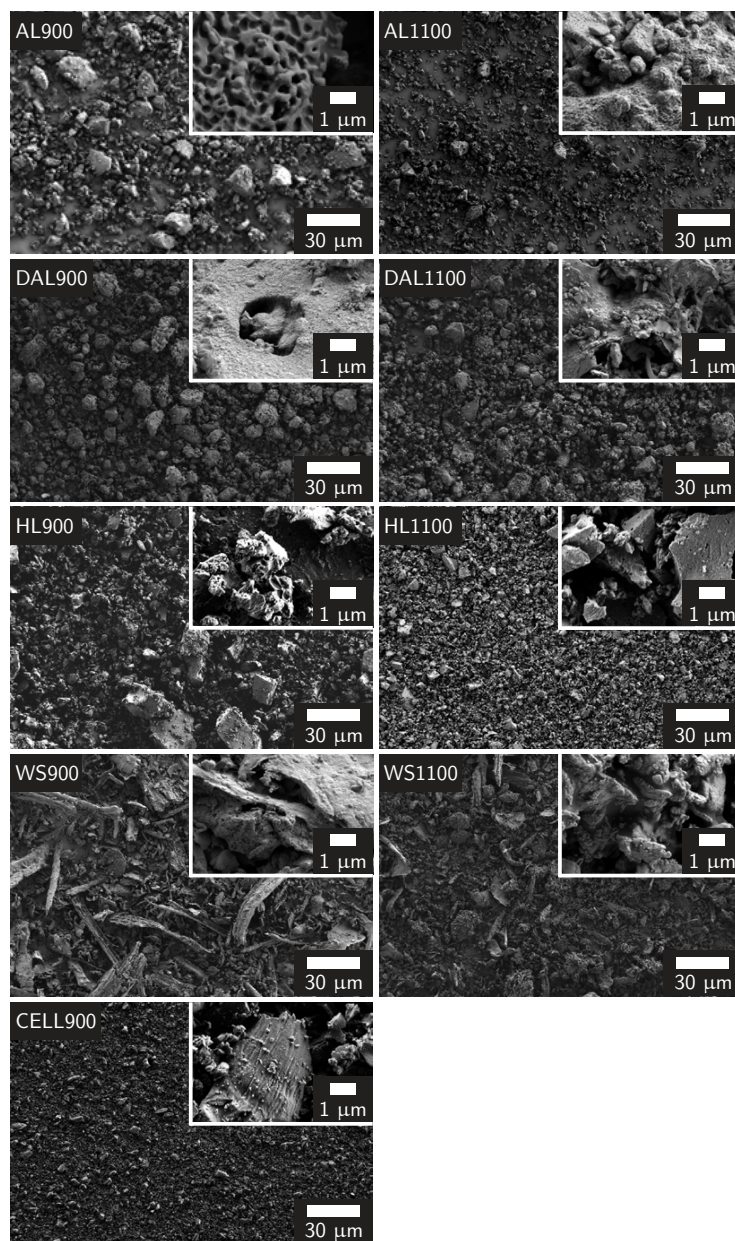


Figure 5.8: FESEM micrographs of biochar produced from all feedstocks and pyrolyzed at 900 °C (left) and 1100 °C (right). Images were acquired at a magnification of 1000 $\times$ for the main image and 25k $\times$ for the inset. Scale bars are 30 μm for the main image and 1 μm for the inset.

CELL900 show average particle sizes of approximately 5 μm . While these two biochars are the smallest size of any measured in this study, their average size is around two orders of

magnitude larger than carbon black [260]. Particle size distributions are shown in Figure C.10. Biochar with smaller particle sizes may be favorable for electrical applications, as electrical percolation thresholds in carbon-filled polymers have been established to decrease with decreasing particle size [261, 262]. Additionally, decreasing particle size is associated with increased mechanical properties of nanofilled composites [263]. Past studies of biochar have examined spray-drying and hydrothermal treatment methods, obtaining biochar particles as small as 21.7 nm [239, 240]. Further ball milling of lignin-derived biochars has shown only minor reductions in particle size [114]. Future work should examine the impact of these treatments on lignin-derived biochar to see if further decreases in particle size can be obtained for these materials.

Biochar surface area was observed to vary by feedstock and pyrolysis temperature. CELL900 has the highest surface area of the biochars produced in this study at 480 m²/g. Except for HL1100, all lignin biochars in this study have surface areas between 10.1 and 27 m²/g. Small decreases in surface area are observed with increasing pyrolysis temperature for AL-, DAL-, and WS-derived biochars. In contrast, HL-derived biochars show an increase in surface area from 18 to 109 m²/g as pyrolysis temperature increases from 900 °C to 1100 °C. Both WS900 and WS1100 biochars show higher surface areas than all lignin biochars except HL1100. Past work has established feedstock lignin content to be inversely correlated with BET surface area in biochar [264]. The results herein support this finding, except for HL1100, providing additional evidence supporting the hypothesis that a shift in structure occurs in HL sourced biochars from 900 °C to 1100 °C, which is not present in the other biochars.

Biochar pore size distributions show that, despite apparent changes in primary pore size in HL1100, only minor changes are seen in pore size distribution (Figure C.8). For most biochars, the smallest pores present in the biochars produced at 1100 °C are not observed in the 900 °C biochars, indicating that changes in porosity between 900 °C and 1100 °C are

due to the formation of pores less than 20 Å in size produced between these temperatures.

In most measurements in this study, HL-derived biochars demonstrate different behavior than AL- or DAL-derived biochars. These differences include meaningfully different FTIR spectra, the highest carbon content, the highest surface area, the lowest O:C and H:C molar ratios, and the lowest content of all metals. In HL-derived biochars I_{DG} ratio decreases as pyrolysis temperature increases from 900 °C to 1100 °C indicating additional graphitization, while AL and DAL-derived biochars show a small increase in I_{DG} ratio with increasing pyrolysis temperature. Additionally, it shows the highest electrical conductivity of any biochar measured in this study. These findings support that a transition in biochar structure has occurred between 900 °C and 1100 °C in HL-derived biochars that benefits electrical conductivity. Between 900 °C and 1100 °C, HL-derived biochar loses the lignin-monomer peaks at 1420 and 876 cm^{-1} seen in HL900 and all other lignin-derived biochars, transitions from 17.97 to 109.1 m^2/g surface area, and loses over half its metal content. In contrast, AL- and DAL-derived biochars decrease in surface area, gain in relative metal content, and show only minor changes in FTIR spectra between these temperatures. This change in HL between 900 °C and 1100 °C does not correspond to a change in TGA slope or any shift in pyrolysis gases released, as measured by TGA-IR. Therefore, we hypothesize that this transition is primarily due to a reordering of the carbon structure of HL between 900 °C and 1100 °C, as indicated by Raman spectroscopy. While the mechanisms behind this shift are not yet fully understood, we hypothesize that shifts in lignin oxygen content, molecular weight, and metal content may be responsible for this shift in pyrolysis behavior.

Relationship between chemical and structural properties of biochar and electrical conductivity

The best fit estimated model determined through a forward, step-wise p-value model selection process, considering O:C molar ratio, H:C molar ratio, inorganic content, particle size (PS), surface area and I_{DG} , is defined as:

$$\sqrt{\hat{\sigma}_{\max,ijk}} = 3.18 - 8.55(\text{O:C}_i) + 3.13(\text{PS}_i^*) + 7.14(\text{PS}_i^*)^2 \quad (5.1)$$

where $\sqrt{\hat{\sigma}_{\max,ijk}}$ is the square root of the mean maximum conductivity of the k th time observation in the j th sample in the i th treatment and PS_i^* relates to the orthogonal polynomial terms for biochar particle size for each treatment i (see Methods and Appendix C for a complete model definition, additionally the full code used to generate this model is available [250]).

Accounting for the random effects sample and time observation and all other respective model terms, strong evidence exists to support a change in the mean $\sqrt{\sigma_{\max}}$ as the O:C molar ratio changes ($t(5)=-4.448$ with an associated $p\text{-value}=0.0067$; standard error (SE) 1.12) and moderate evidence exists to support a change in the mean $\sqrt{\sigma_{\max}}$ as the biochar particle size changes ($t(5)=2.803$ with an associated $p\text{-value}=0.038$; SE 2.5). An effects plot shows a notable decrease in $\sqrt{\sigma_{\max}}$ as the O:C ratio increases. For particle size below approximately 60-70 μm , $\sqrt{\sigma_{\max}}$ decreases as particle size increases. Above 60-70 μm , $\sqrt{\sigma_{\max}}$ begins to increase with increasing particle size (Figure 5.9).

Statistical analyses of the relationship between biochar properties and electrical conductivity were limited by the lack of true replicates for each biochar, as only one batch of material was considered for each treatment. Further, this study was an incomplete factorial design, as CELL1100 produced no biochar. These limitations prevented consideration of interactions during the modeling process. Results may not apply to measurements outside the O:C molar ratio (0.06-0.32) and particle size (4.9-130 μm) observed in this study. Lack of random assignment and random sampling in the experimental design prohibits any causal inference or generalization of results beyond data observed in this study.

The reduction in electrical conductivity with increasing oxygen content observed in this study is strongly supported by past literature. The presence of oxygen in non-graphitizing

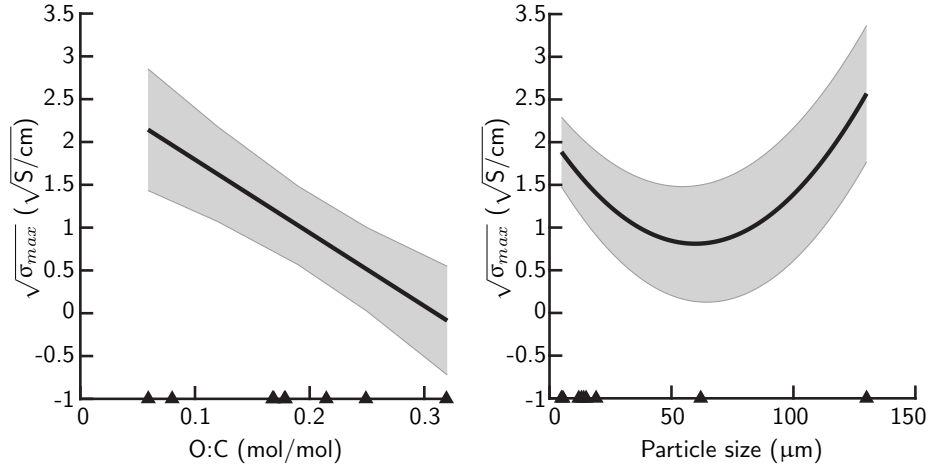


Figure 5.9: Effects plots for the predictor variables O:C ratio (left) and particle size (right). $\blacktriangle$ symbols on the x axis show the position of O:C ratio and particle size observations. Shaded regions represent an estimated 95% confidence interval.

carbons results in distortions in the graphitic structure and increases the presence of sp^3 hybridized carbons. These distortions are expected to reduce the electrical conductivity of the resulting material [102]. Further, the presence of surface oxygen in carbon blacks has been associated with a decrease in electrical conductivity [216]. The model examined in this study does not examine the impacts of inorganic oxygen content, which FTIR spectra show to be present in the form of Na_2SO_4 or Na_2SO_3 in lignin-derived biochars and as Si–O in wheat stem-derived biochar. As these inorganic oxygen groups do not form distortions in the graphitic carbon structure, they are expected to be less impactful on electrical conductivity than organic oxygen. Some factors that are expected to impact electrical conductivity, in particular carbon content and I_{DG} ratio, were not found to be statistically significant in this model. This may be due to oxygen content being a more predictive indicator of both these factors, as increased oxygen content is expected to result in a larger D peak [102] and decreased carbon content.

Past work has shown the electrical conductivity of packed carbon particles to increase with increasing particle size [265]. This increase in electrical conductivity has been attributed

to decreased contact resistance between particles with large particles. In contrast, our results show increases in electrical conductivity at low particle sizes ($< 20\mu\text{m}$) and high particle sizes ($> 100\mu\text{m}$). Both WS900 and WS1100 biochars show oblong geometry rather than the approximately spherical geometry seen in other biochars (Figure 5.8), a broader particle size distribution than was observed in other biochars (Figure C.10), and are the two largest biochars measured in this study. Shifts in particle geometry and particle size distributions are expected to impact particle packing, and electrical conductivity of the packed powder [200, 265]. Particle geometry and particle size distribution were not variables under consideration in this model as they covaried with particle size. As no other biochars show a particle size greater than $20\mu\text{m}$ were examined in this study, examining more biochars of larger particle size would improve understanding of the electrical conductivity behavior of large particle size biochar.

A critical finding of this model is that despite the presence of relatively high quantities of sulfur, alkali metals, and alkaline-earth metals in lignin-derived biochars, inorganic content was not selected in the final, best-fit model. Some studies have proposed the presence of S and Na in lignin-derived biochar as a catalyst for the formation of graphitic regions in lignin-derived biochars [111, 112], while other studies have proposed that the presence of Na inhibits the formation of graphitic regions [113]. Further investigation of the impacts of sodium sulfate and sulfite present on the pyrolysis of lignin is needed to better understand the role they play in lignin pyrolysis.

Lignin-derived biochar measured in this study, and particularly HL1100, show promising electrical conductivity as an alternative to carbon black [141]. This study demonstrates that even in lignin isolated with similar processes, wide variations in electrical conductivity exist in lignin-derived biochars. Therefore, careful selection of lignin feedstocks is needed to produce highly electrically conductive lignin-derived biochar. Based on the results of this study, we hypothesize that reductions in oxygen content of the lignin feedstock may allow

for further optimization of lignin-derived biochar electrical conductivity. This reduction may be achieved by select modification of lignin monomers and linkages to reduce the oxygen content in the feedstock lignin. Optimization of pyrolysis conditions, including maximum temperature, ramp rate, and added catalysts may further reduce oxygen content in lignin-derived biochars. Reduction in oxygen content in lignin-derived biochar will allow for the formation of larger graphitic regions and further improvements in lignin-derived biochar conductivity [19, 102, 146]. Spray-drying methods may achieve further reductions in biochar particle size, with studies examining spray-drying of lignin-derived biochars obtaining particles similar in size to common carbon blacks [239, 240]. We hypothesize that further reductions in biochar particle size may benefit biochar electrical behavior by increasing electrical conductivity and improving percolation behavior in composite materials.

Conclusions

The key finding of this study is that, when controlling for heating rate, catalysts added, and electrical conductivity measurement method, large variations are still seen in the electrical conductivity of biochar produced from lignin feedstocks isolated with similar processes. The wide range of electrical conductivity observed for lignin-derived biochar in this study demonstrates that careful selection of lignin feedstocks is key to producing highly electrically conductive biochar. We demonstrate a maximum conductivity of 18.5 S/cm from a laboratory isolated lignin used as a feedstock for biochar processed at 1100 °C. A shift in biochar structure is seen between pyrolysis temperatures of 900 °C and 1100 °C for HL, the highest electrical conductivity feedstock examined in this study. Further examination of the mechanisms behind this shift may enable the identification of lignin isolation processes to produce highly electrically conductive lignin-derived biochars.

This study found that lignin-derived biochar can obtain a similar range of conductivities to carbon black. Therefore, careful tuning of biochar properties could allow lignin-derived

biochar to fulfill many of the current applications of carbon black. This work highlights the further reduction in oxygen content as an area for potential future improvements in the electrical conductivity of lignin-derived biochar. Careful selection of biomass sources for lignin isolation and lignin isolation processes may reduce biochar oxygen content, potentially allowing for the development of highly electrically conductive biochars for use as a filler material in energy storage applications.

Supporting Information to this Chapter is presented in Appendix C.

PRODUCING MORE GRAPHITIC LIGNIN-DERIVED CARBONS: IMPACTS OF
LIGNIN PROPERTIES ON CARBON STRUCTURE AND ELECTRICAL
CONDUCTIVITY

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Abstract

Lignin is a promising renewable alternative to fossil fuels for the production of carbon materials such as carbon fibers, activated carbons, or carbon blacks. Despite extensive research, lignin-derived carbon materials show limited graphitization relative to comparable petroleum-derived carbons. Further, lignin-derived materials show high variation in graphitization and electrical conductivity depending on the source of the lignin. Herein, nine lignins with various feedstocks and isolation procedures are pyrolyzed to produce biocarbons at 1100 °C. The properties of the lignin and resulting biocarbon are thoroughly characterized and show a range of chemical compositions, structures, and particle sizes. As a result, the pyrolysis behavior of these lignins varies, with powdered, clumped powder, and "foam" biochar morphologies resulting from finely powdered lignin. The resulting biochar varies over two orders of magnitude in electrical conductivity, from 0.19 to 19 S/cm. No statistically significant relationship is identified between lignin properties and biochar electrical conductivity for a broad set of lignin. However, when sodium sulfate is removed from lignin, a significant decrease in electrical conductivity is identified. This decrease in electrical conductivity is accompanied by an increase in graphitic crystallite size. Based on this finding, a relationship between biochar graphitic crystallite size and electrical is proposed that builds on established quasi-percolation models for biochar electrical conductivity.

Introduction

Developing renewable alternatives to petroleum-derived materials is critical to reducing our society's reliance on fossil fuels. Of particular interest are carbonaceous petroleum-derived carbon materials, such as carbon black, carbon fibers, and artificial graphite, whose application is expected to grow rapidly in the coming decades, along with the growth of energy storage and lighter-weight materials. Currently, these materials are highly dependent

on petroleum for their production. Lignin looks to be a promising alternative feedstock to petroleum due to its high aromatic carbon content [130]. Further, 50-100 tons of lignin are isolated annually as a byproduct of paper making and biorefinery industries, 98% of which are currently combusted for energy [266]. This waste stream is anticipated to grow as cellulosic biorefineries continue to expand in the coming decade [127]. However, economic factors primarily limit upcycling of lignin waste streams [137]. As carbon materials are considered some of the most valuable products of lignin upcycling [138], the development of simple processes to convert this lignin to renewable carbon materials has the potential to both reduce reliance on petroleum products and to upcycle this important waste stream.

Lignin-derived carbon materials have been extensively studied [130, 132, 168, 267]. These materials have a graphitic carbon structure, porous morphology, and high electrical conductivity, all important characteristics to replicate the performance of petroleum-derived carbon materials. These materials can be broadly categorized into carbon fibers, activated carbons, and biochars or biocarbons. Lignin-derived carbon fibers have been extensively explored as a renewable alternative to polyacrylonitrile (PAN)-derived carbon fibers [132, 267]. Despite extensive research, lignin-derived carbon fibers show more limited graphitization than PAN-derived carbon fibers, leading to reduced strength and modulus values [132, 267]. Lignin-derived biochars and biocarbons have been examined for a broad set of applications, including electrically-conductive plastic additives, replacements for carbon black, and active materials in battery electrodes [95, 114, 119]. Physical (e.g., with CO_2 or H_2O) or chemical activation (e.g., with KOH) processes can be applied to these biochars to produce high surface area activated carbons. The resulting material has a highly porous physical structure (as high as $2000 \text{ m}^2/\text{g}$) [168]. These lignin-derived activated carbons have been examined in a broad set of applications, including for environmental remediation, as catalysts, and energy storage [168, 268, 269]. Like lignin-derived carbon fibers, both lignin-derived biochars and activated carbons are limited by low graphitization, resulting in

low electrical conductivity. Further, a large range of electrical conductivity is observed for biochars graphitized at above 900 °C, from 0.009 S/cm to 62.96 S/cm for lignins isolated with different processes [143, 270]. Drawing conclusions of the cause of this high variation in electrical conductivity between studies is further complicated by the lack of standardization of electrical conductivity measurement methods for powders, which results in high variation for electrical conductivity measurements of the same carbon powder between studies [141].

These past studies point to lignin as a promising feedstock for various carbon materials; however, its performance is consistently limited by lower graphitization than petroleum-derived carbon materials. Further, wide ranges of electrical conductivity and graphitization have been reported for carbons derived from lignins isolated with different processes. Since graphitization of lignin-derived carbons does not continue to increase above pyrolysis temperatures of approximately 1000 °C, graphitization cannot typically be increased with higher carbonization temperatures [19, 102, 132]. Lignin molecular weight, inorganic content, and particle size have been identified as critical factors that influence the graphitization of lignin during pyrolysis [119, 132, 143]. Further, some studies have found interactions between inorganic compounds present in the as-isolated lignin (i.e., sodium sulfate) and common transition metal catalysts such as iron [119]. These catalysts can be applied to increase the graphitization of lignin, and a more robust understanding of these interactions is key to understanding how this critical lignin waste stream can be upcycled.

In this study, we investigate the role of different lignin isolation procedures, parameters, and feedstocks in the resulting graphitization of lignin-derived biochar. Nine different lignins are characterized for chemical structure, molecular weight, and thermal transitions. These lignins are then pyrolyzed to form biochar at 1100 °C, and the morphology, chemical composition, graphitization, and electrical conductivity of these biochars are investigated. First, the relationship between lignin processing and biochar graphitization is examined. We hypothesize that lignin oxygen content will significantly affect biochar graphitization and

electrical conductivity. Next, the interaction between sodium sulfate (Na_2SO_4) in lignin and a commonly applied catalyst, iron, is investigated. We hypothesize that the presence of Na_2SO_4 in lignin will increase biochar graphitization without an iron catalyst. However, past studies have identified Na_2SO_4 as inhibiting the catalytic effect of iron [119], therefore we hypothesize that in the presence of Na_2SO_4 limited impact will be observed. This work sheds light on the industrial sources of lignin that are most appropriate for converting lignin into highly graphitic carbon materials. Further, the role that the addition of catalysts and interactions between inherent inorganic materials and external catalysts play in this process to better inform how this important waste stream can be upcycled into renewable and high-performance carbon materials.

Materials and Methods

Lignin sourcing

Three commercial lignins were obtained: TCI alkaline lignin (product # L0082) and dealkaline lignin (product # L0045) and Sigma-Aldrich alkali lignin (product # 370959). In addition, six lignins were isolated for this study from a variety of biomass precursors with a variety of separation processes. These lignins vary in feedstock, isolation process, and isolation parameters (Table 6.1).

A95, AP, AC, A115, and A145 lignin were isolated via an alkali process, with the parameters listed in Table 6.2. Biomass was placed in a NaOH solution and heated in a Regmed AU/E-20 Laboratory Digester with TP-2027 lid, and held at temperature. The reactor was then cooled to room temperature, rinsed with DI water, and the remaining wood chips were pressed to recover the dissolved lignin. Sulfuric acid was then added to the lignin solution until the pH of the solution was <2 , and cooled at $4\text{ }^\circ\text{C}$ for 12 hr. Finally, this solution was centrifuged at $4\text{ }^\circ\text{C}$ and 8000 rpm to separate the isolated lignin, and the lignin was air dried at room temperature for 96 hours. Prior to drying additional 1:5 ratio

Table 6.1: Summary of lignin isolation methods and molecular weights. Listed temperatures are maximum processing temperatures.

Abbreviation	Feedstock	Process type	Temperature (°C)	Molecular weight (Da)	PDI (Mw/Mn)
TA	Wood	Commercial, Ligno-sulphonate	Unk.	60000 [271]	
TD	Wood	Commercial, Ligno-sulphonate	Unk.	60000 [271, 272]	
SA	Softwood	Commercial, Kraft	Unk.	28000 [272]	5.6 [272]
AC	Corn stover	Alkali	140		
AP	Poplar	Alkali	140		
A95	Poplar	Alkali	95	43100 [220]	5.34 [220]
HC	Corn stover	Hydrolysis	150	10031.5	2.43
A115	Poplar	Alkali	115	8675	2.51
A145	Poplar	Alkali	145	8443	2.65

Table 6.2: Parameters for isolation of Alkali lignins.

	NaOH loading	l:s ratio	t (hr)	T (°C)	initial mass (kg)
A95	13%	10:1	1	95	1.5
AP	18%	5:1	3	150	3
AC	13%	9:1	0.5	140	2
A115	10%	10:1	1	115	0.15
A145	15%	10:1	1	145	0.15

DI washing and centrifuging steps were applied to AP, AC, A115, and A145.

HCS lignin was isolated using a three step process. Corn stover was subjected to dilute acid pretreatment followed by enzymatic hydrolysis, and finally underwent a NaOH

purification. Pretreatment was conducted using dilute sulfuric acid solution with an initial pH of 1.25 at a 20% solid ratio (wt. dry corn stover/liquid volume). Samples were heated to 150 °C in a Regmed AU/E-20 Laboratory Digester, held for 1 hr, then rinsed with DI water and dried at 50 °C. Next, enzymatic hydrolysis was performed on 1:10 biomass:liquid solution of 25 mg protein/g glucan enzyme loading. The solution was heated to 50 °C for 72 hr, periodically stirred for the first 24 hr, and the pH was periodically adjusted to pH 5.0. Following hydrolysis, the lignin cake was washed four times in 1 L DI water in a centrifuge at 8000 rpm, and dried at 50 °C for 48 hr. Finally, the lignin was extracted in a 1:5 solid:liquid ratio solution of 1 M NaOH. This solution was placed in the digester at 85 °C for 1 hr, and the solution was pressed to separate, the pH was adjusted to pH <2 with H₂SO₄ to precipitate lignin, and the solution was centrifuged to separate lignin and rinsed with DI water.

To examine the impact of particle size, different treatments to reduce lignin particle size prior to pyrolysis are used. The commercial lignins (TA, TD, and SA) are pyrolyzed as provided. BL, AC, and A115 were ball milled (Retsch Mixer Mill 400) for 3 min at 30 Hz (1800 rpm). A115, AP, and TA were ground with a pestle and mortar for 3 min.

Biochar production

All nine lignins were converted to biochar via pyrolysis in a tube furnace. Prior to pyrolysis, all lignins were stored in a drying oven at 105 °C for at least 24 h to reduce moisture content. Approximately 500 mg of lignin was placed in an alumina boat (100 mm × 20 mm × 13 mm) within the tube furnace (Lindberg/Blue M Mini Mite) fitted with an alumina tube. The tube furnace was purged with nitrogen at 100 mL min⁻¹ for 10 min prior to heating. During heating, nitrogen was flowed at 30 mL min⁻¹, and the lignin was heated at 10 °C/min from room temperature to 1100 °C, held for 1 hr, and then allowed to cool to room temperature. After pyrolysis, biochar was ball milled (Retsch Mixer Mill 400) for

3 min at 30 Hz (1800 rpm). Biochar was stored in a drying oven at 105 °C until analysis. A single batch of biochar was produced for each lignin type. To determine pyrolysis yield, samples were weighed both before and after pyrolysis.

Catalyzed biochar production

As a secondary experiment, the impact of metals inherent in the biochar and their interaction with the transition metal catalyst iron was examined. To this end, the A95 lignin was triple washed and centrifuged in 1:50 DI water to remove Na_2SO_4 following established procedures [273]. Biochars were then prepared with this lignin with and without 30 wt.% iron catalyst, and compared against unwashed A95 biochar with and without an iron catalyst. After pyrolysis, this biochar was washed with 37% HCl at a 1:25 biochar to solution ratio to removed the catalyst. The electrical conductivity of these biochars were then compared to determine the impact of the catalyst and the interaction between the catalyst and the Na_2SO_4 present in the biochar and the carbon structure was analyzed with Raman spectroscopy and XRD.

Lignin and biochar characterization

Biochars from the two TCI lignins were produced and characterized in previous work [143]. Production yields, and mass percentages of C, H, N, S, Na, Ca, Mg, K, and O for those biochars are adapted from that study and were measured with the same parameters described herein.

Biochar pyrolysis conditions were simulated in a therogravimetric analyzer (TGA, TA Instruments Q8000IR) to examine the weight loss as a function of temperature. Approximately 5 mg of each lignin was placed in a HT-platinum TGA pan and heated from 30 °C to 1000 °C at a rate of 10 °C/min under a 30 mL/min flow of nitrogen gas. Lignin thermal transitions at low temperatures were examined with differential scanning calorimetry (DSC, TA Instruments Discovery 2500). For DSC, approximately 5 mg of each

lignin was placed in a TZero DSC pan and heated from 30 °C to 400 °C.

Atomic species present in biochar were examined with energy dispersive x-ray spectroscopy (EDX) on a Oxford Ultim Max EDX detector on a Zeiss SUPRA 55VP field emission scanning electron microscope (FESEM). Based on the EDX findings, C, H, N, S, Na, Mg, Ca, and K were selected for quantified analysis. The C, H, N, and S content of all lignins and biochars were characterized with combustion analysis by Atlantic Microlab Inc. (Norcross, Georgia, USA). Lignin and biochar Na, Mg, Ca, and K content was characterized with inductively coupled plasma optical emission spectrometry (ICP-OES). Biochar and lignin samples were digested in trace metal grade HNO_3 (Fisher Scientific, product #A509P500, Pittsburgh, PA USA) on a Mars6 iWave digester at 220 °C with a ramp time of 15 min, a hold time of 15 min, and under 800 psi of pressure. Digested samples and cation standards were run in a matrix of 2% HNO_3 on a SpectroBlue ICP-OES in axial view mode (high sensitivity). Oxygen content was then calculated as the remaining mass not accounted for by combustion analysis or ICP-OES.

The chemical structure of all lignins and biochars were examined with Fourier-transform infrared spectroscopy (FTIR) and x-ray diffractometry (XRD), and biochar was additionally characterized with Raman spectroscopy. FTIR measurements were performed on a ThermoFisher Nicolet iS50 FTIR spectrometer with a Smart iTX attuned total reflectance (ATR) accessory with a diamond crystal. Spectra were collected from wavenumbers of 600-4000 cm^{-1} , at a resolution of 4 cm^{-1} , with 64 scans per sample. XRD of all lignins and biochars was performed on a Bruker D8 Advance powder X-ray diffractometer with $\text{K}\alpha_{1,2}$ radiation, from 2θ values of 10-70° with a step size of 0.02°. Raman spectra were measured on a Horiba LabRam HR Evolution spectrometer with a 50× long-working distance objective and a frequency-doubled Nd:YAG laser (wavelength of 532 nm) at a power of 1 mW. Carbon D and G peaks were deconvoluted as previously described [206, 207].

Lignin particle size was measured on a Malvern Mastersizer 2000 laser particle size

analyzer with water as dispersant at the assumption of spherical particles. Prior to measurement, all samples except TA and TD were placed in DI water and sonicated for 5 min to disperse lignin particles. TA and TD were found to be water soluble, and were placed directly into the particle size analyzer to limit dissolution. Biochar and lignin morphology was examined on a Zeiss SUPRA 55VP field emission scanning electron microscope (SEM) with an EHT of 20 kV and a working distance of approximately 8.2 mm.

Biochar electrical conductivity was measured on 100 mg of biochar with a compressive guard electrode setup, as described in previous work [141]. DC resistance measurements were taken on a Keithly 2540 Sourcemeter from the point of first contact between the electrode and the biochar until no more pressure could be applied. Biochar packing fractions were calculated with the assumption of a skeletal density of 2 g/cm³ for all biochars.

Data analysis

All statistical analyses were performed in Minitab (vers. 19.2020.1, Minitab LLC, State College, PA, USA), with a critical alpha set *a priori* to 0.05. Trends in shifts on the biochar elemental content with lignin elemental content were analyzed with a linear regression, with lignin elemental content as the predictor variable, and biochar elemental content as the response variable. Impacts of lignin properties on biochar electrical conductivity were analyzed with a forward selection regression model. The alpha value for inclusion in the model was set *a priori* to 0.25.

Results and Discussion

Lignin characterization

The lignins examined show a range of weight percentages of atomic species present (Figure 6.5). Carbon is the most abundant element in all lignins, ranging from 46.7 wt.% in TA to 61.7 wt.% in AP. Additionally, all lignins show high oxygen (31.5-43.4 wt.%) and

hydrogen (3.3-6.3 wt.%) content. Lignin inorganic content varies by isolation method. All commercial lignins (SA, TA, and TD), and unwashed alkali lignins (A95) show the presence of sulfur (2.93-5.22 wt.%) and sodium (0.7-1.8 wt.%). In contrast, all other lignins show limited sulfur content (0-0.31 wt.%), and sodium content (0.02-0.19 wt.%). Mg, Ca, and K are present in limited quantities in all lignins (<0.1 wt. %). As a result of the different methods used to reduce lignin particle size, lignins show a range of median particle sizes (8.36-375 μm) and particle size distributions. The three commercial lignins (TA, TD, and SA) all show median particle sizes of approximately 100 μm . Despite their observed water solubility, median particle size values from laser particle scattering for TA and TD are in good agreement with values observed in SEM images, however TA shows large particles not present in other lignins or observed via SEM, which are attributed to agglomeration. All ball milled lignins (A145, HC, and AC) show lower particle sizes than other processing methods at 8-34 μm . Lignins that were ground with a pestle and mortar (AP, A115, and A95) were found to have the highest particle sizes between 160 and 375 μm . Ball milled and commercial biochars show narrower particle size distributions than ground samples. This range of average particle sizes allows for the testing of particle size as a variable that has previously been identified as a key factor impacting biochar electrical conductivity.

FTIR spectra were used to broadly categorize the lignins by their dominant monomer (Figure 6.1a). AL, TD, HL, VWC, D115, D145, HF, and HS show a stronger response for peaks associated with syringyl monomers at 1113 and 1323 cm^{-1} , while SA and VCS show a stronger response in peaks associated with guaiacyl monomers at 1032 and 1323 cm^{-1} [274]. Different lignin isolation procedures have limited impacts on monomer ratios, with no change in primary monomer observed in any groups of lignins from the same feedstock. The presence of hemicellulose contaminants can be observed via the weak peak at 1085 cm^{-1} which corresponds to C-O-C bonds in xylan [131], as a distinct peak in SA and AC, a shoulder in A115, A145, and HC. These contaminants are also potentially observed as peak

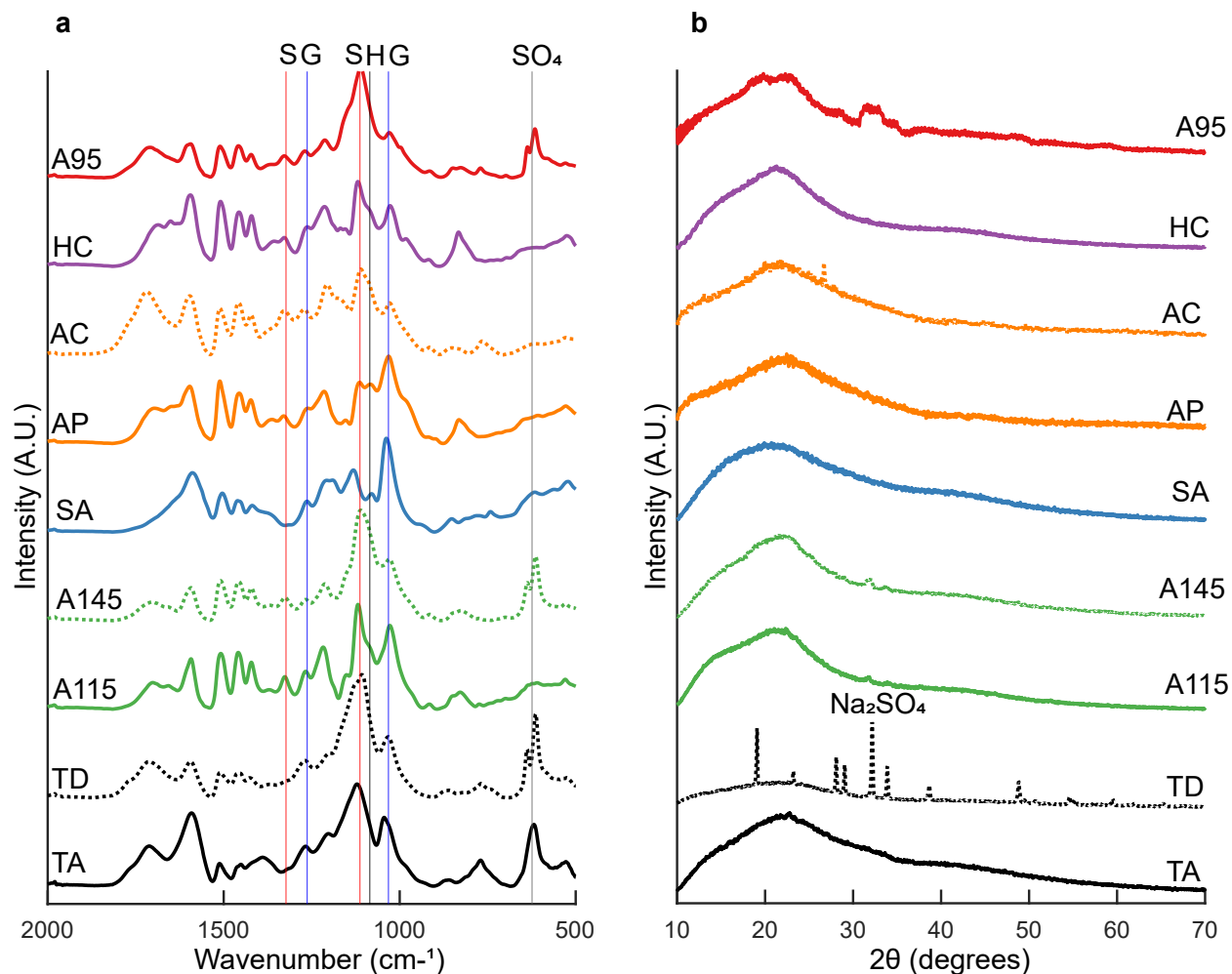


Figure 6.1: (a) FTIR spectra of all nine lignins from 2000-500 cm^{-1} . S labels indicate peaks associated with syringyl monomers, G with guaiacyl monomers, H with hemicellulose contaminants, and SO_4 with sulfate. (b) XRD patterns for all lignins. All crystalline peaks present in TD are attributed to Na_2SO_4 .

broadening in AP, HL, TD, and TA. While the primary Na_2SO_4 peak (1112 cm^{-1}) overlaps with the primary syringyl peak, the presence of Na_2SO_4 can be identified by the secondary SO_4 peak at 627 cm^{-1} [275], present as a strong peak in TA, TD, HL, and A145, with weak peaks present in SA, A115, and AC. This finding is supported by the relative concentrations of Na in these lignins, with high concentrations of Na present in TA, TD, and HL. SA and AC which show stronger guaiacyl peaks are isolated from spruce and corn respectively, rather

than the hardwood feedstocks used for the other lignins [276, 277].

XRD patterns of the lignin show a mostly amorphous structure, with crystalline Na_2SO_4 [275] present in some lignins (Figure 6.1b). Most prominently, TD shows a strong crystalline response that is attributed to Na_2SO_4 , with weaker Na_2SO_4 patterns observed in HL, A115 and A145. Despite high levels of Na and S and FTIR peaks attributed to SO_4 TA does not show a crystalline Na_2SO_4 response in XRD, indicating the presence of amorphous sodium sulfate.

Combined, XRD, FTIR, and chemical composition of lignin indicate that most sodium and sulfur are present in the form of Na_2SO_4 . Therefore, a portion of the oxygen present in lignin is in this inorganic form. Assuming all sodium is in the form of Na_2SO_4 , the amount of lignin oxygen present in the inorganic form ranges from 2.6 wt.% for TA to 0.03 wt.% for AP. In some biochars surplus sulfur is present relative to the amount of Na, for all sulfur to be in the form Na_2SO_4 . This excess amount ranges from 1.9 wt.% for TD (out of 5.2 wt.% total sulfur) to 0.03 wt.% for AP (out of 0.08 wt.% total sulfur). This sulfur is assumed to be present as organic sulfur in the lignin polymeric structure [273]. Additionally, in some biochars (TA, SA, A115, and HC) excess sodium is present for all sodium to form Na_2SO_4 . This sodium may be in other inorganic forms, such as sodium carbonate, at levels that were not detected via XRD or FTIR. The range of organic elemental composition, amount of Na_2SO_4 present, non-lignin contaminants, and dominant lignin monomers present in these lignins allow for how these properties impact the properties of the resulting biochar to be examined.

Lignin thermal transitions and biochar morphology

DSC curves of lignin show two distinct patterns of behavior (Figure 6.2). The hydrolysis lignin and pretreated alkali lignins (HC, A145, and A115) show strong, broad glass transitions at 110 °C. In contrast, the commercial lignins (TA, TD, and SA), and two of the alkali

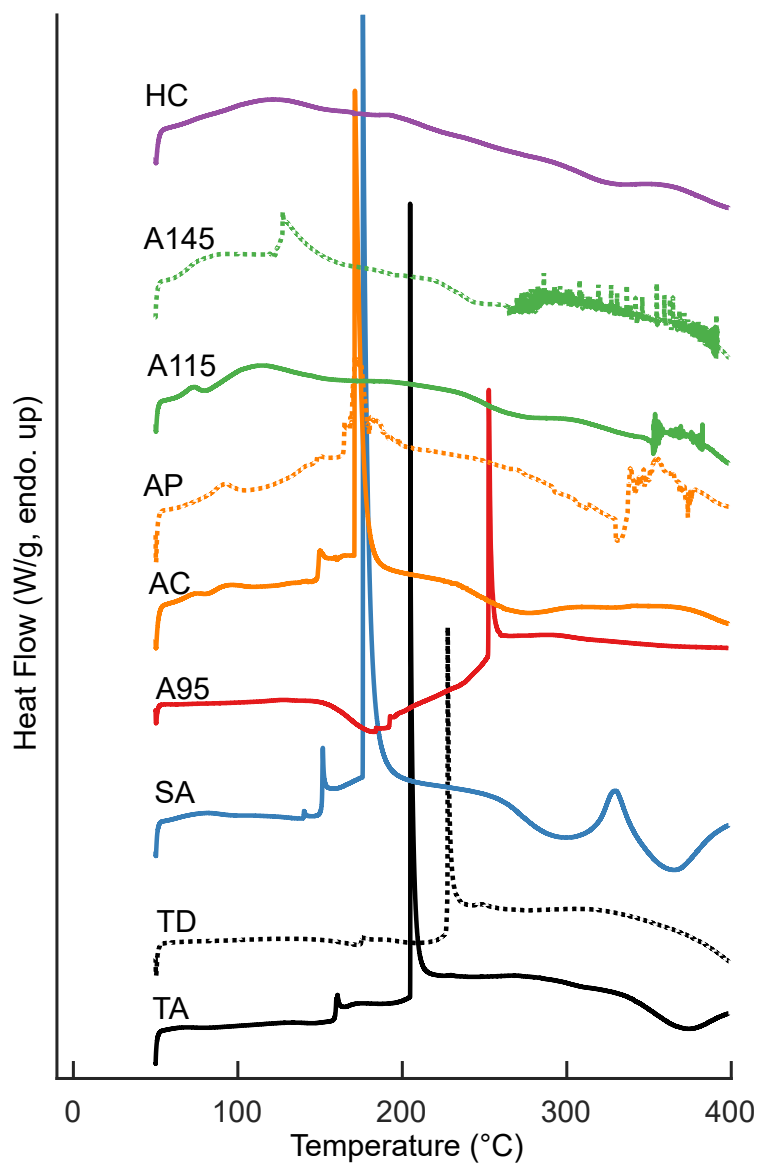


Figure 6.2: DSC curves of all nine lignins, presented endothermic up.

extraction lignins (HL and CS) show sharp, weak glass transitions at approximately 150 °C, or no transition at all. Above this second glass transition, lignins that are high in Na_2SO_4 (as identified by elemental composition, FTIR, and XRD) show a sharp transition that is attributed to a polymorphic transition in Na_2SO_4 [278]. Finally, at high temperatures a lignin softening transition is observed for all biochars [279, 280]. This transition occurs at a

lower temperature (118-200 °C) for hydrolysis lignins than for alkali or Kraft lignins (236-336 °C). In some lignins (A115, A145, AP), the onset of thermal degradation during pyrolysis can be observed as noise at temperatures above 300 °C.

As a result of these differences in lignin thermal behavior, the structure of the biochar post-pyrolysis varies greatly depending on lignin-feedstock (Figure 6.3). In the three commercial lignins (TA, TD, and SA), a powdered structure is observed. In AC, AP, and HC, a clumped particle structure is observed. In contrast, in A95, and A115, A145, a "carbon foam" structure is observed (Figure 6.2.) Optical microscopy and SEM reveal that this "carbon foam" structure does not show distinctions between individual particles, and appears as a single continuous material (Figure 6.3). We hypothesize that this difference in behavior is related to thermal transitions in the lignin. In TA, TD, SA, AP, and AC DSC curves show weak or no glass transition, while AC, A115, A145, and HC all show strong glass transitions. Depending on the strength of these transitions, the structure of the resulting biochar shifts from a powder similar in size to the original lignins to a continuous material. These materials were qualitatively observed to vary in mechanical strength, with biochars that formed a clumped particle structure requiring more force to break prior to ball milling than biochar with a "carbon foam" structure. Notably, all commercial lignins (SA, TA, and TD) and only commercial lignins retain their original particle structure after pyrolysis.

Importantly, past studies have found that particle size may play an important role in graphitization of lignin during pyrolysis [132, 143]. Based on the softening transitions observed and the resulting biochar morphology, we hypothesize that in lignins with a strong softening transition, particle size plays a limited role in resulting graphitization, as this size will have been lost prior to most pyrolysis reactions. Particle size does not appear to play an important role in this transition, as lignins with large differences in size (such as A115 at 19 μm and A145 at 375 μm) have these same thermal transitions and form similar structures. Particle size may still play an important role in pyrolysis of lignins with a weak softening

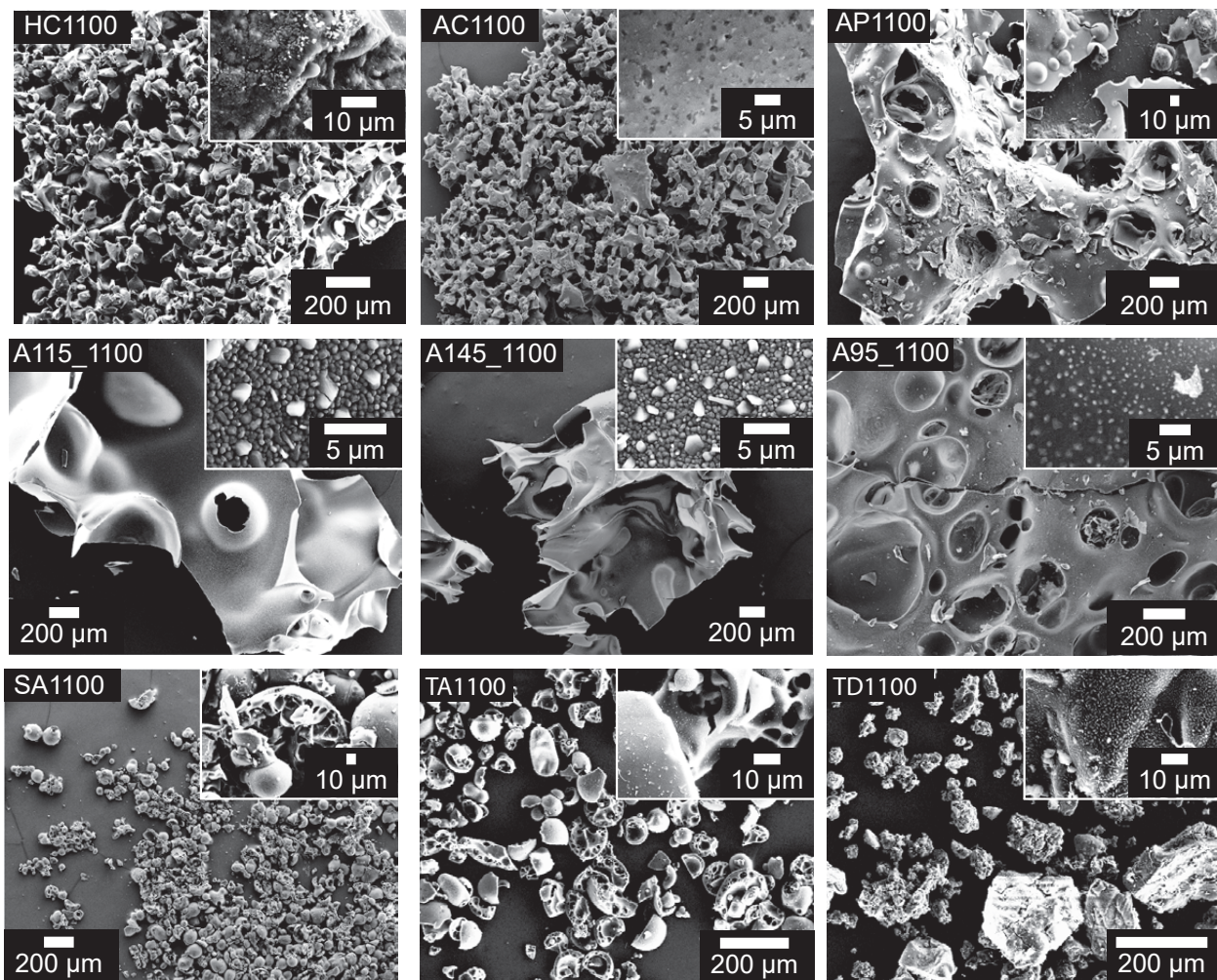


Figure 6.3: SEM micrographs of biochars produced from all lignins. Main images are at 50-250 $\times$ magnification to highlight macroscale features, while insets are at 1000-3000 $\times$ magnification to highlight microscale features.

transition (such as TA, TD, and SA). This softening transition of lignin has previously been identified as a key limiting factor for fast pyrolysis of lignin, which optimizes for biofuel production. Above this transition, softening of lignin results in clogging of continuous fast pyrolysis reactors such as fluid beds or augers [281, 282]. Therefore, slow pyrolysis, batch pyrolysis methods with a focus on development of high-value carbon materials may help to mitigate this issue.

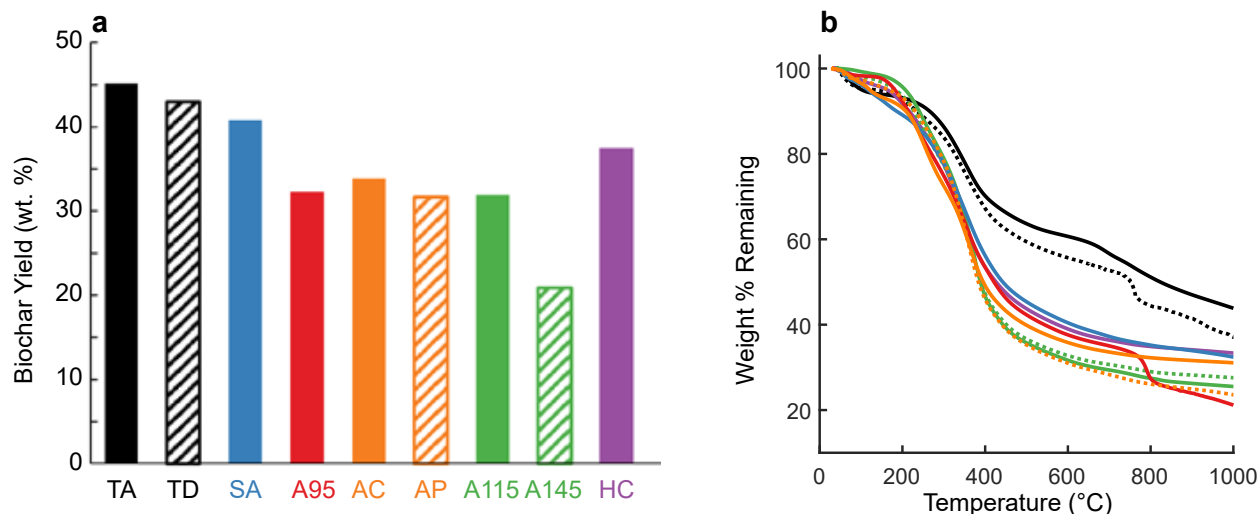


Figure 6.4: (a) Pyrolysis yield for each lignin. (b) TGA curves for each lignin under heating rates replicating tube furnace pyrolysis. Line colors and textures match to labels in (a).

Biochar characterization

Biochar yield varied between 21 and 45 wt.%, depending on lignin feedstock (Figure 6.4a). Typically, lignins with higher sodium content (TA, TD, SA, and A95) resulted in higher biochar yields, which is attributed to the lack of reaction of Na_2SO_4 during pyrolysis. In biochars that formed a "carbon foam" structure, the biochar had expanded out of the alumina boat used, and therefore some biochar was lost during pyrolysis. The reactions responsible for these pyrolysis yields were examined with TGA, with final masses found to generally be in agreement with trends in biochar production yields (Figure 6.4b). At low temperatures (30-110 °C) all lignins show small mass losses (0.9-5.3%) associated with moisture evaporation. At high temperatures, two distinct pyrolysis behaviors are observed - with the two TCI lignins (TA, TD) and the unwashed alkali lignin (HL) all showing degradation in the 600-800 °C region, while other lignins show only minor mass loss in this region. This mass loss is associated with degradation of ether linkages into CO and CO_2 [87].

The carbon, oxygen, sodium, and sulfur content in the biochar is found to be

significantly impacted by the concentration of that element present in lignin ($p < 0.05$, Figure 6.5). Carbon shows a consistent gain of approximately 25 wt.% with pyrolysis. This shift is independent of starting lignin carbon content. Only SA shows a meaningful variation from this trend, gaining approximately 35% carbon. Due to limited evidence for formation of carbon containing inorganic compounds, this carbon is assumed to be entirely organic. Similarly, biochar oxygen content increases with increasing lignin oxygen content, however at a slower rate than carbon, with approximately 44% of the lignin oxygen remaining after pyrolysis on average. Lignin hydrogen content was not found to have a significant impact on biochar hydrogen content ($p = 0.65$). All biochars showed hydrogen content of approximately 0.5 wt.%, while lignin hydrogen content varied from 3.3-6.3 wt.%. This similar hydrogen content indicates that in these biochars, H/C atomic ratios, and therefore inferred graphene structure diameters [283], are driven primarily by carbon content.

All biochars showed low (< 0.1 wt.%) concentrations of Mg, Ca, and K. In contrast, biochars from Kraft and alkali processes without washing steps (TA, TD, AP, and SA) show high concentrations of Na and S. These concentrations are found to be typically significantly higher than the concentration of sodium or sulfur in the lignin feedstock ($p < 0.01$ and < 0.05 respectively). In the case of sodium, this increase in concentration ($3.2\times$), roughly matches the change in mass (average yield of 35%, Figure 6.4), indicating that minimal sodium has reacted off during pyrolysis. Molar ratios of sodium to sulfur show differing shifts, depending on the lignin feedstock. Based on XRD and FTIR spectra of both lignin and biochar, sodium present is assumed to remain as Na_2SO_4 following pyrolysis, as also identified in previous studies of both lignin and lignin-derived biochars [143].

All biochars show sigmoidal electrical percolation behavior as they are compressed (Figure 6.6). At low compressions, all biochars show highly resistive behavior, as the unpacked powder is dominated by the non-conductive air, at around a packing fraction of 0.25 the percolation threshold is reached, and electrical conductivity rapidly increases.

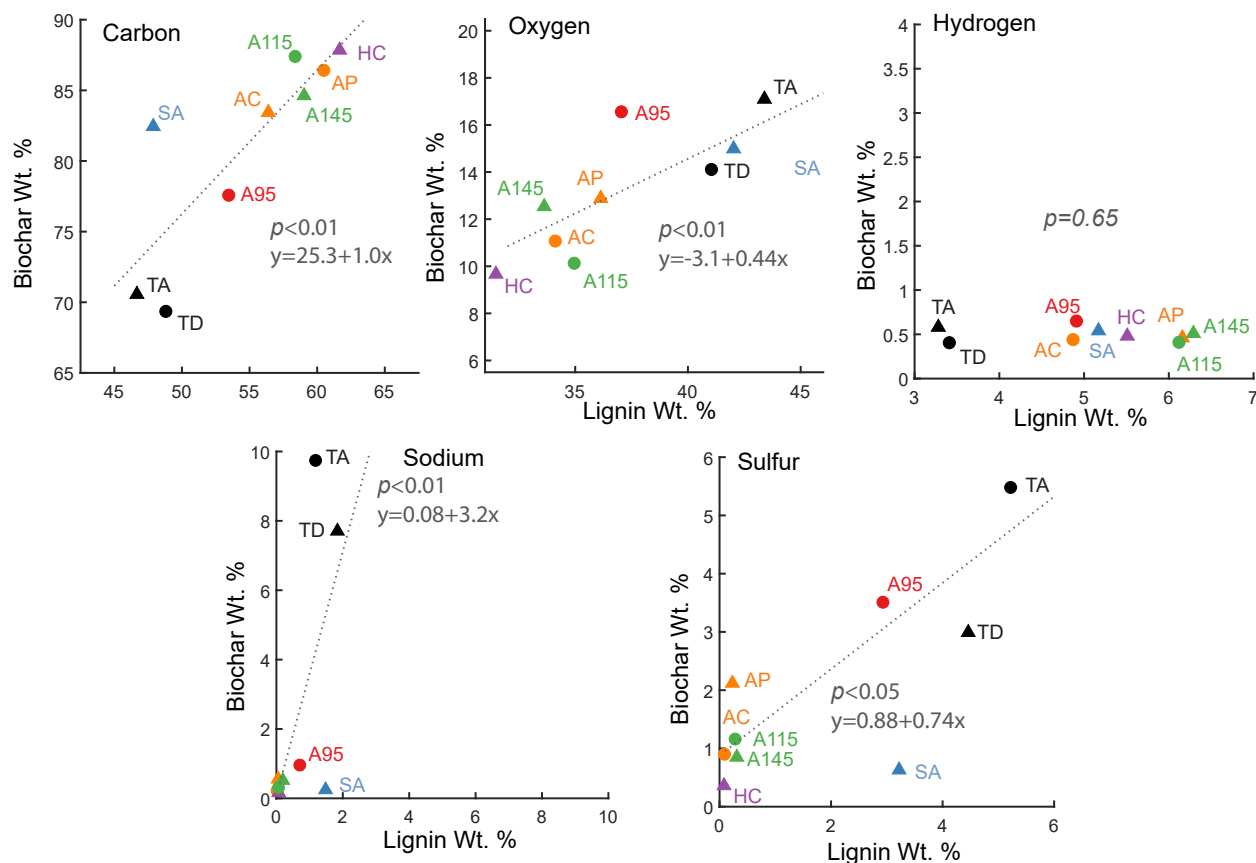


Figure 6.5: Difference in weight % of C, H, O, Na, and S in all lignins before and after pyrolysis at 1100 °C. Linear regression trend lines are shown for all elements with a significant relationship ($p < 0.05$).

The percolation threshold is similar for all biochars, indicating similar particle geometry and packing, despite differences in structure after pyrolysis and before ball milling. The peak electrical conductivity of all biochars varied over two orders of magnitude between biochars - from 0.19 S/cm for TA-biochar to 18.9 S/cm for A95-biochar. These variations are consistent with what has previously been observed for pyrolysis of lignin at 1100 °C with electrical conductivity measured with the same method [143] and in the middle of a range of values observed for all lignin-derived biochars. The upper range (>10 S/cm) of these conductivities are comparable to those of electrically conductive carbon blacks [141, 200], and sufficient for many electrical applications, including anti-static materials, sensors, and

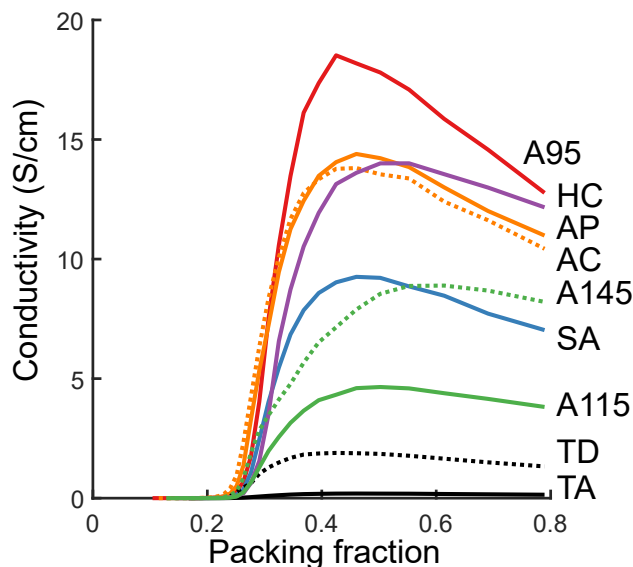


Figure 6.6: Electrical conductivity of all biochars as a function of packing fraction.

conductive additives in batteries.

A number of factors impact biochar electrical conductivity: size of graphitic crystallites, displacements and deformations on those crystallites, biochar surface groups, and biochar particle size [19, 102, 143]. At a pyrolysis temperature of 1100 °C, all biochars are expected to be above the internal percolation threshold between graphitic crystallites, and no increase in electrical conductivity is expected with increasing pyrolysis temperature [19]. XRD patterns of the biochar show variation in the in-plane size of graphitic crystallites (L_a), but minimal shifts in size or distance between sheets in the stacking direction (L_c and d_{002}) with an average of 1.2 ± 0.1 graphene planes per crystallite across all samples. The in-plane size of graphitic crystallites varies from 3.4 Å for TD-biochar to 41 Å for A115-biochar. TA and TD show poor fits relative to other biochar, which is attributed to the high contribution of inorganic components to the XRD pattern in these biochars. Minimal shifts are observed in Raman spectra between samples. All biochars show the typical D and G peaks that are typical for non-graphitizing carbons [206]. The intensity ratio of these peaks (I_{dg}) ranges from 1.03-1.18. In TA, an additional peak is observed at 1058 cm^{-1} , which is attributed to Na_2SO_4 [284].

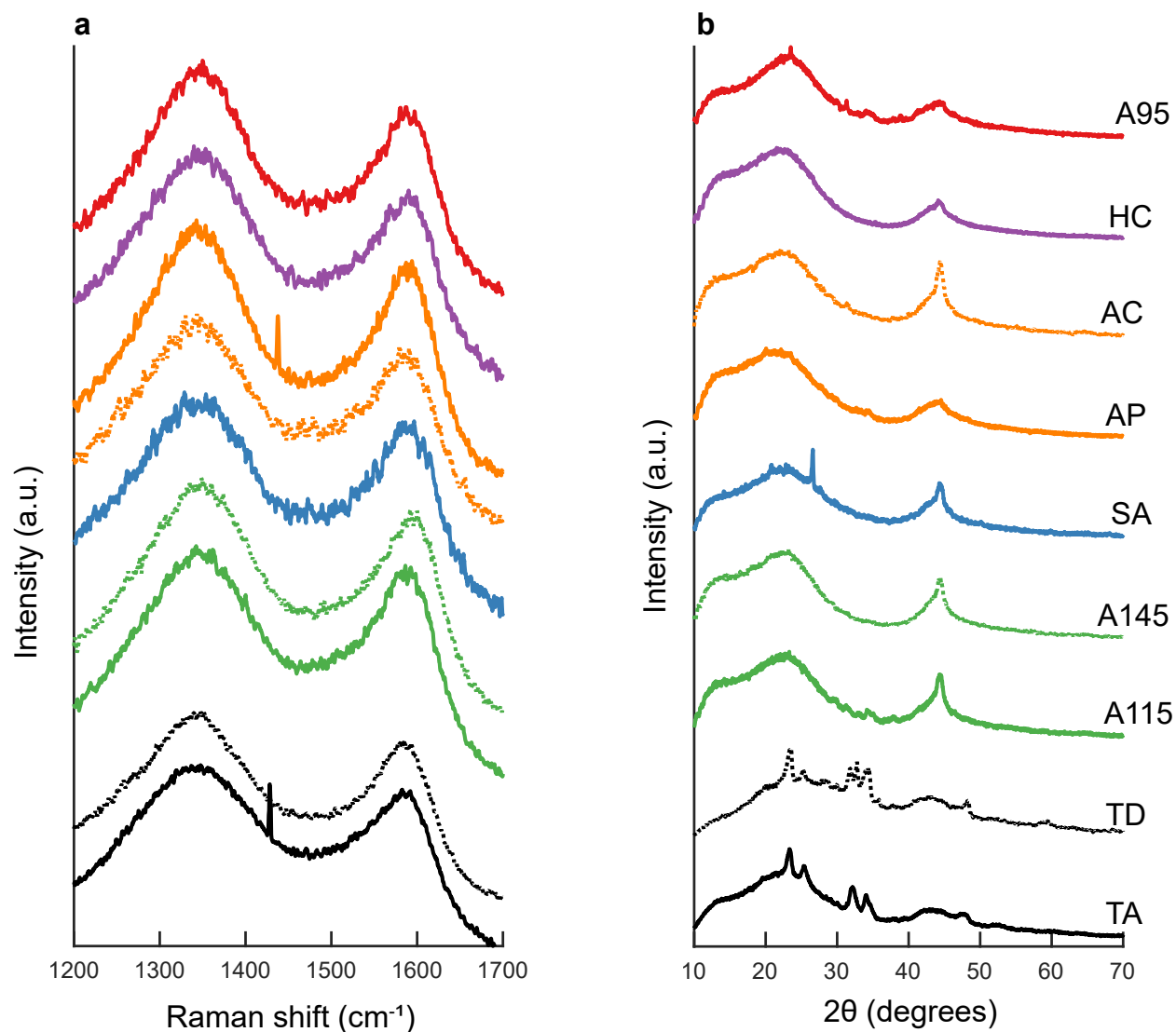


Figure 6.7: Characterization of biochar graphitic structure with (a) Raman spectroscopy and (b) XRD.

TA-biochar and TD-biochar were found to have a shallower valley between the D and G peaks than other biochars. The ratio of this valley depth to the height of the G-peak has previously been correlated with degree of graphitization [285], and combined with limited 10 ℓ peaks in the XRD patterns of TA and TD, and low electrical conductivity demonstrates that these biochars show much lower graphitization than the other biochars examined. A full summary of peak values from XRD and Raman is given in Table 6.3.

Table 6.3: Calculate XRD and Raman values and peak electrical conductivity for all biochar.

	L_a (Å)	L_c (Å)	d (Å)	I_{DG}	W_g	Conductivity (S/cm)
TA	7.8	4.6	4.0	1.1	148.0	0.2
TD	3.4	5.2	3.7	1.1	133.9	1.9
SA	33.1	5.0	4.1	1.1	151.2	9.3
HP	16.2	4.9	4.1	1.2	147.7	14.0
AC	15.2	4.3	4.4	1.1	153.9	14.4
AP	30.9	4.6	4.3	1.1	137.5	13.8
A115	41.2	4.9	4.2	1.0	146.8	4.6
A145	35.9	4.9	4.3	1.1	146.0	8.9
A95	19.5	5.1	4.4	1.2	146.1	18.5
A95-Na	38.3	4.0				7.0
A95-Na+Fe	36.8	4.7				5.2
A95+Fe	12.6	3.9				11.4

Despite the range of properties and electrical conductivity identified herein, no statistically significant relationship was found between any of the examined lignin properties (C, H, O, Na, or S content, molecular weight, particle size, dominant monomer (S or G), and lignin thermal transitions) and biochar electrical conductivity. Individual comparisons can be made based on similar lignins with individual differences in processing. AP and AC show identical processing, but different feedstocks (poplar and corn stover) and particle sizes (34 μm and 160 μm), but the resulting biochars have nearly identical electrical conductivities. In contrast, A95, which shows similar processing to AP, but lower treatment temperature results in higher electrical conductivity. Similarly, A115 and A145 have similar processing and chemical content, with differences in treatment temperature, but A145 shows higher

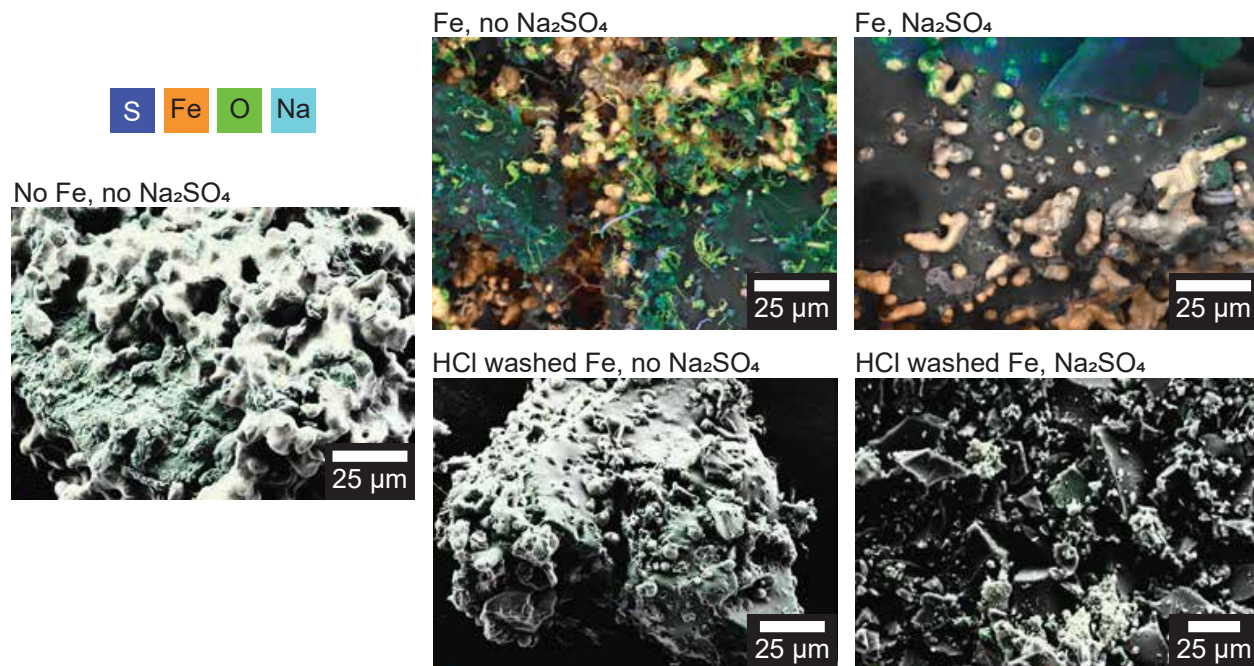


Figure 6.8: EDS maps of oxygen, iron, sodium, and sulfur content for A95-Na, and A95+Fe and A95+Fe-Na before and after washing with HCl to remove iron.

electrical conductivity than A115.

Iron catalyzed pyrolysis and inorganic interactions

A95 biochar, as the highest electrical conductivity biochar was selected for further testing to examine the impact of inherent Na₂SO₄ and its interaction with an iron catalyst. In total four total treatments were examined: as-isolated lignin (A95), lignin with Na₂SO₄ removed (A95-Na), lignin with iron (A95+Fe), and lignin with Na₂SO₄ removed with iron (A95-Na+Fe), with each treatment showing varying inorganic content after pyrolysis (Figure 6.8). After washing with HCl to remove iron, minimal inorganic content was observed in either A95-Fe or A95-Na+Fe.

A two-factor ANOVA assessing the impact of Na₂SO₄ and iron content on biochar electrical conductivity found a statistically significant impact from both Na₂SO₄ and iron, and a significant interaction between the two ($p < 0.01$ for all). A95-biochar had an average

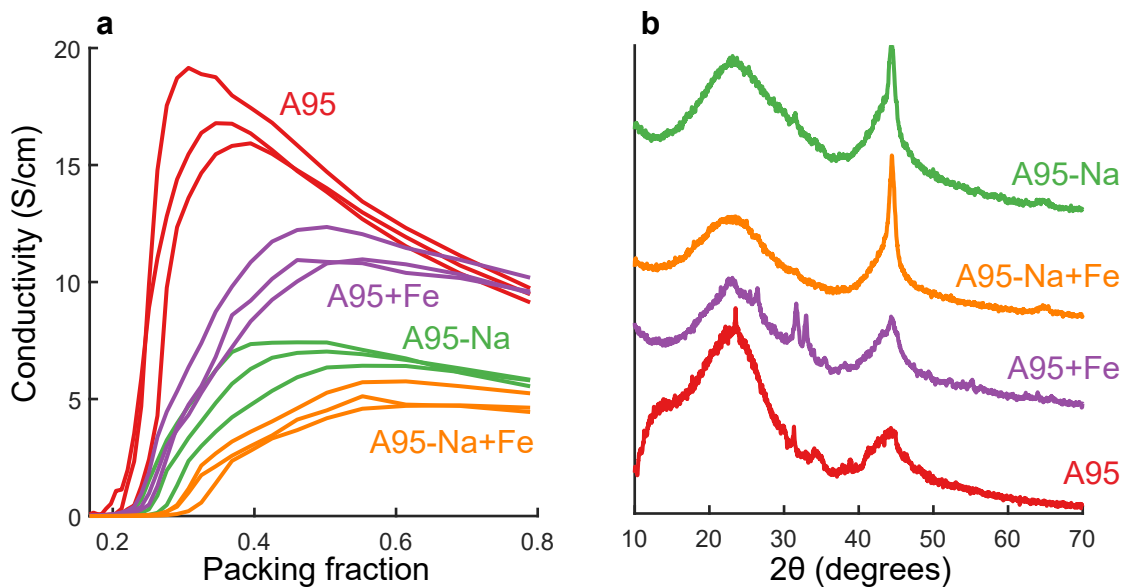


Figure 6.9: (a) Electrical conductivity of A95 biochar with all combinations of Na_2SO_4 and iron examined. Triplicate measurements are shown. (b) XRD patterns of A95 biochar with all combinations of Na_2SO_4 and iron examined.

electrical conductivity of 17 ± 1.6 S/cm (Figure 6.9a). Removing Na_2SO_4 from this biochar. With sodium removed this reduced to 7.0 ± 0.5 S/cm. Similarly, with an iron catalyst the electrical conductivity was 11 ± 0.8 S/cm. With both Na_2SO_4 removed and an iron catalyst, the lowest electrical conductivity was observed at 5.2 ± 0.51 S/cm. Post hoc testing found no significant difference ($p > 0.05$) to exist between the A95-Na+Fe and A95-Na samples, indicating that without Na_2SO_4 the iron catalyst played no role in electrical conductivity.

The mechanisms behind this difference in electrical conductivity was further explored with XRD, finding meaningful differences in crystallite size of the graphitic 10 plane (L_a) for each treatment examined (Figure 6.9b and Table 6.3). A95-biochar shows a crystallite size of $16.2 \text{ \AA}$ on average. With removal of Na_2SO_4 , this greatly increases regardless of the presence of iron to $38.3 \text{ \AA}$ and $36.8 \text{ \AA}$ for A95-Na and A95-Na+Fe respectively. In contrast A95+Fe, shows slightly reduced L_a relative to A95 at $12.6 \text{ \AA}$. In contrast, crystallite size in the stacking 002 direction (L_c) only shows minor shifts between 4-5 $\text{ \AA}$ for all treatments with

approximately 4 Å between each layer indicating an average of . Importantly, this finding indicates that presence of Na_2SO_4 inhibits graphitization in lignin-derived biochars. Iron plays a limited role in graphitization in this study, a finding supported by past studies that find the majority of irons catalytic effect to occur between 1100 and 1200 °C [119].

As biochar graphitic crystallite size only varies in the in-plane direction, the aspect ratio of graphitic crystallites vary greatly between different biochars. This shift in graphitic crystallite size is found to play a key role in biochar electrical conductivity. A strong quadratic relationship is found between (L_a) and biochar conductivity ($p < 0.01$, Figure 6.10). This relationship peaks in electrical conductivity at $L_a=23$ Å. We propose two mechanisms for this behavior, which expand on the previously developed quasi-percolation model for biochar electrical conductivity [19, 146]. At low graphitic crystallite sizes, such as are found in TA- and TD-biochar, limited graphitization has occurred as indicated by both XRD and Raman spectroscopy. Graphitic crystallites in these materials show limited contacts, and are separated by displaced graphitic carbon. As the size of these crystallites expands, such as in AC-, HP-, and A95-Fe biochar, these crystallites grow increasing the number of contacts between electrically conductive regions. These contacts reach a maximum at approximately 23 Å. Above this contact, the high aspect ratio of the crystallites limits contacts between the crystallites resulting in lower electrical conductivity. Peak electrical conductivity occurs at an aspect ratio of approximately 4 $L_a:L_c$; for carbons with larger stacks per crystallite larger L_a sizes may result in higher electrical conductivity. This proposed behavior matches what has previously been observed for percolation in packed powder systems, where higher aspect ratios results in reduced electrical conductivity [200].

This finding highlights development of low aspect ratio, but well graphitized as a potential method to increase the electrical conductivity of carbons produced from non-graphitizing feedstocks. If biochar could be developed with limited disordered and displaced graphitic content, but with graphitic crystallite aspect ratios approaching 1, higher electrical

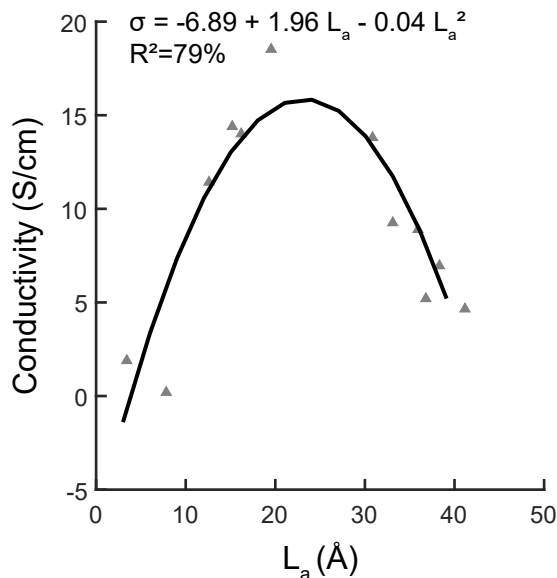


Figure 6.10: Relationship between graphitic crystallite in-plane size (L_a) and electrical conductivity.

conductivities of the bulk material may be possible.

Conclusions

This work highlights that all lignins are not equal for producing electrically conductive biochars, with a $100\times$ difference in electrical conductivity between the most and least conductive biochar measured. The wide range of electrical conductivities observed herein for lignin-derived biochars confirms that similar ranges observed between past studies are not exclusively due to differences in biochar production or electrical conductivity measurement method. Further, important differences in thermal transitions during heating of lignin result in widely varying biochar morphologies. Despite wide ranges in both lignin properties and lignin-derived biochar conductivity, no statistically significant relationships were found between lignin properties and biochar electrical conductivity. However, experimental testing finds that Na_2SO_4 present in lignin inhibits the formation of larger graphitic structures in

lignin-derived biochar.

The aspect ratio of graphitic crystallites in lignin-derived biochar is found to play an important role in electrical conductivity of the resulting biochar, with a quadratic relationship observed with a maximum at a aspect ratio of 4. This finding builds on past quasi-percolation models that describe packing of graphitic crystallites within carbon particles as an important contributor to their bulk electrical conductivity, and can help to inform development of future electrically conductive, non-graphitizing carbons.

BIOCHAR FROM FOOD WASTE AS A SUSTAINABLE REPLACEMENT FOR
CARBON BLACK IN UPCYCLED OR COMPOSTABLE COMPOSITES

Contribution of Authors and Co-Authors

Manuscript in Chapter 7

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Contributions: Conceptualization, Methodology, Investigation, Formal analysis,
Writing - original draft, Visualization.

Author: Cecily Ryan

Contributions: Conceptualization, Resources, Supervision, Writing - review & editing

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Abstract

This study investigates biochar, a carbon-based material produced via pyrolysis, as a filler in two plastics: biodegradable plastic polylactic acid (PLA) and recycled high-density polyethylene (HDPE). Specifically, we examine biochar derived from post-consumer food waste as a method to reuse this large waste stream. We find that pyrolysis of this inhomogeneous waste at 900 °C forms biochar with a graphitic structure and electrical conductivity similar to carbon black. Biochar addition impacts the properties of HDPE and PLA differently, with reduced thermal stability in PLA and only minor impacts on the thermal and mechanical properties of HDPE. In both polymers, agglomeration of biochar particles results in low electrical conductivity of the composites. This study highlights a loss of thermal stability in PLA with the addition of biochar as a critical roadblock to applying biochar as a filler in PLA. We propose that inorganic compounds in the biochar catalyze the thermal degradation of PLA, resulting in shorter PLA chains and reducing the composite's mechanical properties. An important finding of this work is that food-waste-derived biochar increased the degradation rate of PLA under composting conditions, with almost twice the mass loss after 40 days in samples with high biochar loading compared to neat PLA. This study highlights both the promise and challenges of utilizing biochar as a filler in PLA and HDPE. If particle dispersion and thermal stability with PLA can be addressed, biochar has the potential for reuse of a high environmental impact waste stream for a wide range of applications.

Introduction

Food waste is one of society's highest volume and most environmentally impactful waste streams. The development of new methods to upcycle food waste into usable materials is integral to mitigating the substantial greenhouse gas emissions associated with wasted

food [5]. However, chemical or biological conversion of food waste into valuable materials is currently limited by the inhomogeneous nature of post-consumer food waste, making it challenging to economically convert post-consumer food waste into valuable materials [286].

One promising method to upcycle food waste is to convert it to biochar. Biochar is a carbon-based material produced by pyrolysis of biomass that has been widely studied as a method to sequester carbon, produce biofuels, and improve soil health [12, 287]. Biochar is a promising replacement for petroleum-derived fillers (e.g., carbon black) in plastics - at high pyrolysis temperatures ($> 900\text{ }^{\circ}\text{C}$), biochar can be produced with a chemical structure, and electrical conductivity comparable to that of carbon black [19, 99, 114, 143]. Biochar produced at $900\text{ }^{\circ}\text{C}$ typical has electrical conductivities of 0.03-4 S/cm [143], with some higher electrical conductivities reported with the use of catalysts [148]. Biochar's addition to plastics contributes to beneficial properties including reduced weight, improved strength, and high electrical conductivity [18, 56, 88, 181, 183, 184, 188, 255, 266, 288, 289, 290, 291, 292, 293, 294, 295]. For example, past studies have found that addition of 50% wood-derived biochar to HDPE resulted in approximately a 60% increase in flexural strength of HDPE [296] and addition of 20% coffee ground-derived biochar to epoxy results in similar electrical conductivity to 20% carbon black in the same epoxy [103]. If similar performance can be obtained with food waste as other fillers, conversion of food waste to carbon filler will present a combined strategy to upcycle this large waste stream and reduce reliance on fossil fuel-derived carbon filler materials.

The properties of biochar are highly dependent on its feedstock and processing conditions [12, 19, 143, 297]. Previous studies have examined biochar produced from diverse biomass streams, including chicken manure, sewer sludge [291], lignin [114, 143], coffee grounds [189, 295], and agricultural waste [18, 99]. These studies have found that the properties of the resulting biochar are highly dependent on the feedstock [18, 143]. However, no study to date has examined the potential of mixed, post-consumer food waste-derived

biochar as a filler material in plastics. The inhomogeneity of post-consumer food waste, including the inclusion of inorganic components such as bone or table salt (NaCl), poses a unique problem and may produce biochar with varying chemical structures and properties depending on the source of the food waste [286]. Further, food waste has high moisture content, in some cases greater than 80% [234], and may have high energy requirements to dry [286]. If challenges of inhomogeneity of post-consumer food waste can be overcome, we believe food-waste-derived biochar can provide similar benefits as a filler material as other biochars while helping to mitigate the environmental impacts of landfilled food waste.

In this study, we applied food waste-derived biochar as a filler in plastics to replace petroleum-derived carbon with a renewable and waste-derived material. The goal of this work was to characterize the properties of food waste-derived biochar, and its interactions with both recycled and biodegradable plastics. To this end, we produced biochar from post-consumer food waste at a pyrolysis temperature of 900 °C (FW900) for use as a filler material in recycled high-density polyethylene (HDPE) and the compostable plastic polylactic acid (PLA). We hypothesized that the addition of food-waste-derived biochar would increase the flexural storage modulus of both HDPE and PLA and have comparable electrical conductivity to carbon black. Additionally, we examine the impact of biochar addition on the degradation rate of PLA under composting conditions. Based on past studies examining composting of biochar-PLA composites [56], we hypothesize that the presence of food-waste-derived biochar will increase the rate of degradation of PLA under composting conditions. The results highlight how biochar from food waste can add value to plastic composites while reusing a high volume waste stream, as well as the challenges remaining for application of food waste biochar in composites.

Materials and Methods

Materials

PLA pellets (2003D) were provided by Nature Works (melt flow index of 6, Minnetonka, MN, USA [32]). Prior to use, PLA pellets were stored in a desiccator at <5% relative humidity. Recycled HDPE flakes were provided by Northwest Polymers (Molalla, OR, USA). Food waste was provided by Montana State University Culinary Services (Bozeman, MT, USA) and is a random selection of inhomogeneous, post-consumer food waste collected from university dining halls at three different points in time. Non-food-waste contaminants were manually removed from the supplied food waste before biochar production. As a comparison to food-waste-derived biochar, Cabot Vulcan XC-72R carbon black (Boston, MA, USA) was examined.

Biochar production

In order to reduce particle size and moisture content, food waste was blended into a paste and dried at 110 °C for 72 hours. The blended, dried food waste was then ground into a powder with a mortar and pestle and stored in a drying oven at 110 °C.

Biochar was produced via slow pyrolysis in a Thermo Fisher Lindberg/Blue M Mini-Mite tube furnace with an alumina ceramic tube. Approximately 5.8 g of ground and dried food waste was placed into an alumina boat in the tube furnace. Before heating, the tube was purged with nitrogen for 10 min at a flow rate of 100 mL/min. Next, the furnace temperature was ramped at 10 °C/min to a maximum temperature of 900 °C under a 30 mL/min nitrogen flow. The maximum temperature was maintained for one hour and then cooled to room temperature. A small bio-oil sample was collected from the tubing downstream of the tube furnace for further analysis. After pyrolysis, biochar was ball milled in a Retsch Mixer Mill 400 for 2.5 min at 30 Hz with a 50 mL stainless steel grinding jar and a single 25 mm diameter

stainless steel ball to reduce particle size and stored in a drying oven at 105 °C. Pyrolysis of food waste was repeated six times to generate sufficient biochar for all experiments.

Characterization of biochar

The particle size distributions of 0.25 g of biochar and carbon black were measured on a Malvern Mastersizer 3000 laser diffraction particle size analyzer with the assumption of non-spherical particles. Distilled water was used as the dispersant.

The chemical compositions of biochar and carbon black were examined to determine potential chemical differences between the two materials. The relative chemical composition of key inorganic elements was measured with an Oxford Xplore energy dispersive X-ray (EDS) detector on a Zeiss SUPRA 55VP field emission scanning electron microscope (FESEM). Before measurement, samples were placed on carbon sticky dots (Ted Pella, product #16084-3) and samples for imaging were sputter-coated with iridium, while samples for EDS were examined uncoated. FESEM images were captured at 250 $\times$ magnification and a working distance of 8.4 mm with an SE2 detector. EDS spectra were collected over the entire displayed area. Fourier transform infrared spectroscopy (FTIR) was performed to examine biochar and bio-oil functional groups to further examine the chemical structure of the food-waste-derived biochar. FTIR was performed on a ThermoFisher Nicolet iS10 FTIR Spectrometer with a Smart iTX ATR Accessory with a diamond crystal. Spectra were collected from 600 to 4000 cm^{-1} at a resolution of 4 cm^{-1} , and with 32 scans per sample. In addition, biochar Raman spectra were collected to examine displacements and defects in the graphitic structure of the FW900 biochar. Confocal Raman spectroscopy was performed on a Horiba LabRam HR Evolution NIR. Samples were measured with a 50 $\times$ LWD objective, 1800 gr/mm grating, and a 532 nm laser at 3.2% filter. The Raman spectra were deconvoluted into their constituent D and G peaks in MATLAB (Mathworks inc., R2020a, v. 9.8.0.1380330) to determine the D and G peak ratio. A linear baseline correction was applied, the D peak was

fit with a Lorentzian function, and the G peak was fit with a Breit-Wigner-Fano function [206, 207]. The intensity ratio of the D and G peaks (I_{DG}) was calculated as the ratio of the height of the fit D and G peaks. X-ray diffraction patterns were collected on a Bruker D8 Advance powder X-ray diffractometer with Cu $K\alpha_{1,2}$ radiation, from 5-70° with a step size of 0.02° per step.

Biochar and carbon black electrical conductivities were characterized with a guard electrode compression setup [141]. Resistance measurements were taken every 0.0127 cm (0.005 in) of compression with a Keithly 2450 Sourcemeter from the lower current limit of the source meter until no more compression could be applied.

Composite fabrication

Composites were prepared for 0 wt.%, 2.5 wt.%, 5 wt.%, 10 wt.% and 20 wt.% FW900 biochar with the remainder either PLA or HDPE. Composites were mixed in a Thermo Fisher Scientific HAAKE Minilab II dual screw extruder at 100 rpm and 170 °C for PLA and 190 °C for HDPE for 5 min. Rheology data were collected during extrusion. Compounded composite melt was injected into a Thermo Fisher Scientific DMA sample mold (Part #557-2295, 60 mm × 10 mm × 1 mm) with a Thermo Fisher Scientific Minijet Pro injection molder. PLA samples were injected with a barrel temperature of 175 °C and a mold temperature of 90 °C. HDPE samples were injected with a 190 °C barrel temperature and a 60 °C mold temperature. Injection molding temperatures were determined based on polymer manufacturer specifications, and PLA's temperatures were iteratively reduced with the goal of minimizing thermal degradation during processing. High mold temperatures were required due to the thin mold used for DMA flexural samples. An injection pressure of 750 bar was applied for 10 s, followed by a post pressure of 450 bar for 60 s. For all biochar loadings of PLA, 12-13 injection molded samples were prepared from four extrusion runs, while for HDPE, 7-9 injection molded samples were prepared from three extrusion runs. After

injection, molds were cooled at room temperature for 1 min before demolding. Composite samples were stored in a desiccator at less than 5% relative humidity until testing.

As a follow-up experiment to examine the impact of particle size on electrical conductivity, FW900 biochar was ball milled as in Section 7 for an additional 3.5 min (6 min total), and three additional composite samples of PLA and HDPE and 20 wt.% FW900 were produced with this smaller biochar size and the same extrusion and injection molding parameters as above. To further examine the percolation behavior of FW900-PLA composites, samples were produced with 30 wt.% of the smaller biochar and PLA. These samples were only characterized for electrical conductivity.

Composite characterization

The flexural stiffness of FW900 composite samples was tested in a three-point bending fixture of a TA Instruments Q800 dynamic mechanical analyzer (DMA). The storage modulus (E'), loss modulus (E''), and the tangent of delta ($\tan \delta$) of each composite were measured as a function of temperature. All samples were tested at a frequency of 1 Hz, amplitude of 20 μm , and a force track of 125%. The temperature was equilibrated at 30 °C for 5 min, then ramped to 140 °C for PLA and 120 °C for HDPE at a constant rate of 5 °C/min. DMA measurements were taken in triplicate.

Charpy impact testing was performed on a P.A. Hilton (Hampshire, U.K.) HSM4 pendulum impact tester, with a procedure adapted from ASTM D6110 [298]. A 0.39 kg impact weight and 79.21° initial angle were used for PLA samples and 1.02 kg and 114.21° for HDPE samples. Injection molded flexural samples for both PLA and HDPE at all biochar loadings were notched with a Boss LS1420 65 W laser cutter at 40% power at a speed of 20 mm/s. Samples were notched on the midpoint of the 10×60 mm surface, with a 2 mm 45° v-notch (Supplemental Figure D.11). All Charpy impact strength values were taken in triplicate.

Biochar dispersion in both HDPE and PLA was examined via imaging with FESEM as described in Section 7. Prior to imaging HDPE and PLA samples with 0%, 20%, and 20% reduced size FW900 were cryofractured in liquid nitrogen, and the fracture surface was examined.

The electrical conductivity of biochar composites was measured using a linear four-probe setup (Supplemental Figure D.1). Impedance spectra of the composites were measured on a Gamry Reference600 Potentiostat with a voltage amplitude of 2000 mV from 0.1 to 1 Hz. Impedance spectra were collected in three positions on each of three different samples for HDPE and PLA composites at 20 wt.% FW900 loading. Electrical conductivity was measured of 20 and 30 wt.% Vulcan XC-72R carbon black and PLA samples as a comparison.

Changes in the chemical and crystalline structure of the composite samples were examined with FTIR, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). FTIR spectra were collected as in Section 7 on all composite samples. TGA was performed to determine the effect of biochar addition on the thermal degradation of the polymers. To determine the impact of biochar addition on sample thermal degradation, TGA was performed in a TA Instruments Q5000 IR. Approximately 15 ± 1 g samples of all extruded composites were placed in TA Instruments HT platinum pans and ramped at 10 °C/min from 30 °C to 900 °C under a nitrogen flow of 25 mL/min. To determine the impact of FW900 on PLA and HDPE crystallinity, melt temperature, and glass transition temperature, DSC was performed on a TA Instruments Discovery DSC 250 with a RSC90 cooling unit (minimum temperature -90 °C). Additionally, non-extruded samples with 0 wt.% and 20 wt.% FW900 were added to approximately 10 mg of polymer in a TA Instruments DSC Tzero pan. For both HDPE and PLA, two consecutive heating samples were examined, and all heating rates were 10 °C/min. PLA samples were heated from 20 °C to 190 °C, down to -20 °C then back up to 220 °C. HDPE samples were heated from 20 °C to 250 °C, down to -80 °C then back up to 250 °C. Sample crystallinity was calculated as defined by Kessler

[299], with values of 93.7 J/g and 293 J/g for the 100% crystalline enthalpies of PLA and HDPE respectively. A single measurement of each sample was taken for TGA, FTIR, and DSC measurements of composites.

Aerobic biodegradation was performed with a composting process approximating ASTM D5338 with measurements of sample mass loss [300]. Compost inoculum was obtained from Happy Trash Can (Bozeman, MT, USA). This inoculum had an initial dry solids content of 84.7% and a pH of 8.4. Next, DI water was added to compost to obtain a dry solids content of 55%. Five replicates of PLA-FW900 composites at all FW900 loadings (0%, 2.5%, 5%, 10%, and 20%) were placed in polyester 100 μm mesh bags, and the bags were melted closed in order to collect undegraded remnants (Figure D.2). Samples and 1 kg of compost were placed in 2 L polycarbonate containers, with 8-9 PLA composite test samples, and control samples of an HDPE sample, an HDPE with 20% FW900 sample, and a sample of Whatman cellulose filter paper (Marlborough, MA, USA, part #1541-185) cut and folded to approximate the geometry and weight of the PLA samples per container. The addition of these samples resulted in a compost to sample weight ratio (including mesh bags and control samples) of 18.5 g sample to 1 kg compost. These containers were placed in a Queue Cell Culture Incubator at 58 °C with a 2 L/min ambient airflow. Samples were weighed before composting. On days 1, 10, 20, 30, and 40, samples were lightly rinsed, air-dried, and weighed. After measurement, the compost was stirred, the dry solids content of the compost was measured, and if needed, additional DI water was added to maintain a dry solids content of 55%. Sample weight remaining was calculated as:

$$Wt.\% = \frac{W_n - (W_{n=1} - W_S)}{W_S} \quad (7.1)$$

Where W_n is the weight of the bag and sample at day n, and W_S is the weight of the sample before being placed in the compost. $W_{n=1} - W_S$ is removed to account for the weight of the

mesh bag and the moisture gain of the sample after one day in compost. After 40 days of composting, sample residue was removed from the mesh bags, dried at 110 °C for 24 hr, and weighed to determine the sample's final weight.

Results and Discussion

Biochar characterization

Pyrolysis of food waste produced an average biochar yield of $28.07\% \pm 1.22\%$ with the variation representing a single standard deviation. Therefore, a majority of the initial food waste mass formed the co-products of biogas and bio-oil. The FTIR spectrum of the bio-oil (Figure D.3) shows the presence of complex organic compounds, with aromatic carbons, methyl groups, carbonyl, alkane, alkene, alcohol, and amine bonds all observed [301, 302, 303, 304, 305]. The primary peaks at 2914 cm^{-1} , 2849 cm^{-1} , and 1709 cm^{-1} suggest the presence of high quantities of fatty acids, which may be upgraded into valuable biofuels [306]. The composition of the gas pyrolysis products was not examined in this study but is expected to be primarily composed of methane, hydrogen, carbon dioxide, carbon monoxide, and water [12, 143, 301, 307]. In order to maximize the efficiency of the pyrolysis process, these bio-oil and gas products, as well as excess heat generated during pyrolysis, should be applied for valuable applications [12].

FW900 biochar was found to have a majority carbon content, with oxygen, sodium, phosphorous, chlorine, potassium, and calcium also present (Figure 7.1a). Relative to Vulcan XC-72R carbon black, EDS measurements show FW900 biochar had 9.9% higher oxygen and 7% higher inorganic content, a finding which has been observed in past comparisons of biochar and carbon black [114, 143]. The high inorganic content and the variety of inorganic elements observed are attributed to the inhomogeneity of post-consumer food waste and inorganic components, such as bones and table salt, present in the initial food waste. Both XRD patterns and EDS maps show sodium and chloride to be present as NaCl in the final

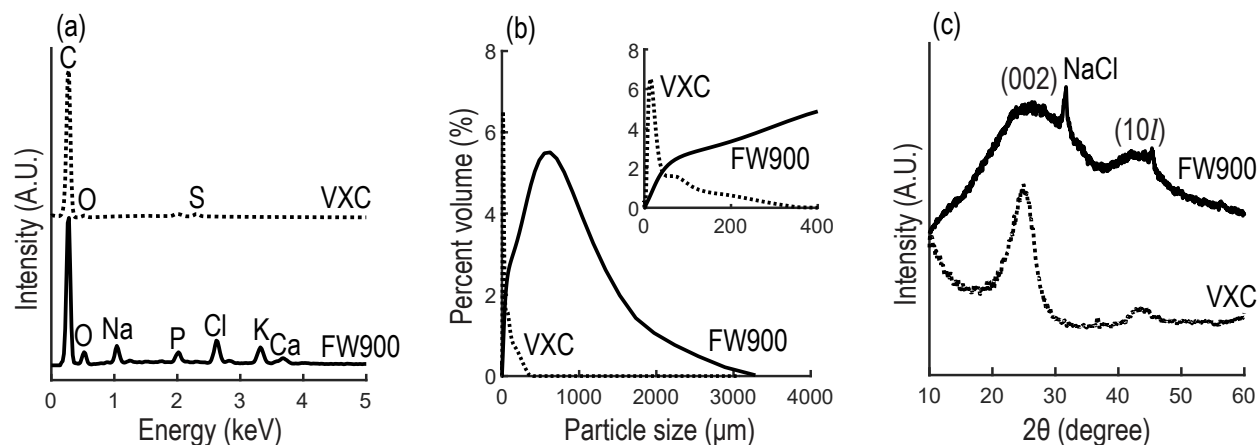


Figure 7.1: Characterization of the chemical composition and physical structure of FW900 biochar and Vulcan XC-72R carbon black. (a) Stacked EDS spectra of FW900 biochar and Vulcan XC-72R carbon black (VXC). Labeled peaks indicate primary elements associated with those peaks. (b) Particle size distribution of FW900 biochar (solid line) and Vulcan XC-72R carbon black (dashed line). FW900 biochar has a median particle size of 320 μm , and VXC has 14.5 μm . (c) XRD patterns for FW900 biochar and Vulcan XC-72R carbon black, with the turbostratic graphite peaks (002) and (10l) and the primary peak associated with NaCl labeled.

biochar (Figure 7.1c and Supplemental Figure D.4). Notably, the FW900 biochar shows much higher particle sizes (average 320 μm) than Vulcan XC-72R carbon black (average 14.5 μm , Figure 7.1b and 7.3). Another iteration of size reduction was performed to address this difference in particle size. This additional ball milling produced a food-waste derived biochar more similar in size to carbon black (Figure 7.3). FTIR measurements of the food waste-derived biochar prior to baseline correction show limited peaks and a large baseline shift, a spectrum seen in past FTIR measurements of biochar, and have been identified as indicative of graphitic carbon in biochar and carbon black [19, 102, 114, 198]. After baseline correction, a peak is observed at 1034 cm^{-1} in both FW900 biochar and Vulcan XC-72R carbon black. This peak has previously been attributed to -OH groups on carbon rings in biochar. Additionally, in both materials, a pair of overlapping peaks is observed at 1443 cm^{-1} and 1563 cm^{-1} and attributed to C-H bonds on aromatic carbon rings (Figure

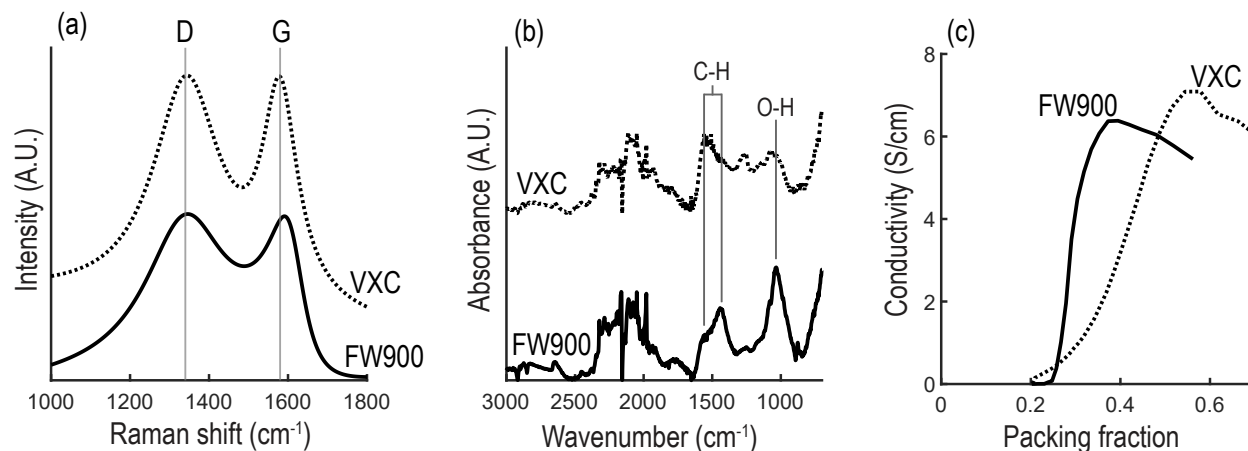


Figure 7.2: Characterization of FW900 biochar chemical properties. (a) Stacked fit Raman spectra of FW900 biochar (solid) and Vulcan XC-72R (VXC, dashed) carbon black, with D (1340 cm^{-1}) and G bands labeled (1580 cm^{-1}) [206]. (b) Stacked and baseline corrected FTIR spectra for FW900 biochar (solid), and Vulcan XC-72R (VXC, dashed) carbon black. Labeled peaks correspond to O-H substitutions on graphitic rings (1080 cm^{-1}) and C-H bonds on aromatic carbon rings (1440 cm^{-1} and 1560 cm^{-1}) [19]. (c) Conductivity compression curve for FW900 biochar.

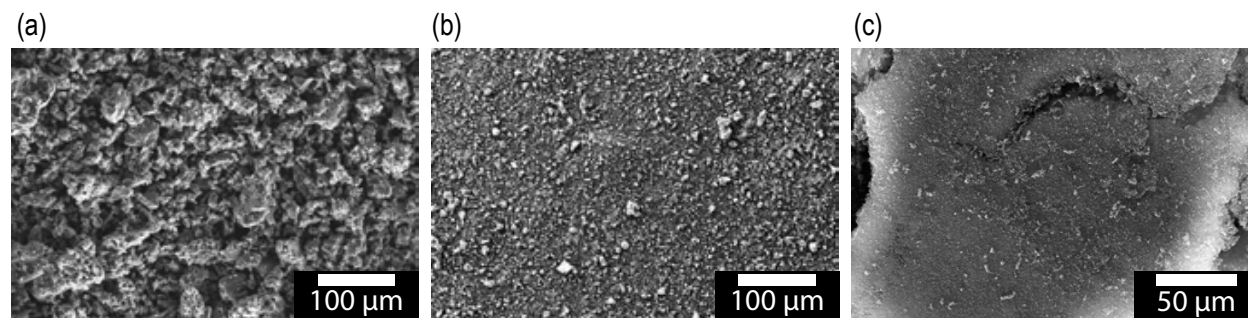


Figure 7.3: SEM micrographs of (a) FW900 biochar at $250\times$ magnification, (b) reduced size FW900 biochar at $250\times$ magnification, and (c) Vulcan XC-72R carbon black at $1000\times$ magnification.

7.2b) [19]. The FW900 spectrum is similar to those previously reported for other biochars produced at $900\text{ }^{\circ}\text{C}$ or above from more homogeneous feedstocks, with typically few peaks observed due to the highly graphitic structure [19, 114, 143, 198]. The Raman spectrum for FW900 biochar shows both G (1583 cm^{-1}) and D (1340 cm^{-1}) peaks with an intensity

ratio of $I_{DG}=1.008$ (Figure 7.2a). As a comparison, Vulcan XC-72R carbon black was had $I_{DG}=1.028$, indicating that FW900 and Vulcan XC-72R have similar graphite crystallite sizes [206]. FW900 biochar shows a higher response between the D and G peaks ($\sim 1400\text{ cm}^{-1}$), a region which has previously been attributed to the presence of five-carbon rings adjacent to graphitic structures or out of plane deformation of sp^2 carbons near defects in the graphitic structure [308]. Similarly, the XRD pattern of FW900 shows a similar structure to Vulcan XC-72R, with both showing (002) and (101) reflections characteristic of turbostratic graphite that have previously been observed in both carbon blacks and biochar [19, 309]. FW900 shows crystalline peaks at 2θ values of 31.7° and 45.5° , which are attributed to sodium chloride (NaCl, pdf #97-024-05989).

The FW900 biochar was found to have an electrical conductivity (6.38 S/cm, Figure 7.2c) that was high relative to other biochars (0.003 – 4 S/cm) produced at 900°C without the addition of catalysts, and comparable to that of common carbon blacks and biochar produced at higher temperatures [99, 111, 114, 143, 149, 153, 156]. Combined with the low I_{DG} ratio and relatively high carbon content, this electrical conductivity indicates that graphitic crystallites of sufficient size have formed in the food-waste-derived biochar to allow for percolation between these electrically conductive regions [19, 102]. While the pyrolysis reactions behind this high electrical conductivity were not examined in detail in this study, past studies have proposed that the presence of inorganics in biochar feedstocks, as observed in FW900, may be responsible for catalyzing the formation of a graphitic structure, which would result in the relatively high electrical conductivity for biochar produced at 900°C [102, 111, 112, 147].

Combined, the EDS, XRD, FTIR, Raman spectra, and electrical conductivity of the FW900 biochar indicate that inhomogeneous food waste is a non-graphitizing feedstock that has formed small graphitic crystallites, surrounded by defected graphitic structures with oxygen or hydrogen substitutions. This structure has previously been observed in

chars produced from other feedstocks, indicating that a similar degree of graphitization and electrical performance can be obtained from post-consumer food waste as from more homogeneous feedstocks [19, 102, 114]. In addition, higher quantities of inorganic compounds are present in FW900 biochar than in carbon black, and a wider variety than in other biochars, which past studies have found to play a role in forming a more graphitic biochar structure during pyrolysis [111, 112, 147]. Past studies have proposed that inorganics may be responsible for catalyzing the formation of graphitic crystallites in the biochar, resulting in higher electrical conductivity than other biochars produced at 900 °C from more homogeneous feedstocks [99, 111, 114, 143, 149, 153, 156]. The particle size is an important difference between FW900 biochar and Vulcan XC-72R carbon black. Past studies have found that smaller particles are expected to have better dispersion in polymer matrices, resulting in a lower percolation threshold for electrical conductivity of the composite [261, 262], therefore FW900's large size may negatively impact particle dispersion and composite electrical conductivity. After additional ball milling, FW900 shows a meaningful reduction in particle size to approximately 10 μm (Figure 7.3b), which is more comparable to biochars examined as a replacement for carbon black in past studies [114, 143].

Composite characterization

The impact of FW900 on polymer thermal degradation and melt viscosity differed between PLA and HDPE. In PLA, thermal degradation temperature decreased with the addition of FW900, with larger decreases observed at higher additions of FW900. In contrast, HDPE showed no change in thermal degradation temperature with the addition of FW900 (Figure 7.4d). Additionally, PLA saw a decrease in the melt viscosity during extrusion with the addition of FW900, with 10% and 20% biochar addition causing a greater loss in viscosity than 2.5% or 5% addition. Conversely, in HDPE, an increase in viscosity was seen with increasing biochar loading (Figure 7.4e).

DSC results show no shift in glass transition temperature ($\sim 57^\circ\text{C}$) or melt temperature ($\sim 153^\circ\text{C}$) for non-extruded PLA with the addition of 20 wt.% FW900 (Figure 7.4a and Table 7.1). However, after extrusion, a consistent decrease in glass transition temperature, melt temperature, and cold crystallization temperature was observed with increasing biochar content (Figure 7.4c). Decreases in these transition temperatures have previously been associated with decreasing molecular weight in PLA [33]. These decreased transition temperatures relative to non-extruded samples, even at 0% biochar addition, indicate that some degradation of the PLA has occurred during the extrusion of PLA and that this impact is exaggerated by biochar addition. Combined with the observed decreases in PLA thermal degradation temperature and viscosity, these results indicate a decrease in molecular weight of the PLA with extrusion and increased biochar content. The decrease in transition temperatures with extrusion was accompanied by a meaningful shift in thermal behavior, with increased cold crystallization enthalpy relative to non-extruded samples and the formation of a double melt peak. The double melt peak and increase in cold crystallization temperature is attributed to the formation of both α and α' crystalline structures in the PLA [310]. This behavior is not observed in non-extruded PLA samples and is attributed to a slow cooling rate in the mold for injection molded samples [311]. As biochar content increases, both of these melt peaks shift to lower temperatures and the temperature range between these two peaks increases (Figure 7.4c) providing further evidence for decreased molecular weight and increased polydispersity.

For the first heating cycle for injection molded samples, PLA crystallinity increased with increasing biochar content. This increase is primarily due to a decrease in the enthalpy of the exothermic cold crystallization peak (Figure 7.4f) that is greater than the decrease in melt enthalpy. In the second heating cycle, an increase in crystallinity with increasing biochar content is still observed; however, the overall degree of crystallinity is much lower (Table 7.1), indicating that the slower cooling rate during injection molding meaningfully impacts

PLA crystallinity both with and without biochar. Notably, the addition of biochar still improved crystallization relative to neat PLA in the second heating cycle despite potential further polymer degradation by the biochar.

In contrast, biochar addition has minimal impact on recycled HDPE. HDPE shows minimal shifts in its melting temperature with the addition of FW900 ($\sim 131^{\circ}\text{C}$). The glass transition for HDPE could not be captured due to HDPE's low glass transition temperature ($< -80^{\circ}\text{C}$, Figure D.5). Like PLA, non-extruded HDPE saw slight increases in crystallinity after two heating cycles with the addition of FW900 from 57.46% crystallinity for neat HDPE to 64.09% crystallinity for HDPE and 20 wt.% FW900. In extruded samples, biochar addition was found to have only a minor impact on crystallinity, with $< 2\%$ difference between samples with 0% and 20% biochar addition (Table 7.1). Past studies have found biochars from other feedstocks to act as a nucleating agent in HDPE, resulting in increased crystallinity [185, 296]. While a slight increase in crystallinity is observed for non-extruded HDPE samples, the minimal change in crystallinity for injection molded HDPE samples with FW900 addition indicates that the role that FW900 may have played as a nucleating agent in injection molded samples, was likely offset by other mechanisms [312].

The degradation of PLA by FW900 can also be observed in FESEM micrographs (Figure 7.5c). PLA with 20% FW900 is observed to have a highly porous surface, with clear gaps surrounding biochar particles. This texture stands in contrast to the smooth surface of neat PLA samples (Figure D.10). Composites of HDPE and 20% FW900 show a flat surface, with minimal gap between biochar and plastic. These micrographs show generally good dispersion of both the larger FW900, and the reduced size FW900 in HDPE, as shown by the textured surface (Figure 7.5b) attributed to smaller biochar particles that has previously been observed in well dispersed carbon fillers in polymers [92]. This texture is not present in neat HDPE or PLA (Supplemental Figure D.10).

The increase in crystallinity observed with the addition of FW900 to PLA is consistent

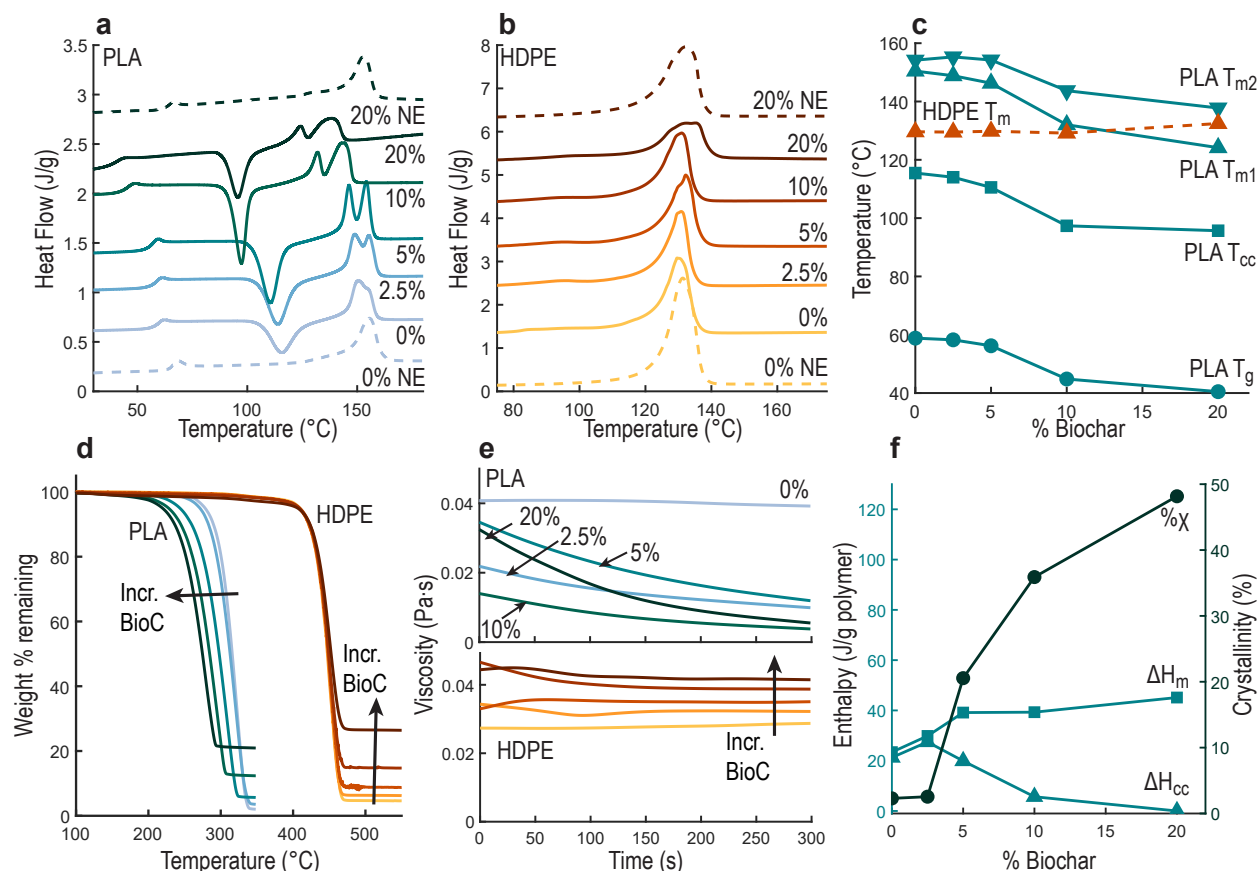


Figure 7.4: DSC curves for composites for (a) the first heating cycle of PLA, (b) the second heating cycle of PLA, (c) First heating cycle shifts in melt temperature (T_{m1} and T_{m2}), glass transition temperature (T_g), and cold crystallization temperature T_{cc} for PLA and melt temperature for HDPE (T_m) at each level of biochar loading. (d) TGA curves for both PLA (blue) and HDPE (orange) from 0% (lightest color) to 20% (darkest color) biochar addition, PLA follows a trend of increased biochar loading as you move left, while HDPE follows a trend of increased biochar loading as you move up in the >500 °C region. (e) Melt viscosity during extrusion of FW900 composites for both PLA (top) and HDPE (bottom) for all biochar loadings. (f) First heating cycle shifts in melt enthalpy (ΔH_m), cold crystallization enthalpy (ΔH_{cc}), and % crystallinity (% χ) for PLA with the addition of biochar. Additional DSC data is shown in Figure D.5

with past literature showing minor increases in crystallinity of PLA with the addition of biochar [181, 182, 313]. Studies examining biochar and other carbon powders' impacts on HDPE crystallinity are mixed, with different studies showing a decrease, increase, or no change in the crystallinity of HDPE with the addition of carbon powders [185, 296, 314,

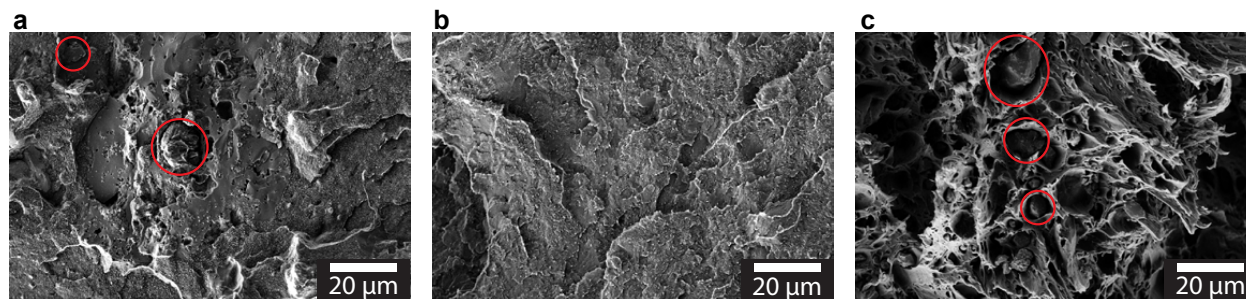


Figure 7.5: FESEM micrographs of composites of (a) HDPE and 20% FW900, (b) HDPE and 20% reduced size FW900, and (c) PLA and 20% FW900 at $2500\times$ magnification. Larger ($>10\ \mu\text{m}$) biochar particles are highlighted by red circles, while smaller ($>1\ \mu\text{m}$) biochar particles are present as the textured surface.

315, 316]. Studies that find a decrease in crystallinity in HDPE with the addition of carbon powders have proposed that the carbon powder inhibits polymer chain mobility during the formation of crystalline regions. As the biochar examined in this study is much larger than typical carbon blacks, we hypothesize that there may be a size effect on the impact of carbon powders on the crystallinity of HDPE. The increase in crystallinity observed in FW900 and PLA or HDPE composites may indicate that FW900 acts as a nucleating agent in PLA and HDPE, facilitating the formation of larger crystalline regions. This finding is particularly important in PLA, where we would expect a reduction in crystallinity due to the shortened polymer chains and where increases in crystallinity may improve the heat deflection temperature and strength, resulting in a material that is viable or more applications [317, 318]. If reductions in PLA polymer chain length by biochar during extrusion can be mitigated, biochar may further increase the crystallinity and mechanical properties of PLA.

Biochar's impact on the polymer chain length of PLA is not reflected in the FTIR spectra of the FW900 and PLA composites. In both PLA and HDPE composites, no change in FTIR spectra is observed with increasing biochar content (Supplemental S6). This lack of change indicates that the observed decrease in melt viscosity of the PLA-FW900 composites

Table 7.1: Polymer glass transition temperate (T_g), melt temperature (T_m), melt enthalpy (ΔH_m), and % crystallinity (% χ) for the first heating cycle of both HDPE and PLA at all loadings of extruded FW900 and the second heating cycle of non-extruded (NE) HDPE and PLA with 0% and 20% FW900.

	T_g (°C)	T_{cc} (°C)	ΔH_{cc} (J/g)	T_m (°C)	2nd T_m (°C)	ΔH_m (J/g)	% χ
NE PLA	58.14	130.07	1.9928	153.47	None	2.2506	0.28
NE PLA & 20% FW900	59.02	146.21	1.8712	152.86	None	2.2953	0.57
PLA	61.64	111.42	21.26	156.54	150.48	23.41	2.29
PLA & 2.5% FW900	61.4	108.72	26.77	155.55	148.86	29.1	2.55
PLA & 5% FW900	61.55	110.3	18.898	157.96	150.01	37.19	20.55
PLA & 10% FW900	57.05	104.64	5.0972	152.99	145.26	35.37	35.90
PLA & 20% FW900	54.26	None	None	152.61	147.66	36.104	48.16
NE HDPE	<-80			130.27		168.35	57.46
NE HDPE & 20% FW900	<-80			130.92		150.22	64.09
HDPE	<-80			129.57		130.32	44.48
HDPE & 2.5% FW900	<-80			130.89		129.5794872	44.23
HDPE & 5% FW900	<-80			132.2		135.9263158	46.39
HDPE & 10% FW900	<-80			130.97		134.5	45.90
HDPE & 20% FW900	<-80			135.22		134.375	45.86

is due to chain scission (rather than changes in the polymer backbone or functional groups), which would not result in meaningful changes to FTIR spectra, apart from minor increases in peaks associated with the ends of polymer chains.

Similarly, DMA results show different shifts in behavior with the addition of biochar in HDPE and PLA (Figure 7.6). In PLA, the storage and loss moduli are reduced relative to neat PLA at temperatures below the glass transition temperature. We hypothesize that this loss of stiffness is due to the degradation of the polymer chain by the biochar, as observed by the reduced thermal degradation temperature and melt viscosity. Additionally, PLA shows a slight reduction in average glass transition temperature with increasing FW900

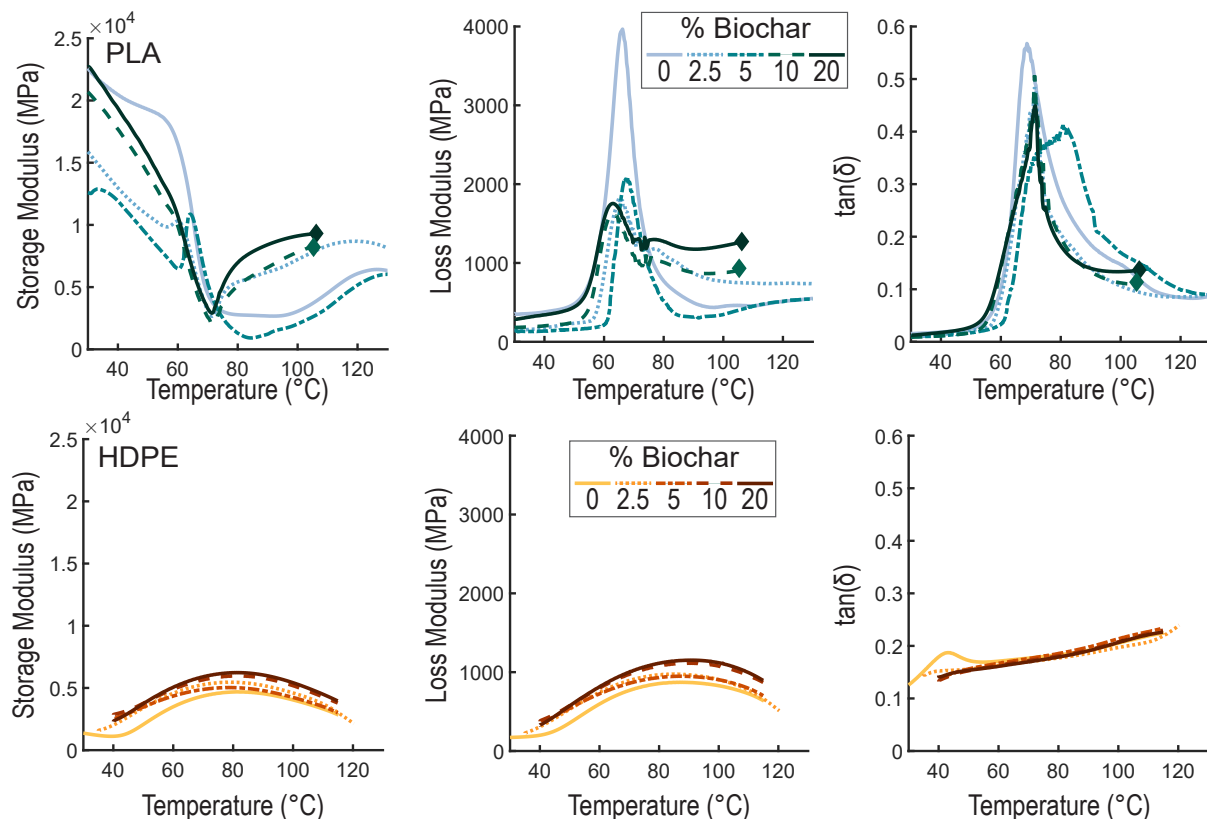


Figure 7.6: DMA results for storage modulus (left), loss modulus (center) and $\tan\delta$ (right) for both PLA (top, blue) and HDPE (bottom, orange) at all biochar loadings. HDPE samples were measured from 30 to 100 °C while PLA samples were measured from 30 to 140 °C due to their higher melt temperature. ♦ symbols indicates the values at which PLA with 10% and 20% FW900 failed. All DMA replicate curves are shown in Figure D.7.

loading (from 68.4 °C with 0% FW900 to 64.1 °C with 20% FW900, Supplemental Table S1), and a decrease in the height of the loss modulus peak as composites passed through the glass transition region. This reduction in glass transition temperature matches the behavior observed via DSC. All samples of PLA-FW900 composites with 10% and 20% FW900 failed before reaching 140 °C, indicating a loss in flexural strength of PLA composites with high loadings of biochar. This finding highlights the impact of the thermal degradation of PLA with the addition of FW900 on the mechanical properties of PLA-biochar composites and the need to address the decreased thermal degradation temperature of PLA with the addition

of biochar in order to produce viable PLA-biochar composites.

In contrast, HDPE composites are observed to have minimal changes in loss and storage moduli with the addition of FW900 biochar. Both HDPE and PLA composites show increased storage and loss moduli with high levels of biochar loading above approximately 80 °C, which may indicate an improvement in the heat deflection temperature at high loadings of biochar. The loss modulus of HDPE and FW900-HDPE composites shows a slight peak at approximately 80 °C, which is attributed to an α -transition [319, 320, 321]. This transition is observed at similar levels for neat HDPE and HDPE-FW900 composites. A $\tan \delta$ peak corresponding to this transition is observed in some, but not all replicates (Figure D.7). The storage modulus of HDPE shows a slight peak that corresponds with the temperature of the α -transition peak in loss modulus. Shifts in storage modulus with an α -transition has not been the focus of past work examining the α -transition of HDPE. However, it is observed in all replicates and biochar loadings in this study, and peaks in storage modulus between 20 °C and the melt temperature have been observed in past DMA measurements of some neat HDPE and HDPE composites [322, 323]. Past studies have not examined the mechanism responsible for this peak in storage modulus.

As with DMA, impact testing shows that addition of FW900 affects the mechanical properties of HDPE and PLA differently. In PLA, at 2.5% biochar addition, a large increase is observed in Charpy impact strength, from an average of 6.7 kJ/m² to 13.1 kJ/m² (Figure 7.7). Beyond this point, impact strength decreases with increasing FW900 content, to a minimum of 1.3 kJ/m² at 20% FW900 addition. This result indicates that FW900 provides a reinforcing effect at low additions, where limited degradation is observed with DSC and TGA. However, as the thermal degradation of the PLA by FW900 progresses at higher FW900 loadings, the loss of mechanical strength due to degradation of the polymer overcomes the increase due to biochar addition. HDPE shows a similar increase at 2.5% biochar addition, from 1.2 kJ/m² to 5.9 kJ/m² (Figure 7.7). This finding is consistent with past studies, which

find an increase in impact strength with the addition of biochar for a variety of polymers, and a decrease in the mechanical properties of PLA at high biochar loadings [292, 324, 325]. However, at higher loadings HDPE maintains a relatively steady impact strength. Of note is that the highly ductile HDPE did not fracture at all loadings of 10% FW900 addition or below and instead deformed out of the test fixture. Therefore, the values reported herein represent minimum values of Charpy impact strength. Samples of HDPE and 20% FW900 did fracture, indicating more brittle behavior at higher biochar loadings, consistent with past studies of 20% biochar addition to HDPE [326].

The HDPE-FW900 composites examined in this study show a more limited change in flexural stiffness and impact strength than HDPE-biochar composites examined in past studies [185, 290, 296]. This difference is attributed to the limited change in crystallinity with the addition of biochar, relative to past studies. We hypothesize that this limited change is due to the relatively large particle size of FW900 making it less facile at nucleating crystal growth. However, differences in particle geometry or stiffness relative to homogeneous feedstocks could also be responsible for this limited impact. Further, past studies have found biochar addition to increase other mechanical properties of HDPE, including tensile strength and modulus, and creep resistance [185, 266, 290, 296]. While these properties were not examined in this study, given the similar chemical structure of FW900 to other biochars and limited change in thermal properties, a similarly limited impact is expected on these properties.

Despite the high electrical conductivity of FW900, both 20% FW900 loadings in both PLA and HDPE were measured to have high electrical resistance, above the upper limit of the Gamry Potentiostat used ($> 1.5 \text{ G}\Omega$). In contrast, the addition of 20 wt.% Vulcan XC-72 carbon black to PLA results in resistance at least eight orders of magnitude lower ($21 \text{ }\Omega$) when measured with the same four-probe method and geometry. We hypothesized that this high electrical resistance is due to the aggregation of the FW900 particles and the

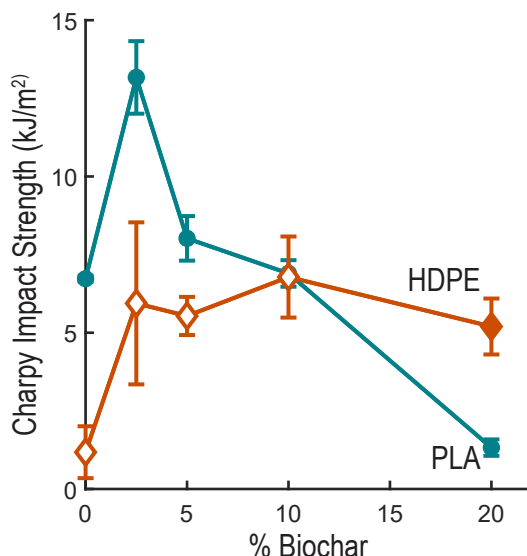


Figure 7.7: Charpy impact strength of composites of HPDE and PLA for all loadings of biochar. Samples indicated with an open symbol (0-10% FW900 and HDPE) did not fail brittley, and instead deformed out of the test fixture.

large particle size of FW900 biochar relative to carbon black and that the FW900-biochar composites were below their percolation threshold at 20 wt.% due to biochar's high density and inorganic content relative to carbon black [143]. The aggregation of biochar particles can be observed in PLA samples via optical microscopy (Figure D.8). To further test this hypothesis, we measured the electrical conductivity of PLA and FW900 composites (20% and 30%) produced with food waste that had been ball milled for an additional 3.5 min. At 20% FW900 and smaller particle size, we found no measurable improvement in the electrical conductivity with a decrease in particle size, with resistance still above the upper limit of the instrument ($> 1.5 \text{ G}\Omega$). This low electrical conductivity, and visually well dispersed particles (Figure 7.5) indicate that particle size may not be the primary factor in the poor electrical conductivity of FW900 composites. In contrast to the 20 wt.% samples, samples produced with 30 wt.% reduced particle size biochar and PLA show a large increase in electrical conductivity over the 20 wt.% samples, with a conductivity of 0.184 S/cm . This conductivity is comparable to samples produced with 30 wt.% carbon black, which had

an electrical conductivity of 0.305 S/cm. Due to this increase in electrical conductivity, we hypothesize that FW900 biochar composites have a higher percolation threshold than carbon black composites. While FESEM micrographs show biochar to be well dispersed, electrical percolation of food-waste biochar composites still remains a key drawback to this material relative to carbon black. This increase in percolation threshold could be due to agglomeration that was not visually observed via FESEM, the higher bulk density of biochar, differences in particle geometry between biochar and carbon black (Figure 7.3) or the high inorganic content of FW900. In all cases, increasing the volume of the composite filled with electrically conductive graphitic carbon and improving particle dispersion can reduce the percolation threshold.

The observed decrease in thermal degradation temperature and mechanical properties of PLA with the addition of biochar highlights the challenges of using biochar as a filler material in PLA. The decrease in thermal degradation temperature and viscosity of PLA with the addition of biochar has been observed to varying extents in all past studies examining these properties of PLA and biochar composites [88, 92, 181, 182, 183, 184, 186, 188, 189, 266, 327]. As in this study, past studies have found that a decrease in mechanical properties accompanies this decrease in thermal degradation temperature [184, 295]. Several hypotheses have been proposed for these decreases in PLA thermal degradation and viscosity, the most common being that oxygen or water trapped in the porous structure of the biochar leads to chain scission of the PLA via oxidative degradation and hydrolysis [181]. However, this scale of decrease in viscosity and thermal degradation of PLA has not been observed in past studies examining the addition of carbon black and similar porous carbon materials [92, 328], and in some cases, increases are reported [329]. Therefore, we propose an alternative hypothesis; that PLA thermal degradation is catalyzed by alkaline earth and alkali metal compounds present in the biochar. This effect increases with increased loading of these inorganic compounds (either via higher biochar addition or increased inorganic content)

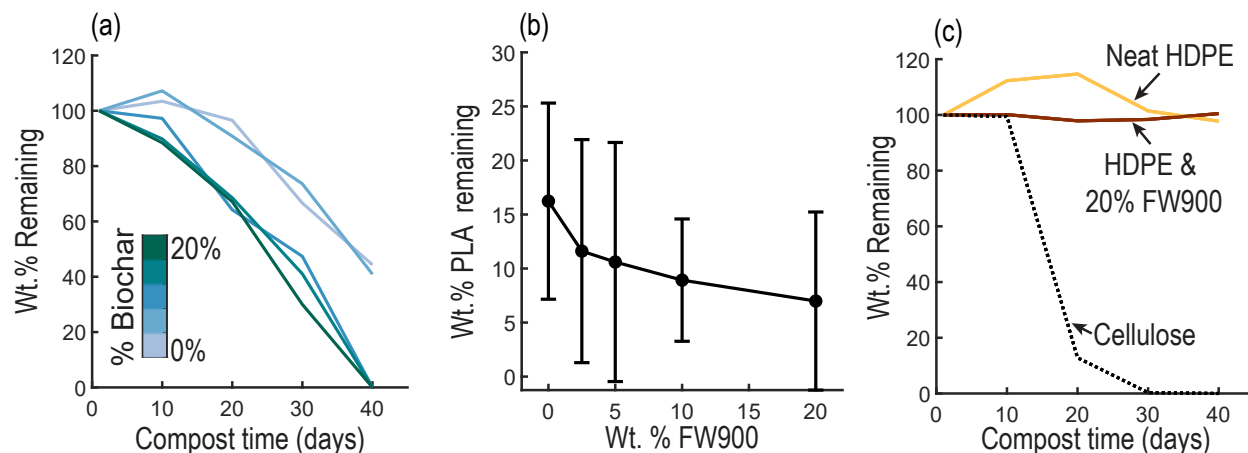


Figure 7.8: (a) Mean weight loss of PLA-FW900 composites over the 40-day composting period. 5%, 10%, and 20% FW900 samples were observed to degrade faster than 0% and 2.5% FW900 samples. Photos of samples at 0, 20, and 40 days are shown in Figure D.2 (0 days) and Figure D.9 (20 and 40 days). (b) Mean difference in weight of PLA remaining after drying as a function of FW900 content after 40 days of composting. Error bars display one standard deviation. (c) Weight change of the control samples cellulose (dashed line), Neat HDPE (yellow line), and HDPE with 20% FW900 (red line) samples during composting.

and is present even when these inorganics are present in relatively low quantities ($< 1\%$). This hypothesis is further supported by past studies, which have identified metal-containing compounds as effective catalysts for depolymerization of PLA [330, 331]. To remedy this issue, future studies should examine the removal of inorganics (e.g., with washing with water or acid [116]) from biochar or biochar feedstocks.

Improvements were observed in PLA composting rates with the addition of biochar (Figure 7.8a). 5, 10, and 20% FW900 composites all display similar degradation rates from day 10 on, reaching 0% weight remaining by day 40. In contrast, 0% and 2.5% FW900 samples degrade slower and have approximately 40% of the original weight remaining after 40 days. When measured after drying, this same trend is observed, with decreasing weight of PLA remaining with increasing FW900 content (Figure 7.8b). High variations in weight remaining (Figure 7.8b) are attributed to the use of mass loss measurement (rather than measurement of gas products), which has potential for variation due to loss of sample, gain

of moisture, or residual compost on the sample [332, 333, 334, 335]. Control samples of both neat HDPE and HDPE with 20% FW900 show limited change in mass after 40 days of composting, while cellulose degrades at a more rapid rate than PLA, with <1% of the original mass remaining after 30 days (Figure 7.8c). We propose two potential mechanisms for the observed increase in composting rate of PLA with the addition of biochar. First, the observed thermal degradation of PLA and FW900 during extrusion resulted in shorter polymer chains that could more easily be degraded during composting. Second, the presence of biochar improved the water permeability of PLA, leading to more rapid degradation of the polymer, as previously observed in PLA and natural fiber composites [336]. This hypothesis is supported by the highly porous structure of PLA after the addition of biochar (Figure 7.5c), which would allow for increased water adsorption. Increased moisture absorption has previously been observed by Ho et al. along with the increased composting rate of PLA with the addition of bamboo char [56]. In that case, less thermal degradation of the PLA during extrusion is observed than in FW900 and PLA composites, supporting the hypothesis that both degradation of biochar during extrusion and increased moisture absorption may play a role in the increased rate of composting observed in this study.

The high electrical conductivity and graphitic structure of FW900 identified in this study highlight it as a promising material to replace petroleum-derived carbon fillers. When applied as a filler material in HDPE, the increase in impact strength, and minimal impact on polymer stiffness, crystallinity, and thermal degradation highlight biochar as a promising filler. However, the differences between PLA and HDPE identified in this study highlight the challenges of applying biochar as a filler material in PLA. Careful feedstock selection or development of procedures to minimize metal content are needed to avoid detrimental thermal degradation of PLA. Importantly, this study shows that even at processing temperatures (170 °C) well below the onset of thermal degradation of PLA (201 °C at 20% FW900 addition), chain scission reactions catalyzed by the presence of metals

in biochar can meaningfully reduce the mechanical properties of PLA-biochar composites. In addition, this study's high biochar electrical conductivity and low composite electrical conductivity highlight the need for new processing methods to reduce the percolation threshold of biochar composites if biochar is to be applied as a replacement for carbon black in electrical applications.

Further, several processing challenges remain for applying food waste-derived biochar as a filler material. Primary among these are challenges with collecting and transporting food waste for processing. Past studies have proposed that distributed pyrolysis facilities for food waste may be more efficient than a centralized facility to minimize the time between food waste production and pyrolysis [286]. Additionally, food waste is higher in moisture content than other feedstocks that have been considered as promising feedstocks for biochar [286]. Removal of this moisture is required prior to pyrolysis. However, past studies have found the excess heat produced during pyrolysis sufficient to dry food waste, minimizing the external energy required [286].

Conclusions

For the first time, post-consumer, inhomogeneous food waste-derived biochar is examined as a filler material in plastics. Food waste-derived biochar is a promising waste-derived and renewable replacement for petroleum-derived carbon materials due to its high electrical conductivity and graphitic structure. However, despite food-waste-derived biochar's high electrical conductivity, a composite with PLA shows a higher percolation threshold than carbon black filled samples. We hypothesize that this high percolation threshold is due to the higher density of food-waste-derived biochar and the presence of inorganic compounds with lower electrical conductivity than the carbon structure.

Importantly, this work highlights the challenges of applying biochar as a filler material in PLA. We find that increasing biochar content decreases the onset of thermal degradation and

melt viscosity in PLA and hypothesize that the presence of inorganics in biochar catalyzes the thermal decomposition of PLA. In contrast, in HDPE, the addition of food-waste-derived biochar was found to have limited impacts on thermal degradation. We attribute the decreased mechanical performance of PLA with the addition of food waste-derived biochar to this decomposition and identify this decomposition as a critical roadblock to developing high-performance PLA and biochar composites. We also attribute the poor mechanical performance of PLA-biochar composites to a reduction in PLA polymer chain length during the extrusion and injection molding process. We found that the addition of food waste-derived biochar to PLA improves the degradation rate of PLA under composting conditions, which may be beneficial in single-use plastic products, where improved degradation rates can improve the viability of composting PLA. This work highlights the promise of food-waste-derived biochar as a filler material and its challenges, notably poor dispersion and increased thermal degradation in PLA. If these challenges can be addressed, food-waste-derived biochar-filled composites could be applied to upcycle food waste in a diverse set of applications, from food packaging to additive manufacturing of electrically conductive parts.

Supporting Information to this Chapter is presented in Appendix D.

BIOCHAR-FILLED BIOPLASTICS: A NEW CLASS OF BIOCOMPOSITES FOR
ELECTRICAL APPLICATIONS AND BEYOND

Contribution of Authors and Co-Authors

Manuscript in Chapter 8

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Contributions: Methodology, Conceptualization, Investigation, Writing - original draft, Writing - review & editing, Visualization

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Contributions: Investigation

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Manuscript Information

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Abstract

Biodegradable and electrically conductive materials have application in 3D printed sensors for a variety of applications. While common biodegradable plastics are used extensively in 3D printing, the conductive additives currently used to create electrically conductive filaments are not biodegradable or bio-compatible. Biochar, a carbon material produced by the pyrolysis of biomass, has been extensively explored as a biobased, electrically conductive material. However, addition of biochar to common biodegradable polymers reduces their thermal stability, resulting in unacceptable material properties. The mechanism responsible for this reduction in thermal stability is debated. Herein, the mechanisms responsible for this decrease are investigated and a method to eliminate this deleterious thermal degradation is developed. Then, the electrical conductivity of composites of a biodegradable polymer blend and biochar are examined. The unique combination of biodegradability and electrical conductivity demonstrated make this new class of biocomposites uniquely positioned to reduce the environmental impacts and costs of sensors across agricultural, biomedical, and environmental applications.

Introduction

3D printable, electrically conductive, and biodegradable materials can improve the sustainability and reduce costs of sensors in agricultural, environmental, and biomedical applications. A promising method to develop materials for these applications is adding electrically conductive filler materials to biodegradable plastics. However, commonly used electrically conductive fillers, such as petroleum-derived carbon black or metals are not biodegradable [180, 337]. Interest in applying biochar as an alternative to these filler materials has increased rapidly in recent years, with more studies published in 2020 and 2021 than in all previous years combined [11]. In addition to being a promising bio-

based alternative to carbon black, biochar provides post-degradation benefits when added to biodegradable plastics [2, 12, 56, 114, 338]. Whereas carbon black is produced by pyrolysis of petroleum [2], biochar is produced from biomass via a pyrolysis reaction which sequesters carbon and has been broadly examined for soil amendment applications [12]. With optimal pyrolysis conditions, this process results in a carbon material with electrical conductivity comparable to petroleum-derived carbons [114, 141, 143, 149, 153, 339]. When incorporated into plastics, these composites perform comparably to commercial conductive fillers in sensing applications [56, 109, 182, 183, 289, 291, 294, 339, 340, 341, 342, 343].

However, addition of biochar to the common biodegradable plastics polylactic acid (PLA) and poly(hydroxybutyrate-*co*-hydroxyvalerate) (PHBV) results in reductions in many material properties. Every study examining biochar fillers in PLA and PHBV has found that the addition of biochar decreases the thermal degradation temperature of the polymer, in some cases by as much as 72 °C (Supplemental Table E.1). This decrease in thermal degradation temperature is accompanied by decreases in molecular weight and mechanical strength [189, 266, 338]. Due to the limited temperature range for melt processing of PLA and PHBV [10], further reductions in thermal stability with the addition of biochar result in an unprocessable material [92]. This thermal degradation creates a critical roadblock to applying biochar as a conductive additive in biodegradable polymers.

The cause of this reduction in thermal degradation is debated. Most studies hypothesize that this decrease in thermal degradation is an inherent issue with biochar. Potential hypotheses include an increased mobility between polymer chains with biochar addition, shear heating local to the biochar during polymer extrusion, catalysis of chain decomposition by inorganics, and thermo-hydrolysis and oxidative degradation of the polymer by water and oxygen in the biochar’s pores [56, 181, 183, 266, 344]. However, no study has systematically examined these mechanisms for two of the most prevalent bioplastics, PLA and PHBV.

Herein, we examine the impact of biochar addition on the thermal degradation of PLA

and PHBV to improve the applicability of biochar-filled composites with the specific goal of creating electrically conductive, bio-based 3D printer filament. A two-pronged statistical and experimental approach is taken to investigate the multiple hypotheses proposed in past studies. First, we measured the effect of the addition of ten biochars on the crystallinity and thermal degradation temperature of PLA and PHBV. These biochars were produced from five feedstocks (three lignins (AL, DAL, and HL), wheat stems (WS), and synthetic cellulose (C)) at pyrolysis temperatures of 900 and 1100 °C (biochars are abbreviated by feedstock and temperature as e.g., AL900 or WS1100) and have been characterized in past work [143] and one commercial biochar (CT). Based on these observations, we examined a suite of hypotheses for the decrease in thermal degradation of PLA and PHBV with a simple regression model to correlate the properties of biochar to decreases in thermal degradation. We then modify the properties of these biochars to test promising hypotheses directly. Finally, we developed and applied simple, green chemistry processes to increase the thermal stability of biochar-filled biodegradable plastics and demonstrate their viability in high-value sensing applications.

Results & Discussion

The physical and chemical structure of the biochars applied in this study have been thoroughly characterized in past work [143]. These biochars have a range of physical and chemical properties allowing for all hypotheses for reduced PLA and PHBV thermal degradation proposed in past studies to be examined. Specifically, past characterization of these biochars shows varying degrees of electrical conductivities, graphitization, porosity, pH, and particle size; and various species and levels of inorganics present. These inorganics are present primarily as sodium sulfate (Na_2SO_4) in lignin-derived biochars and potassium and silica in wheat stem-derived biochars. A complete summary of the past characterization of physical and chemical properties of the biochars examined in this study is provided in

Extended Data Table E.2. Both thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements of biochar show no changes that could be responsible for the later discussed impacts on PLA and PHBV structure and thermal degradation.

Impact of biochar on PHBV and PLA

Thermogravimetric analysis (TGA) of biochar and PHBV composites show a decrease in onset and peak thermal degradation temperature (T_{10} , measured as 10% mass loss and T_{deg} , measured as the maximum of the derivative) with the addition of all biochars except C900 and CT (Figure 8.1a). These decreases range from 5.2 °C for WS1100 biochar to 28.8 °C for AL900 biochar relative to neat PHBV. In contrast, CT and C900 biochars increase thermal degradation temperature by 11 °C and 15°C, respectively. The kinetics of thermal degradation are further examined for neat PHBV and PHBV with the highest and lowest thermal degradation temperature and highest electrical conductivity (C900, AL900, and HL1100 respectively, Figure 8.1f). Biochar composites with similar or higher thermal degradation temperature values to PHBV show similar activation energies at 236 kJ/mol for neat PHBV, 243 kJ/mol for C900, and 216 kJ/mol for HL1100. In contrast, AL900 shows a 29 °C decrease in thermal degradation temperature but an activation energy of 332 kJ/mol. Accompanying this increase in activation energy for low thermal degradation temperature composites is a shift in degradation products, as measured with TGA with infrared spectroscopy (TGA-IR). For all biochar additions, the main products of PHBV thermal degradation are crotonic acid and CO₂ (Figure 8.1b). In neat PHBV, as well as in PHBV with WS900, WS1100 CT, C900, or HL1100 biochar added - the five biochars with the least reduction in thermal degradation temperature - CO₂ and crotonic acid peak gas evolution temperatures coincide. In PHBV with AL900, AL1100, DAL900, DAL1100, or HL900 - the five biochars with the largest reduction in thermal degradation temperature - the CO₂ peak occurs at an approximately 30 °C lower temperature than the primary

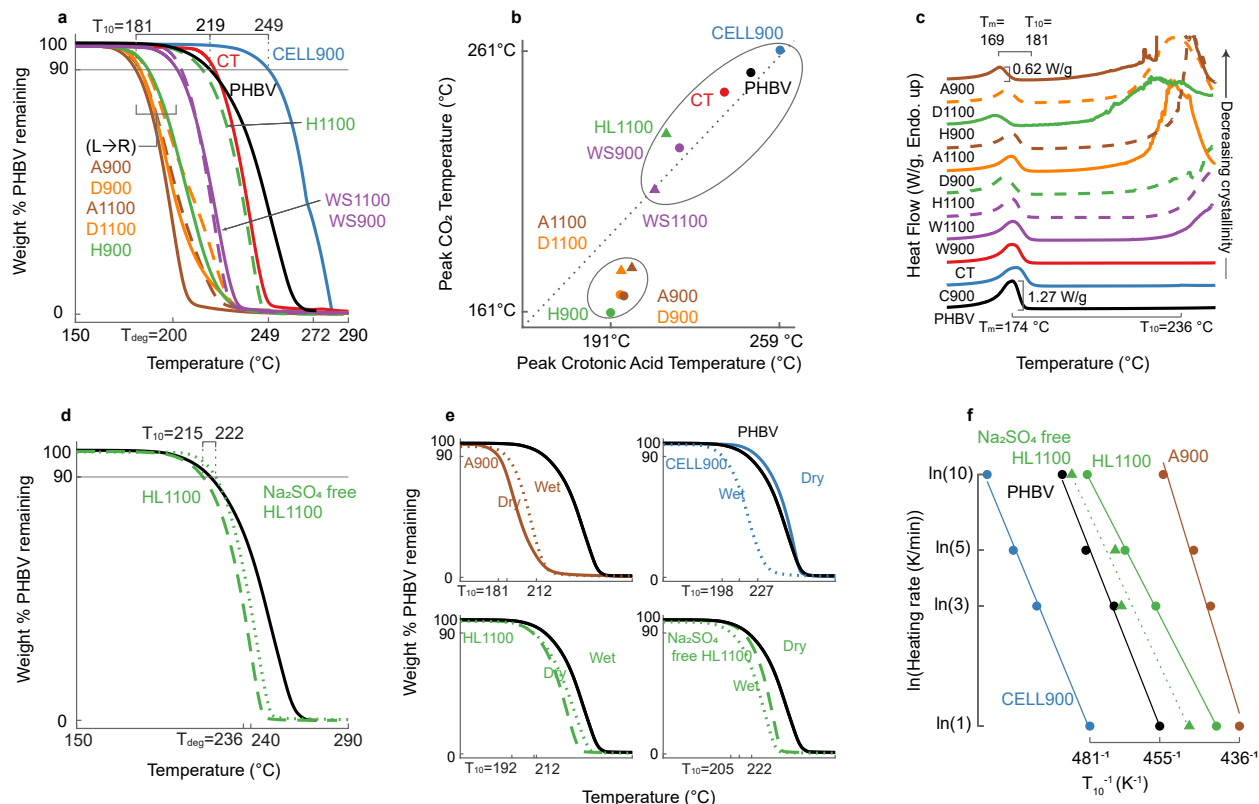


Figure 8.1: Thermal behavior of PHBV with the addition of various biochars. (a) TGA curves for PHBV with 20 wt.% of all biochars, with the onset (10 wt.% loss, T_{10}) and peak (max derivative, T_{deg}) for the lowest temperature degrading material (PHBV and AL900), control (PHBV), and highest temperature degrading material (PHBV and C900) marked. (b) Peak temperatures of crotonic acid vs. CO₂ thermal degradation product release for all biochar additions, as measured with TGA-IR. Two distinct mechanisms are highlighted. (c) Stacked DSC curves for melt and degradation of PHBV with all biochars. The range between melt temperature (T_m) and thermal degradation temperature as measured by TGA and melt peak heights highlighted for neat PHBV and PHBV with AL900. Curves are stacked in order of polymer crystallinity. (d) TGA curves showing the impact of removal of sodium sulfate (Na₂SO₄) from lignin-derived HL1100 biochar on thermal degradation behavior of PHBV with HL1100. (e) TGA curves showing the impact of storing biochar in a dry or wet environment on the thermal degradation behavior of AL900, C900, HL1100, and Na₂SO₄-free HL1100 with PHBV. (f) Arrhenius plot showing the kinetics of thermal degradation of composites of PHBV with C900, Na₂SO₄-free HL1100, HL1100, and AL900 biochar.

crotonic acid peak (Fig.8.1b). This CO₂ peak occurs at a lower temperature than thermal degradation temperature, indicating that this reaction is primarily due to the release of

CO₂ due to chain scission at the ester bond in PHBV, and is accompanied by limited mass loss, but results in a reduction in PHBV molecular weight. The increase in activation energy of PHBV with AL900 is attributed to this shift in mechanism requiring higher energy than the primary thermal degradation reaction of neat PHBV.

Addition of biochar to PLA was found to have similar trends in reduction in thermal degradation as PHBV (Figure 8.2a). A decrease in thermal degradation temperature is seen for all biochars except C900 and WS1100 relative to neat PLA, with decreases higher than 50 °C observed for most lignin-derived biochars (AL900, DAL900, DAL1100, HL900 and WS900). However, the kinetics of thermal degradation in PLA differ from PHBV, with decreased activation energy with decreasing thermal degradation temperature, from 300 kJ/mol for neat PLA to 180 kJ/mol for PLA with AL900. Unlike PHBV, no shift in PLA degradation products is seen with the addition of biochars that cause large decreases in thermal degradation temperature - for all biochar additions the primary gas evolution products of CO₂ and lactide peak at the same temperature. Combined, the kinetic behavior and thermal degradation products of PLA with biochar addition indicate that despite similar reductions in thermal degradation temperature to PHBV, the mechanisms that contribute to this reductions differ. Where as PHBV see difference in degradation products and increased activation energy in the lowest thermal degradation temperature biochar additions, PLA shows a decrease in activation energy and the same products.

To further explore biochars impact on PHBV and PLA, the impact of the addition of biochar to PHBV and the subsequent thermal degradation on the crystallinity and thermal transitions of PHBV was examined via DSC. Biochar additions that resulted in a large loss in thermal degradation temperature (AL900, DAL900, AL1100, HL900, DAL1100) decreased PHBV crystallinity relative to neat PHBV, with reductions between 14.8% crystallinity (DAL900) and 23.6% crystallinity (AL900) (Figure 8.1c). Samples with small losses or no change in thermal degradation temperature (WS900, WS1100, HL1100

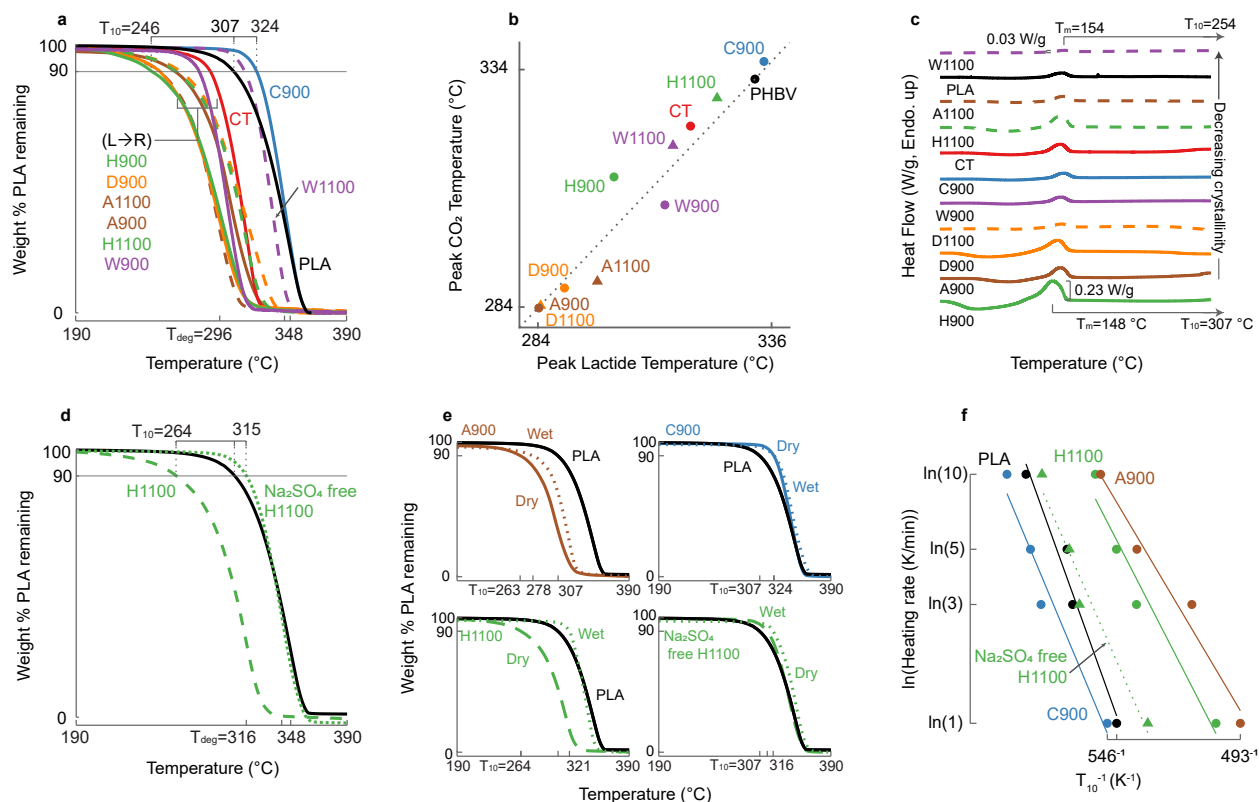


Figure 8.2: Thermal behavior of PLA with the addition of various biochars. (a) TGA curves for PLA with 20 wt.% of all biochars, with the onset (10 wt.% loss, T_{10}) and peak (max derivative, T_{deg}) for the lowest temperature degrading material (PLA and HL900), control (PLA), and highest temperature degrading material (PLA and C900) marked. (b) Peak temperatures of lactide vs. CO₂ thermal degradation product release for all biochar additions, as measured with TGA-IR. (c) Stacked DSC curves for melt and degradation of PLA with all biochars. The range between melt temperature (T_m) and thermal degradation temperature as measured by TGA and melt peak heights highlighted for PLA with HL900 and WS1100. Curves are stacked in order of polymer crystallinity. (d) TGA curves showing the impact of removal of sodium sulfate (Na_2SO_4) from lignin-derived HL1100 biochar on thermal degradation behavior of PLA with HL1100. (e) TGA curves showing the impact of storing biochar in a dry or wet environment on the thermal degradation behavior of AL900, C9000, HL1100, and Na_2SO_4 -free HL1100 with PLA. (f) Arrhenius plot showing the kinetics of thermal degradation of composites of PLA with C900, Na_2SO_4 -free HL1100, HL1100, and AL900 biochar.

and CT) all show modest (<7%) crystalline losses relative to neat PHBV and C900 gains 3% crystallinity relative to neat PHBV. Above the melt peak, the addition of all lignin and wheat stem-derived biochars results in a second phase transition in this region which

is attributed to thermal degradation. Neat PHBV and PHBV with biochars that increased thermal degradation temperature did not show the second transition in this region, a finding consistent with their higher thermal degradation temperatures. Notably, during the cooling cycle, no crystallization peaks were observed in PHBV samples with lignin or wheat-stem-derived biochars. Additionally, small decreases in PHBV melt temperature (3-6 °C) were found for the five biochars with the largest reduction in thermal degradation temperature (HL900, DL900, AL900, AL1100, and DL1100), indicating a reduction in polymer molecular weight [33]. In PLA, a more amorphous polymer than PHBV, limited shifts in crystallinity are observed (Figure 8.2c). However, for biochar additions that resulted in large losses in thermal degradation temperature, reductions as high as 6 °C are observed in the glass transition temperature and the melt temperature, indicating reductions in molecular weight of the PLA below the onset of thermal degradation [58, 59]. Only WS900, WS1100, and C900 show an increase in glass transition temperature relative to neat PLA and only WS1100 and C900 addition result in an increase in melt temperature, both of which increase thermal degradation temperature relative to neat PLA.

Combined, DSC and TGA-IR data indicates that the addition of most biochars examined result in a loss in molecular weight in PHBV and PLA that occurs at temperatures commonly used for melt processing. In PHBV composites with most lignin-derived biochars thermal degradation begins within 5 °C of the melting temperature, eliminating any possibility of melt processing the material without thermal degradation. This finding is supported by reduced thermal degradation temperature, crystallinity, glass transition temperature, and melt temperature and increased CO₂ release during heating of PHBV or PLA with addition of these biochars. However, the severity of this impact varies by biochar, with some biochars - in particular C900 improving thermal stability of PHBV. This finding provides evidence against the hypothesis that observed reductions in thermal stability are an inherent issue with biochar. As the samples examined herein were never

extruded, the hypothesis that increased degradation is due to shear heating during extrusion can be rejected as the sole mechanism for losses in thermal degradation. Further, that some biochars increase thermal stability, as well as past studies that finding mechanical interlocking between biochar and polymers [16] provide evidence against the hypothesis that biochar improves chain mobility of polymers.

A regression model and further TGA experiments were used directly test the two other hypotheses: that moisture and oxygen trapped in the pores of the biochar increase rates of hydrolysis and oxidative degradation and that metals present in biochar catalyze thermal degradation. A regression model considering the impacts of biochar surface area, particle size, moisture content, and metal content on thermal degradation of PHBV or PLA was applied to test these hypotheses. This model found that decreasing biochar surface area and increasing metal content significantly reduced the thermal degradation of PHBV ($p < 0.01$ for both) and that increasing biochar metal content and particle size significantly reduced the thermal degradation temperature of PLA ($p < 0.05$ for both).

To experimentally test the impact of metals, 95% of the sodium present in the highest electrical conductivity biochar (HL1100) was removed with a simple washing procedure (Extended Data Figure E.1). The resulting biochar (Na₂SO₄-free HL1100) slightly increased the thermal degradation temperature of both PHBV and PLA compared to a slight decrease for untreated HL1100, supporting this hypothesis (Figure 8.1e). To examine the impact of biochar moisture content on PHBV and PLA, AL900, C900, HL1100, and Na₂SO₄-free HL1100 biochar samples were stored in a humid environment, resulting in a moisture content of approximately 25%, compared to an average of 3% for biochar stored in a drying oven (Extended Data Table E.2). The impact of this treatment on PHBV and PLA thermal degradation varied by biochar. In AL900 and HL1100, which showed decreases in thermal degradation temperature when dry, moisture treatment increased thermal degradation temperature in both neat PLA and PHBV, in the case of HL1100 to a higher level than neat

PHBV and PLA. In contrast, in C900 and Na₂SO₄-free HL1100 moisture treatment slightly decreased thermal degradation temperature for PHBV, and no change is observed for PLA. This difference in behavior is attributed to inadvertent washing of Na₂SO₄ out of AL900 and HL1100 during moisture treatment. In contrast, in C900 and Na₂SO₄-free HL1100 no metals were present to be removed, and increasing the moisture present decreased the thermal degradation temperature of PHBV. Following removal of Na₂SO₄, activation energy of PLA with HL1100 increased from 209 kJ/mol to 247 kJ/mol, further indicating an increase in thermal stability. Combined, these experiments provide evidence supporting the hypothesis that metal content is the primary factor driving reductions in thermal stability of PHBV with the addition of biochar. Moisture content may have some additional impact, but can be mitigated with proper storage of biochar in a low-moisture environment.

The findings of the statistical model and experimental testing are supported by past work examining the impact of metal ions on the thermal degradation of PHBV and PLA. The presence of hard Lewis acid metal ions Ca²⁺ and Mg²⁺ catalyze the thermal degradation of PHBV by acting as electrophiles that catalyze scission of the polymer chain [345, 346]. Na⁺, which is present in lignin-derived biochars in the form of Na₂SO₄ is also a hard Lewis acid and a stronger electrophile than Ca²⁺ [347]. Therefore, we conclude that the presence of Na⁺ ions from sodium sulfate are responsible for the decrease in thermal degradation temperature observed with the addition of lignin-sourced biochars to PHBV, and similarly with K⁺, Ca²⁺, and Mg²⁺ ions present in WS based biochars. In contrast, C900 and CT, both showed an increase in thermal degradation temperature and contained limited levels of Ca²⁺, Mg²⁺, and Na⁺. The simple, green chemistry process of water and centrifugation was used herein to remove sodium sulfate from lignin-derived biochar is similar processes have already been applied at scale to remove sodium sulfate from lignin and inorganics from biochar for agricultural application [116]. This process has the potential to be scalable and economically viable. Similar processes could be developed to remove Lewis acids from

biochar feedstocks other than lignin, allowing for a diverse set of biochars to be applied as a filler material in biodegradable plastics without decreases in their thermal degradation temperature.

Combined, the statistical and experimental results provide strong evidence in support of the hypothesis that inorganic compounds present in the biochar catalyze the thermal degradation of PLA and PHBV. The finding that C900, CT, and lignin-derived biochar with inorganics removed can increase the thermal degradation temperature of PLA and PHBV provides evidence against the currently accepted hypothesis that decreased thermal degradation temperature is an inherent issue with biochar-filled PLA and PHBV. As past studies have found that this decrease in thermal degradation temperature negatively impacts the mechanical properties of biochar-PLA composites [189, 338], this finding not only improves the ease of processing of biochar-PLA and PHBV composites but improves their final material properties, allowing for them to be applied to a larger set of applications. Using the methods developed herein to reduce biochar metal content, or by selecting metal-free biochar feedstocks, biochar-filled PLA or PHBV can be applied to improve the viability of a new class of biocomposites. Improvements in mechanical properties with biochar addition have been broadly examined [11], allowing for higher strength biocomposites than previously available. Further, addition of biochar to PLA and PHBV can meaningfully reduce the greenhouse gas emissions associated with production of these plastics and biochar is currently available at lower cost than either PLA or PHBV, improving cost competitiveness of these materials with conventional plastics [326]. The unique combination of a biodegradable plastic and biochar soil amendments can be applied in agricultural applications to both improve PLA biodegradation rates, reduce agricultural plastic pollution, and deliver a soil amendment. In food packaging, biochar-PLA composites have shown improved anti-microbial properties compared to neat PLA, and in agricultural applications, biochar has potential to both act as a filler in the plastic and as a soil amendment once the plastic degrades [180]. Biochar has

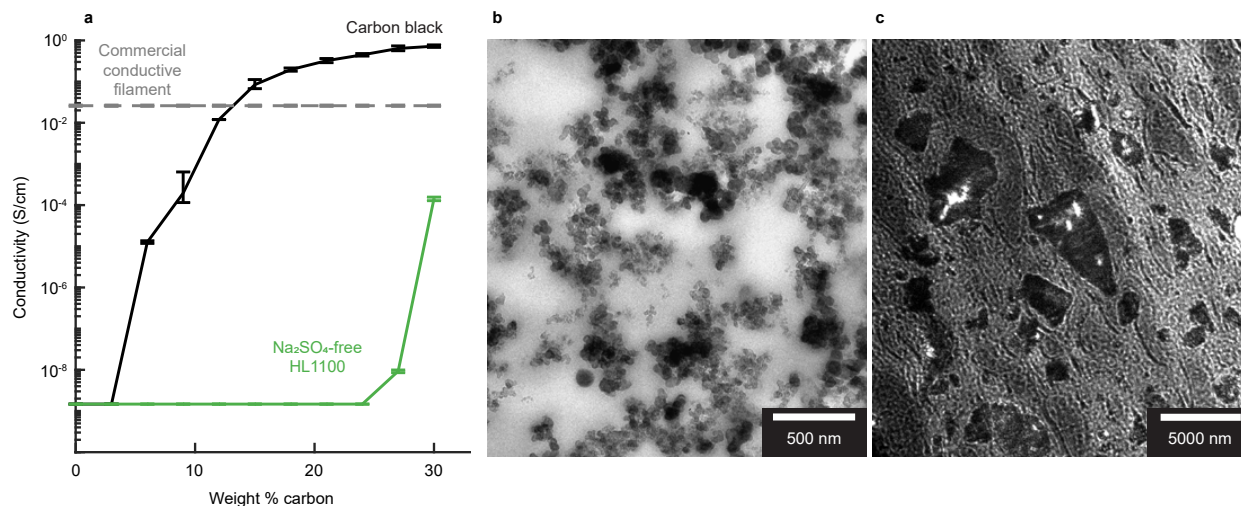


Figure 8.3: (a) Electrical conductivity of composites of an 80:20 PHBV:PLA blend with Na₂SO₄-free HL1100 or carbon black, compared to a commercial electrically conductive filament, which is independent of the x-axis. Error bars represent one standard deviation in resistance, calculated from three replicates. (b,c) TEM images of (b) carbon black and (c) Na₂SO₄-free HL1100 at 15 wt.% loading in 80:20 PHBV:PLA blends.

previously been found to increase the biodegradation rate of PLA [56, 338] - if this finding is maintained without the reduction in molecular weight, biochar addition may improve degradation rates of PLA in the natural environment.

Application of biochar-PHBV/PLA composites to produce electrically conductive materials

To demonstrate biochars promise in electrically conductive applications a composite sample of a polymer blend of 80 wt.% PHBV and 20 wt.% PLA, which has been shown to reduce the percolation threshold of carbon black relative to un-blended polymers [92], was prepared with 0-30 wt.% Na₂SO₄-free HL1100. At 30 wt.% biochar addition the electrical conductivity of this composite was 1.4×10^{-4} S/cm (Figure 8.3). In contrast, a similar composite prepared with electrically conductive carbon black was found to have an electrical conductivity of 0.72 S/cm - approximately four orders of magnitude higher. Further the onset of percolation in the carbon black composite is observed at 6 wt.% carbon black addition, while with biochar the onset of percolation occurs at 27 wt. % addition, and the

electrical conductivity is still in the percolation region at 30 wt. % addition. The composite containing carbon black have higher electrical conductivity than the commercial electrically conductive filament above 15 wt.% carbon black addition, with a 280% improvement in electrical conductivity at 30 wt.% carbon black. Addition of higher loadings of biochar to further improve electrical conductivity is limited by processing challenges of 3D printing high filler loading materials.

As this carbon black and biochar have similar electrical conductivities [141], we attribute the drastic difference in electrical conductivity between these two composites to geometric differences that remain between carbon black and biochar. Transmission electron microscopy images of 15 wt.% carbon black and biochar composites show clear differences in morphology (Figure 5.4b and c). Carbon black shows its expected, "fluffy" aggregate morphology with nodules sizes on the order of 100 nm and aggregate sizes on the order of 1 μm [348], leading to good dispersion in the polymer that is hypothesized to result in its low percolation threshold. In contrast, the biochar has a blocky morphology and particle sizes of 5.5 μm as a result of the ball milling procedure used. This blocky structure results in biochar particles not creating an electrically conductive network at low biochar loadings, resulting in the observed poor electrical conductivity and high percolation threshold.

While this study has resolved thermal issues with biochar as a sustainable alternative to carbon black, further development remains limited by biochar's blocky morphology. This critical issue prevents development of unique, electrically conductive, biodegradable, and 3D printable materials from biochar. Spray pyrolysis methods, such as those used to produce carbon black, may provide an alternative processing method to produce "fluffy" biochar with a nodule structure more similar to carbon black. The high solubility and softening behavior of lignin make it a promising feedstock for spray pyrolysis, as it may be more easily converted to a liquid form than other biomass waste streams.

Conclusions

Alkali and alkaline earth metals present in biochar were identified as critical factors that reduces the thermal degradation of PLA and PHBV. In lignin-derived biochars where these metals are present as sodium sulfate, these metals are easily removed with water, allowing for the creation of a new class of biocomposites with unique properties. By applying this finding, biochar fillers can be applied in PLA and PHBV to improve the mechanical properties of biocomposites relative to natural fibers, reduce environmental impacts and costs of PLA or PHBV, or to improve biodegradation rates and act as a soil amendment at the materials end-of-life. The high electrical conductivity of biochar shows promise for the creation of unique, 3D printable and biodegradable electrically conductive materials from composites of PLA and PHBV with biochar. However, the percolation threshold of ball milled biochar is much higher than that of carbon black. This results in poor electrical conductivity of biochar composites at loading levels required for additive manufacturing. If a method can be developed to produced biochar with morphology more similar to carbon black, this unique combination of electrical conductivity and biodegradability has the potential for reduced costs and environmental impacts across a broad range of sensing applications in the agricultural and environmental industries. As demand continues to rise for alternatives to conventional plastics, the findings herein create a path for biochar to play an important role in expanding the application of PLA and PHBV across a diverse set of industries and applications.

Methods and Materials

Materials

Alkaline and dealkaline lignin were purchased from TCI America (Portland, OR, USA). Solid stem wheat was provided by the Montana State University Agricultural Research and

Teaching Farm (Bozeman, MT, USA). Cellulose was purchased from Sigma-Aldrich (St. Louis, MO, USA). Laboratory isolated lignin was provided by the Dr. David Hodge Research Group (Montana State University, Bozeman, MT). This lignin was isolated with an alkali process, as described in detail in previous work [220]. All biochar feedstocks were stored in a drying oven at 105 °C until use.

A commercially produced biochar, CoolTerra, was used as a point of comparison for the laboratory produced biochars. It was provided by CoolPlanet (Greenwood Village, CO, United States).

PHBV pellets and powder (ENMAT Y 1000p and ENMAT Y1000, >98% purity) were provided by Tianan (Nigbo City, China). PLA pellets (2003D) were provided by Nature Works (Minnetonka, MN, USA). PLA and PHBV were stored in a desiccator at <5% relative humidity prior to use.

Biochar production

Biochar was produced in a tube furnace with a heating rate of 10 °C/min, a maximum temperature of 900 or 11100 °C and a dwell time of 1 hr as previously described [143]. The physical and chemical structure of all lab-produced biochars have been previously characterized [143]. The commercial biochar, CT, was characterized with identical methods used for other biochars. A summary of the chemical and physical structure of biochars is shown in Table E.2.

Characterization of biochar impact on PHBV and PLA

The effects of biochar on the thermal properties of PLA and PHBV is examined with thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA was performed on a TA Instruments Q5000IR TGA, with evolved gas measured by a Thermofisher iS10 Fourier transform infrared spectrometer, with TGA-IR accessory. For all samples 8 ± 0.1 mg of PLA or PHBV was combined with 2 ± 0.05 mg biochar, and stored in a desiccator

until immediately prior to measurement. Samples were heated from 30 °C to 900 °C with a heating rate of 10 °C/min in HT-platinum pans, under a 25 mL/min flow of nitrogen gas.

To determine activation energy of thermal degradation, TGA was ran on samples of PLA or PHBV with AL900, HL1100, Na₂SO₄-free HL1100, and C900 with the parameters described above, but with a heating rate of 1, 3, 5, or 10 °C/min. Activation energy was calculated with a critical degradation level of 20%, with the Ozawa-Flynn-Wall method [349].

Differential scanning calorimetry was performed on a TA Instruments Discovery DSC 250. For all samples 8 ± 0.1 mg of PLA or PHBV was combined with 2 ± 0.05 mg biochar in a TZero DSC pan. Both PLA and PHBV samples were heated from 25 °C to 190 °C, then cooled to -20 °C and heated back to 250 °C before cooling back to 25 °C at a rate of 10 °C/min under a 10 mL/min flow of nitrogen gas. The crystallinity of each polymer sample was determined as described by Kessler [299], with 100% crystallinity values of 146 and 93.7 J/g for PHBV and PLA respectively.

In addition, TGA and DSC were performed on 10 mg of neat biochar sample with the same procedure, to identify any thermal transition or degradation inherent in the biochars.

Composite production and electrical conductivity

Composites of biochar or carbon black (Cabot Vulcan XC-MAX22) and a 80 wt.% PHBV-20 wt.% PLA polymer blend were melt compounded (Thermo Fisher Scientific HAAKE Minilab II dual screw extruder) at 190 °C and 50 rpm for 5 min, and injection molded (Thermo Fisher Scientific Minijet Pro injection molder) into a flexural mold (Thermo Fisher part #557-2295) with a injection pressure of 750 bar, a post-pressure of 450 bar, an injection temperature of 190 °C and a mold temperature of 60 °C. Composites were produced from 0-30 wt.% carbon additive every 3 wt.%. The electrical conductivity of the resulting composite material was characterized with a four-point probe via a Keithly 2540 Sourcemeter. Electrical conductivity was measured in triplicate for all samples.

As a comparison, an injection molded sample is prepared from a commercial electrically conductive filament (Protopasta Electrically Conductive Composite PLA) and the electrical conductivity is measured.

Extended data to this chapter is shown in Appendix E

REDUCING THE ENVIRONMENTAL IMPACTS OF PLASTICS WHILE INCREASING
STRENGTH: BIOCHAR FILLERS IN BIODEGRADABLE, RECYCLED, AND
FOSSIL-FUEL DERIVED PLASTICS

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Abstract

In this study, material characterization and a cradle-to-gate life cycle assessment methodology are applied to examine how the addition of biochar as a filler in recycled plastics (rHDPE) influences material properties and environmental burdens. Environmental impacts for these composites are then compared to biochar fillers in virgin HDPE and bio-based polylactic acid (PLA) and polyhydroxybutyrate (PHB). At 40% biochar addition to rHDPE, biochar increased the tensile strength by 45%, stiffness by 126% and flexural storage modulus by 79% but resulted in a more brittle material. Biochar addition detrimentally effects the thermal degradation of both PLA and PHB, resulting in reduced mechanical properties. Increased biochar loading linearly reduced the global warming potential of all plastics relative to neat plastic by up to 3.3 kg CO₂ eq. per kg of composite, with a dual benefit of reducing the amount of plastic used and creating a net-uptake of carbon in the biochar. Similarly, biochar decreased the fossil fuel depletion of PLA, PHB, and HDPE, but additional transportation-related emissions and the low fossil fuel depletion for neat rHDPE caused biochar addition to increase fossil fuel depletion for rHDPE. While changes in material application and end-of-life were outside the scope of this study, biochar is expected to provide further end-of-life benefits to the biodegradable PHB or PLA. Importantly, this study demonstrates that biochar can be applied to produce carbon-neutral composite materials when added to a wide variety of plastics and demonstrates the potential of biochar to reduce the environmental impacts of plastic materials.

Introduction

Plastics are one of the most ubiquitous materials in modern society, but their production is highly dependent on petroleum resources, and they are currently responsible for notable environmental impacts [350, 351, 352]. As the use of plastic products continues to grow,

forecasts indicate that plastic production will be responsible for more greenhouse gas emissions than coal by 2030 [353] and the majority of the growth in global fossil fuel use by 2050 [350]. To address these challenges, new approaches are needed to mitigate these impacts and reduce reliance on fossil resources during the manufacturing of plastic products.

One strategy proposed to reduce the negative environmental impacts of plastics is the addition of biochar as a filler material in the plastic. Biochar is a high carbon-content material produced by pyrolysis of biomass and has been extensively studied as a method to sequester carbon [12, 98, 287]. The material properties of biochar vary based on its feedstock and processing; with optimal processing, biochar can be produced with comparable properties to standard fossil fuel-derived carbon filler materials (e.g., carbon black) [19, 114, 143]. Because of these beneficial properties, biochar has been widely studied as a filler material in plastics. Typically, the addition of biochar improves the strength and stiffness of fossil-fuel-derived plastics, across a wide variety of plastic types and biochar feedstocks [11, 18, 174, 185, 255, 290, 291, 292, 343, 354]. For example, a recent study found that addition of 50 wt. % rice husk-derived biochar to HDPE results in a 146% increase in flexural strength, a 200% increase in tensile modulus, an 11% increase in tensile strength, and a 40% increase in tensile modulus [185]. In contrast, the addition of biochar to biodegradable plastics (e.g., PLA or PHB) reduces the thermal stability of the material, resulting in decreased mechanical properties of the biodegradable plastics [56, 92, 181, 183, 184, 189, 266, 338].

Numerous life cycle assessments have examined the environmental impacts of wood-plastic composites (WPCs) and shown the relative GHG reductions compared to neat petroleum based plastic polymers [355, 356, 357, 358]. Despite the environmental benefits of WPCs, various limitations include inferior mechanical properties and dimensional instability which could reduce the service life of these materials, leading to potentially higher environmental impacts due to product replacement [109]. Biochar offers numerous mechanical and environmental benefits over wood, including increased flexural and tensile

strength [109, 289, 291], utilization of a wider variety of waste materials, and the propensity to sequester carbon for a longer period of time due to biochar's high chemical stability [359]. Past life cycle assessment studies have found that biochar can reduce certain environmental impacts of plastic products relative to petroleum-derived filler materials [178, 179, 360]. However, these studies have been limited in scope to automotive products and have not examined waste-derived biochar (such as biochars from agricultural or forestry waste that have been commercialized for soil amendment and carbon sequestration). Further, these studies have only examined biochar addition to polypropylene. The environmental impact of biochar addition to other petroleum derived plastics and recycled or biobased plastics remains a crucial gap to understanding how biochar can be utilized to drive reductions in the environmental impacts of plastics and their products.

In this study, we conduct both mechanical property and environmental impact comparisons between recycled high-density polyethylene (rHDPE) with and without biochar filler. Specifically, tensile and flexural properties are assessed with varying filler levels, and we apply a cradle-to-gate environmental impact assessment methodology to examine the environmental impacts of biochar as a filler material. To draw comparisons and elucidate additional environmental benefits that could be achieved with biochar as a filler, its application in two biodegradable plastics (polylactic acid (PLA) and polyhydroxybutyrate (PHB)), and a fossil-fuel derived plastic (HDPE) are also examined through environmental impact assessments; however, experimental analysis of the material properties of these additional composites is outside the scope of this work. We hypothesize that the addition of biochar would decrease the global warming potential, as well as other environmental impacts, for all non-recycled plastic types by replacing virgin material with a waste-derived material. Given the recent, rapid growth in interest in applying biochar as a filler material in plastic, this study builds a vital platform to begin to understand how biochar can be applied to reduce the environmental impacts of a diverse set of plastic products.

Methods

Experimental methods

Composite production Composites of biochar and rHDPE were produced to examine the impact of biochar addition on plastic mechanical behavior. Pacific Biochar (Santa Rosa, CA, USA [361]) supplied wood-derived biochar (85% carbon with an O/C molar ratio of 0.21) produced from forestry residues. Prior to extrusion, this biochar was ball milled for 2.5 min at 30 Hz (1800 rpm) in a Retsch Mixer Mill 400 to reduce particle size, a ball milling procedure which has been previously shown to reduce biochar particle sizes to $<10\ \mu\text{m}$ [143] and dried at 105 °C to reduce moisture content. Recycled high-density polyethylene (rHDPE) was provided by Northwest Polymers (Moalla, OR, USA). To demonstrate the impact of Pacific Biochar on the thermal degradation of biobased plastics, PLA was supplied by NatureWorks (2003D, Minnetonka, MN, USA) and PHB was supplied by Tianan (ENMAT Y3000P, Ningbo City, China).

Composite materials of rHDPE with 0%, 20%, and 40% biochar addition were prepared to represent a range of biochar addition (no, medium, and high amounts). Composites were compounded in a Thermo Fisher Scientific HAAKE Minilab II dual screw extruder for 5 minutes, at a speed of 100 rpm and a temperature of 190 °C. Rheology data were collected during extrusion to verify sample mixing and consistent biochar addition between batches (Supplemental Figure F.2). Samples were extruded into a Thermo Fisher Scientific MiniJet Pro injection molder and injected into Thermo Fisher Scientific DMA three-point bending sample mold (Part #557-2295, 10 mm $\times$ 60 mm $\times$ 1 mm) or Thermo Fisher Scientific ASTM D638 Type V tensile test mold (Part #557-2299). Samples were injection molded with a 190 °C barrel temperature and a 60 °C mold temperature. An injection pressure of 750 bar was applied for 10 s, followed by a post pressure of 450 bar for 60 s. Samples were produced in triplicate for both bending and tensile tests.

Composite testing The impact of biochar on the thermal degradation temperature of rHDPE, PLA, and PHB with 0%, 20%, and for rHDPE 40% biochar addition were measured with thermogravimetric analysis (TGA) on a TA Instruments Q5000 IR, with 20 mg samples. Samples were heated from 30 °C to 900 °C at a rate of 10 °C/min. Differential scanning calorimetry (DSC) was used to measure shifts in the melt peak and melt enthalpy on injection molded rHDPE samples with 0%, 20%, and 40% biochar addition on a TA instruments Discovery DSC 2500. Samples were heated from −80 °C to 250 °C, then cooled to −20 °C at 10 °C/min. Sample crystallinity was determined based on the ratio of sample melt enthalpy to 100% crystalline melt enthalpy (293 J/g for HDPE) [299].

The tensile and flexural strength and modulus of the biochar-filled plastics were examined for changes to strength as a function of filler content. A three-point bending fixture measured the flexural dynamic modulus with a TA Instruments Q800 dynamic mechanical analyzer (DMA). Samples of HDPE and 0%, 20%, and 40% biochar were heated from 30 °C to 100 °C, with a frequency of 1 Hz, amplitude of 20 μ m, and a force track of 125%. Tensile strength and modulus were measured on an MTS C43 load frame with a load rate of 5 mm/min and a gauge length of 35 mm from clamp to clamp. All DMA and tensile tests were measured in triplicate for each sample type.

Environmental impact assessment methods

Environmental impact assessments were conducted in four stages: goal and scope, life cycle inventory analysis, impact assessment, and interpretation of results. The goal of this assessment was to examine how plastics with different origins are impacted by biochar addition. Four plastics (rHDPE, HDPE, PLA and PHB) were analyzed with 0, 20, and 40 wt. % biochar-filler on a cradle-to-gate scope, with use phase and end-of-life being excluded. This system boundary is depicted in Figure 9.1. The inventory flows for this model included the material flows and energy requirements associated with bio-based and

petroleum plastic production, plastic and biochar extrusion and molding, and transportation impacts for a functional unit of 1 kg of material (plastic with or without biochar filler). The PLA production inventory was based on data from NatureWorks, which is the largest producer of PLA in the US [64]. The inventory for PHB was based on values from Miller et al. [67] due to the lack of available industry data. The carbon feedstocks for PLA and PHB were assumed to be corn and sugarcane, respectively. The inventories for HDPE and rHDPE were based on data from a US LCI database [3]. The electricity grid for all plastic production inventories was based on the 2015 US Energy Information Association (EIA) electricity grid data [362]. The inventory for biochar was based off of a study by Peters et al. [363]. However, changes were made to account for the fact that biochar is a waste residue rather than a by-product of poplar cultivation. In addition, unlike in the inventory from Peters et al, a credit was not applied to the syngas for the displacement of natural gas. Detailed inventories for each of the bioplastics as well as the biochar are provided as Supplemental Files [326]. The inventory for the injection molding process was based on the NREL US LCI database, but a California electricity grid mixed was used [364]. The inventory for transportation impacts were derived from Kamau-Devers and Miller 2020 [66].

For this work, biochar was modeled as being produced from biomass residues, and therefore no environmental burdens associated with biomass production were allocated to the char. However, it was assumed that the organic carbon present in the biochar is representative of the carbon dioxide (CO₂) taken up during photosynthesis. The amount of CO₂ taken up by the biochar was calculated using Equation 9.1 (where C_b is the carbon content in biochar (kg C/kg biochar)).

$$CO_2_{stored} = C_b * \frac{1molC}{12kgC} * \frac{1molCO_2}{1molC} * \frac{44kgCO_2}{1molCO_2} \quad (9.1)$$

The heating requirements for the pyrolysis process were assumed to be met using the

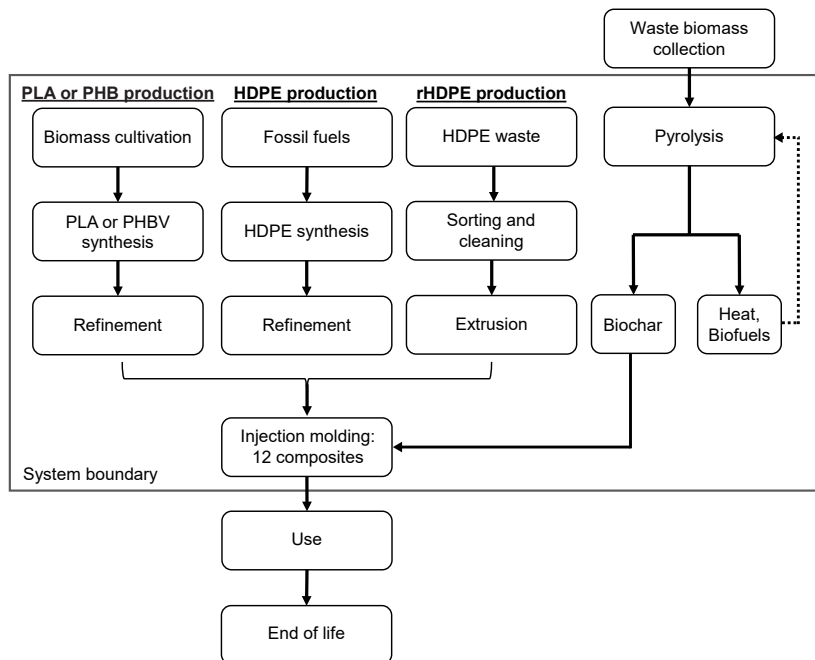


Figure 9.1: System boundary of this cradle-to-gate study.

gas and heat resulting from the pyrolysis process itself, therefore negating the necessity for external heat sources such as natural gas [363]. It was assumed that the biochar and plastics were each pelletized before being compounded together. The pelletization of the plastics was part of the inventories selected, and the pelletization of the biochar was modeled based on pelletization following extrusion melt blending with plastic [364]. The plastics and biochar were modeled as being combined via injection molding. If biochar and plastic were prepared at the same location, biochar addition and plastic pelletization could be combined as a single step process, improving the overall efficiency of the process [3]. The injection molding requirements for bioplastics with and without biochar were assumed to be the same given the negligible difference in heating requirements. Transportation assumptions were derived from Kamau-Devers and Miller 2020 [66]. The plastics and biochar were assumed to travel 200 km and 3340 km respectively to the composite manufacturing site.

The characterization factors from the Tool for the Reduction and Assessment of

Chemical and other environmental Impacts (TRACI) from the US Environmental protection agency were used for the environmental impact assessment [365]. This impact assessment method differs from others in that it utilizes input parameters based specifically on US data. This method was chosen due to the abundance of US based data in the life cycle inventories of the materials analyzed. The interpretation of results included an uncertainty analysis, which was conducted using input parameters from Kamau-Devers and Miller 2020 [66] who used a quantitative uncertainty method based on pedigree matrices [366, 367]. These uncertainties were modeled using distributions for each input, and Monte Carlo simulations were run to determine distributions of anticipated environmental impacts ($n = 10,000$). Median outputs from these simulations are presented in the results.

Results

Experimental results

Addition of biochar to rHDPE had a minimal effect on the thermal degradation temperature of rHDPE (Figure 9.2a). Only limited ($<3\text{ }^{\circ}\text{C}$) shifts were seen in both onset and peak thermal degradation temperatures for 20% and 40% biochar addition relative to neat rHDPE. Small mass losses ($<2\%$) were observed in both 20% and 40% biochar samples prior to the onset of rHDPE thermal degradation, which are attributed to increased moisture adsorption with the addition of biochar, as has been observed in past studies examining biochar addition to plastics [56]. Similarly, addition of biochar has minimal impact ($<1\text{ }^{\circ}\text{C}$) on the melting and crystallization temperatures of rHDPE. The glass transition temperature of rHDPE and its composites were not measured, due to the typically low glass transition temperature of HDPE ($<-80\text{ }^{\circ}\text{C}$). In contrast, biochar addition had a meaningful impact on the crystallinity of rHDPE - as biochar loading increases from 0% to 40% crystallinity increased from 54% to 81% (Supplemental Table 7.1). This increase in crystallinity is consistent with what has previously been observed for addition of biochar to petroleum-

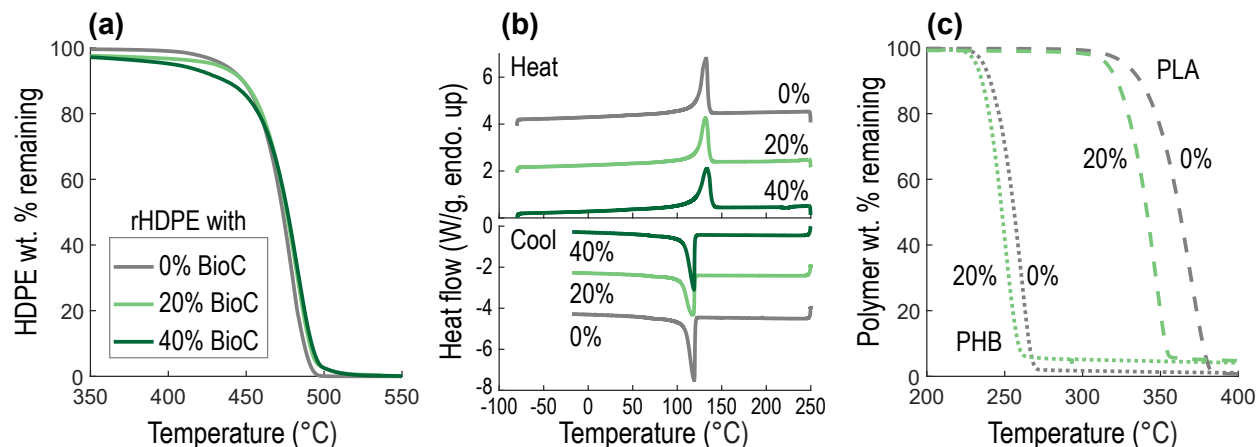


Figure 9.2: Thermal characterization of rHDPE and biochar composites with 0%, 20%, and 40% biochar addition showing (a) TGA curves in the region of rHDPE degradation, (b) DSC heating (top) and cooling (bottom) curves, and (c) TGA curves for composites of PLA and PHB with 0% and 20% biochar addition, showing the decrease in thermal degradation temperature with the addition of biochar.

derived plastics [291, 338]. TGA measurements of PLA and PHB with biochar addition highlight the challenges of applying biochar as a filler material in these plastics. In both cases the addition of 20% biochar reduces the peak temperature of thermal degradation, by 7 °C in PHB and by 23 °C in PLA. This decrease has previously been widely observed in studies examining biochar and PLA or PHB composites and has been attributed to alkali and alkaline earth metals (e.g., Na or Ca) catalyzing the thermal degradation of PLA or PHB, resulting in reduced polymer chain length and poor mechanical properties [92, 184, 295, 338]. Therefore, the mechanical properties of biochar-filled PLA or PHB are not examined in this study.

The tensile behavior of the rHDPE was notably altered by the inclusion of biochar (Figure 9.3). The addition of biochar at both 20% and 40% levels increased the tensile strength and stiffness of rHDPE. The tensile strength increased from an average strength of 22.19 ± 0.81 MPa for neat rHDPE to 28.06 ± 0.88 MPa at 20% biochar addition and to 32.29 ± 0.70 MPa at 40% biochar addition, with variations representing one standard deviation

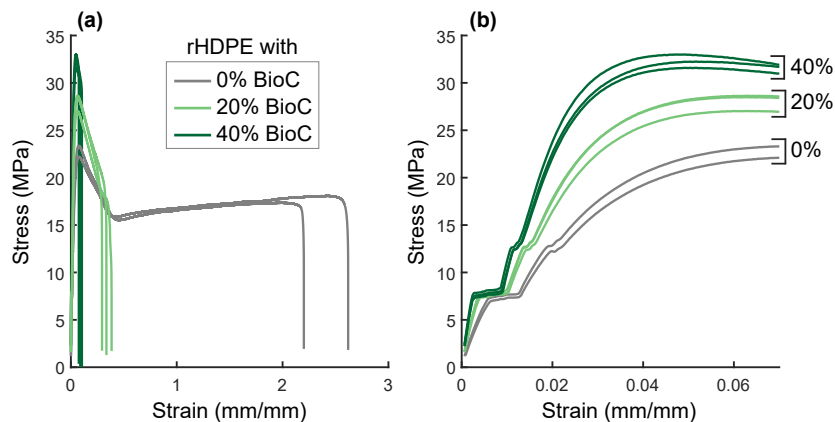


Figure 9.3: Stress-strain curves from tensile test data of rHDPE with 0%, 20%, and 40% biochar addition, with (a) the full range of strain and (b) a detailed view of the initial loading region, prior to peak stress.

between the three measured samples. A similar trend is seen in the tensile modulus, with average Young's modulus values and standard deviations of 606 ± 2.50 MPa, 859 ± 81.7 MPa, and 1371 ± 51.8 MPa at 0%, 20%, and 40% biochar addition, respectively. Along with these increases in strength and stiffness, the addition of biochar modified the failure behavior of rHDPE. For the neat rHDPE, after the peak in tensile stress ($\epsilon=0.07$ mm/mm), a period of strain softening is observed (from $\epsilon=0.07$ to 0.4 mm/mm), followed by a period of mild strain hardening until failure, consistent with expected failure behavior for rHDPE [368]. In contrast, our results showed samples with 20% biochar addition fail immediately following the strain softening phase, and samples with 40% biochar addition exhibit brittle failure immediately following the peak in stress. Accompanying this greater degree of brittleness with biochar is a decrease in strain to failure, from 2.41 ± 0.30 mm/mm at 0% biochar addition to 0.089 ± 0.015 mm/mm at 40% biochar addition. The improvements in strength and stiffness of rHDPE with the addition of biochar are consistent with past studies examining biochar addition to HDPE and other fossil fuel-derived plastics [174, 175].

Like the tensile results, flexural DMA results show that increasing biochar content increases the loss and storage moduli of rHDPE (Figure 9.4). At low temperatures (30 °C),

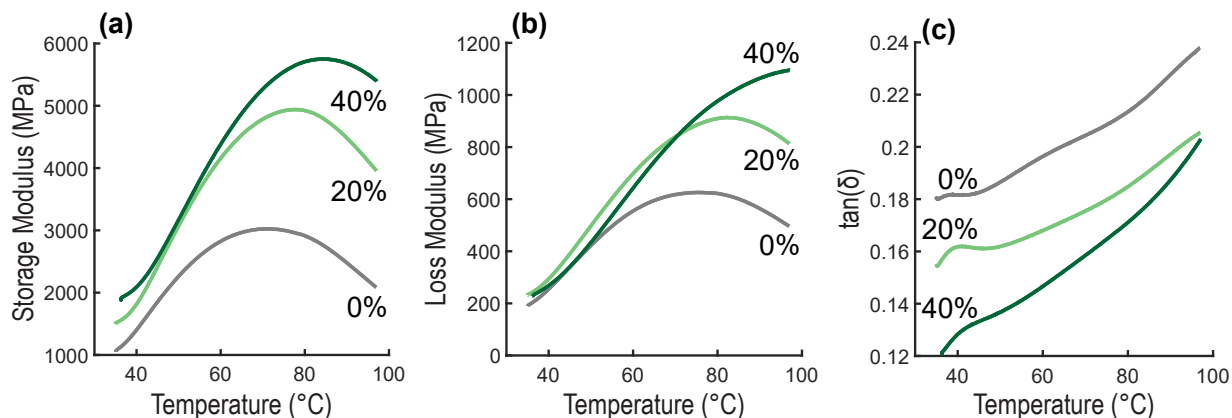


Figure 9.4: DMA data for rHDPE composites with 0%, 20% and 40% biochar, showing (a) storage modulus, (b) loss modulus and (c) $\tan(\delta)$ as a function of temperature (see Supplemental Figure F.3 for replicate curves).

the differences between 0%, 20%, and 40% biochar addition are small relative to higher temperatures, with an increase of 43% and 79% of the storage modulus of neat rHDPE for 20% and 40% biochar addition, respectively. Similarly, relatively minor differences are seen in the loss modulus at lower temperatures. As temperature increases, differences between storage modulus at 0%, 20%, and 40% biochar content also increase, indicating that the addition of biochar may also improve the heat deflection temperature of rHPDE. The tangent of delta decreases with increasing biochar content, indicating a more elastic response, a finding consistent with the increase in elastic modulus observed via tensile testing.

Life cycle assessment results

For all plastic types, the addition of biochar decreases the global warming potential of the material, with a linear relationship between the amount of biochar added and the reduction in global warming potential (Figure 9.5a). The addition of biochar to plastic materials provides a dual benefit of reducing both the global warming potential associated with plastic production and creating a net-uptake of CO_2 in the biochar. This dual benefit results in approximately twice the percent reduction in GWP as percent addition

of biochar (e.g., a 20% biochar addition results in an approximately 40% reduction in global warming potential). The highest percent change is noted for rHDPE, which has limited GWP associated with plastic production, and for which the utilization of a biochar filler at 40% suggested the potential for net-uptake composites. In contrast, PHB had the lowest percentage change as it has the highest GWP associated with plastic production and as a result, maintained relatively high global warming potential even with biochar filler. For most plastic types, a similar trend to GWP is seen for fossil fuel depletion (Figure 9.5b). However, rHDPE shows a negligible increase in fossil fuel depletion with biochar addition; this result is a function of the production of the material, which requires little fossil fuels relative to the additional transportation step. The addition of biochar to PLA, rHDPE, and HDPE contributes to limited change in acidification and respiratory effects (Figures 9.5c&d). However, in PHB, the addition of biochar results in decreases in these impact categories. This decrease is due to the relatively large acidification and respiratory effects associated with PHB production relative to PLA or petroleum-derived plastics [67]. Other environmental impact indicators (ozone depletion, smog formation, eutrophication, human health cancer, human health noncancer, and ecotoxicity) were examined (Supplemental Figure F.4) and showed similar trends to those of acidification and respiratory effects.

For all plastics except rHDPE, the magnitude of the impact is dominated by the production of the plastic (Figure 9.6). This constituent production makes up over 70% of the global warming potential and 60% of the fossil fuel depletion for all percent biochar additions, with the percentage increasing with increasing biochar content. Similar trends are seen for acidification, respiratory effects, and other impact indicators (Figure 9.6 and Supplemental Figure F.5). Conversely, in rHDPE, this relationship is not present as the sorting and recycling process requires less energy than the production of virgin HDPE, PHB, or PLA. For rHDPE, the global warming potential and fossil fuel depletion values are driven by the energy required for injection molding and the negative global warming

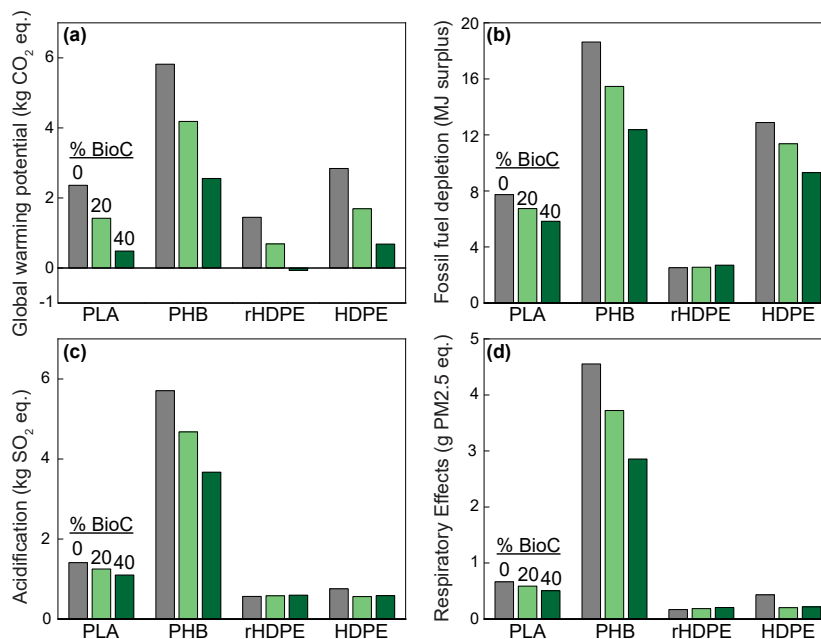


Figure 9.5: Environmental impact assessment results for PLA, PHB, rHDPE, and HDPE for 0%, 20%, and 40% biochar addition. Impact indicators of (a) global warming potential, (b) fossil fuel depletion, (c) acidification, and (d) respiratory effects are shown. Other impact indicators in the TRACI weighting schemes are presented in Supplemental Figure F.4.

potential of the biochar. Differences in total impact between each plastic type, regardless of impact category, are primarily a result of differences in plastic production. The increased transportation-related impacts required to transport biochar for the addition were minimal relative to these differences between plastics.

Discussion

The increase in strength and stiffness of HDPE with the addition of biochar is consistent with the findings in past studies [174, 175]. These studies have identified that the addition of biochar results in increased modulus and strength via three mechanisms: changes in polymer crystallinity, the high modulus of biochar, and polymer interlocking with the porous structure of biochar [16]. The large increase in crystallinity observed in this study is consistent with

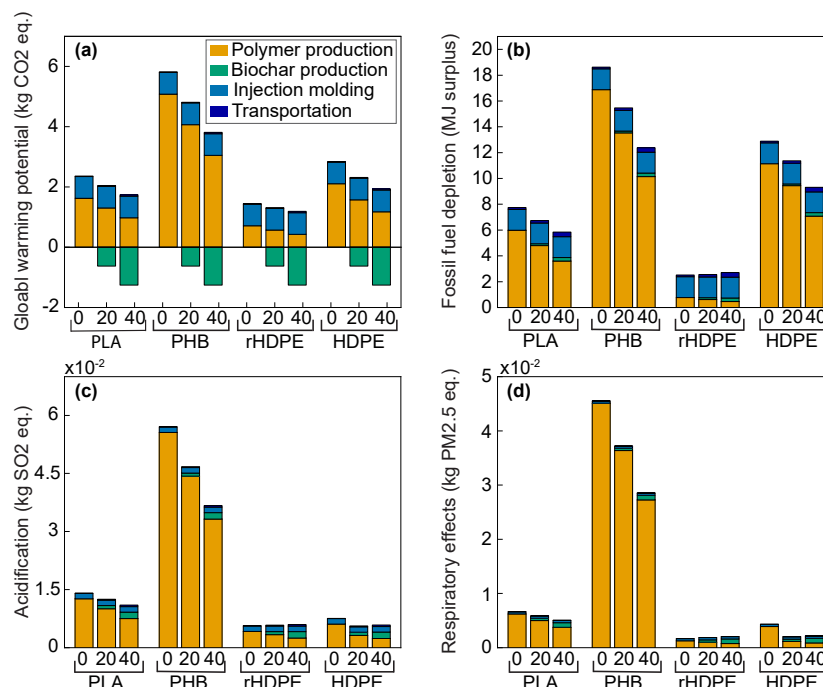


Figure 9.6: Stacked bar plots of (a) global warming potential, (b) fossil fuel depletion, (c) acidification and (d) respiratory effects by constituent and processing step for composites of 0%, 20%, and 40% biochar with HDPE, rHDPE, PLA and PHB. Other impact categories are shown in Supplemental Figure F.5.

these mechanisms and would be expected to result in a stronger and more brittle material as observed in this study [369, 370]. As biochar has previously been found to have a high modulus relative to polymers [16], the increase in stiffness of rHDPE with the addition of biochar is jointly attributed to the increase in crystallinity of rHDPE and reinforcement by the biochar particles. The morphology of biochar composites was not examined in this study, but past studies of wood-derived biochar have found the highly macroporous structure of biochar to interlock with the polymer matrix, resulting in a good interface between the materials, which is expected to contribute to strong mechanical performance [289, 291, 354]. Further, past studies have found biochar addition to improve mechanical properties that were not examined in this study, including creep resistance, impact resistance, and flexural strength [17, 174]. While the impacts of biochar addition on virgin HDPE were not examined

in this study, it is expected to result in similar shifts in mechanical behavior as in rHDPE.

A key finding of this study is that biochar could provide sufficient reduction in global warming potential to produce a cradle-to-gate carbon-neutral or negative material when added to plastic, while increasing plastic strength. The amount of biochar needed to reach carbon neutral varies depending on the plastic-type used. For example, the rHDPE examined in this study reaches 0 kg CO₂ equivalent with less than 40% biochar addition, while PLA and HDPE would require 50% and 52% biochar addition, respectively. While the mechanical properties of composites containing higher biochar loadings were not examined in this study, past studies have shown similar strength and stiffness between 40% and 50% biochar addition in HDPE [174]. In contrast to the other plastics, PHB requires 72% biochar to reach 0 kg CO₂ equivalent global warming potential, which would be expected to result in a significant reduction in composite strength.

Forestry residues were examined as the feedstock for biochar in this study, and they were assumed to have no emissions for production (other than the uptake of CO₂ during photosynthesis that resulted in the carbon content of the biochar). However, many studies, including past life cycle assessment studies of biochar-filled composites, have examined the growth of biomass specifically to produce biochar [178, 179, 360]. These studies have identified crop cultivation as a critical area to reduce emissions in biochar production, which is avoided by using waste-derived feedstocks [98, 178]. If biomass were cultivated for biochar production, additional emissions and land-use changes would need to be considered beyond what is shown in this work. Further, in this study, the avoided impacts of decomposition of the feedstock were not considered and may vary depending on how waste feedstocks would otherwise be disposed. This consideration may be more critical for high environmental impact waste feedstocks, such as food waste, where conversion to biochar may provide further reductions in global warming potential by avoiding the greenhouse gas emissions associated with the decomposition of the feedstock.

In addition to global warming potential considerations, shifts in material performance must be considered. The improvement in strength and stiffness of rHDPE with the addition of biochar and the brittle behavior at 40% biochar may change the target applications for the rHDPE-biochar composites. For example, the brittle behavior of 40% biochar is more similar to neat polyethylene terephthalate (PET) or polypropylene (PP) than neat HDPE, and high biochar content composites may be more desirable in applications where high failure strain is not needed [371]. In some applications, the impact on strength and stiffness from using biochar may allow for lower quantities of material to be used to meet the loading requirements, thus further reducing the environmental impacts of the final product.

If impacts are considered with a functional unit of volume per unit strength (e.g., m^3/MPa), rather than mass as used in this study, rHDPE and biochar composites can achieve greater reductions in global warming potential. Namely, with a 20% biochar filler content, the rHDPE composites achieve a 62% decrease in global warming potential on a strength basis relative to unfilled rHDPE, relative to a 48% decrease on a mass basis. Combined, the materials characterization and environmental impact assessment in this study highlight how biochar may be applied to result in a stronger material, with lower environmental impact. In common applications of disposable plastic, such as food packaging or takeout containers, biochar could be applied as a filler to fulfill multiple roles – for example acting as a colorant, increasing strength, increasing heat deflection temperature, while also reducing reliance on petroleum-derived materials and reducing total greenhouse gas emissions for the product. The improved properties of rHDPE with the addition of biochar could shift the polymer used in these applications, for example allowing for biochar-filled rHDPE to be used in takeout food packaging in place of PP, due to its higher stiffness and heat deflection temperature. If challenges with the thermal degradation temperature can be overcome, and similar mechanical increases to rHDPE achieved, this finding is particularly important for PLA and PHB, as more limited ranges of material properties are available for biodegradable

plastics than petroleum-derived plastics [372].

The observed increase in strength with the addition of biochar is particularly important for rHDPE, as plastic recycling typically decreases the strength of the plastic [373]. The improved strength of rHDPE with the addition of biochar may expand the applications for which rHDPE has sufficient strength. Further, as the biochar examined in this study is currently inexpensive relative to rHDPE, biochar addition to plastic may improve the economic viability of the recycling industry [374, 375]. Replacement of virgin HDPE or other plastics with rHDPE filled with biochar may further reduce the environmental impact of these materials as rHDPE had lower environmental impacts across most impact categories studied.

Despite these benefits to the mechanical properties of fossil-fuel-derived plastics, past studies have shown that the addition of biochar to PLA and PHB reduces the thermal degradation temperature and molecular weight of these polymers, resulting in poor mechanical properties and processing challenges [17, 92, 181, 183, 184, 189, 338]. This decrease has been hypothesized to be due to the presence of inorganic compounds in the biochar catalyzing chain scission of the polymer [189, 338]. As the Pacific Biochar examined in this study contained inorganics (Supplemental Figure F.6), the mechanical properties of PLA and PHB were not studied herein. These inorganics may be removed with washing steps (e.g., with water or hydrofluoric acid) [116], but this processing step was not considered in our environmental impact assessment, as the exact processing depends on the biochar feedstock and desired level of inorganic removal. However, the addition of these processing steps would be expected to result in an increase in certain environmental impact categories (e.g., increased water use, additional energy required to heat water, or energy required to separate biochar after washing). Addressing this issue remains a key gap to the application of biochar as a filler material in PLA or PHB.

Importantly, as this study focused on the cradle-to-gate impacts of biochar addition

to plastics, any changes to the material use phase or end-of-life impacts were not examined in this study. Depending on the desired application for biochar-filled plastic, it may be necessary to examine changes in material environmental wear and fatigue failure to determine the full life cycle impacts of biochar addition. Further, the biochar addition may impact the material's end-of-life depending on the disposal method. If the plastics are landfilled (rHDPE, HDPE, PLA, or PHB), composted (PLA or PHB), or degrade in the environment (PLA or PHB), the carbon in the biochar is expected to remain sequestered, and in the case of composted PLA or PHB, to positively benefit both the rate of composting [56, 338] and the eventual compost application to agriculture [12]. However, if the material is combusted, the carbon in the biochar will not remain sequestered, potentially increasing the overall greenhouse gas emissions of the material. Further, the addition of biochar to plastic currently makes the material challenging to recycle [376], and therefore may reduce recycling rates for otherwise commonly recycled plastics, such as HDPE.

Conclusions

The environmental impact assessment conducted in this study highlights the potential for biochar to reduce certain environmental burdens, particularly the global warming potential and fossil fuel depletion, of a broad set of plastic materials. Further, our work suggests the addition of biochar improves the strength and stiffness of rHDPE, with a 45% increase in tensile strength and a 126% increase in tensile modulus at 40% biochar addition. A key finding of this study is that in rHDPE, HDPE, and PLA, biochar addition can result in a carbon-neutral material at the factory gate at 40-50 wt.% biochar addition. While use-phase and end-of-life stages were outside the scope of our environmental impact assessment, biochar addition to biodegradable plastics can increase biodegradation rates, while in landfilled plastics the biochar will continue to sequester carbon stored in biochar. This work supports the rapidly growing interest in applying biochar as a filler material in

plastics by quantifying the potential environmental benefits of using biochar filler in a variety of plastics in addition to modifying the material properties.

BIOCHAR AS A RENEWABLE SUBSTITUTE FOR CARBON BLACK IN
LITHIUM-ION BATTERY ELECTRODES

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Manuscript Information

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Abstract

Lignin-derived biochar was prepared and characterized towards potential applications as a conductive electrode additive and active lithium host material within lithium-ion batteries (LIBs). This biochar was specifically selected for its high electrical conductivity, which is comparable to that of common conductive carbon black standards (e.g., Super P). As an active material, this biochar exhibits a higher lithiation capacity than graphite under high current rates relevant to rapid-charging applications, though not as high as other biochars optimized for high surface area. Further biochar optimization would be needed to retain a higher capacity as an active electrode material while maintaining a low average anodic potential and minimal overpotential. Nevertheless, owing to its high electrical conductivity, this biochar serves as an effective conductive additive within electrodes comprised of graphite as the active material, demonstrating slightly improved cell efficiency and rate capability over electrodes using carbon black as the additive. Despite its effectiveness as a conductive additive in LIB anodes, preliminary results show that the biochar developed in this work is not suitable as a direct replacement for carbon black as a conductive additive in LiFePO_4 (LFP) cathodes. This latter insufficiency may simply be due to differences in particle geometry between biochar and carbon black; further optimization is necessary to permit the application of biochar as a general-purpose conductive additive in LIBs. Nevertheless, these investigations combined with an environmental impact assessment show that replacing carbon black with biochar can be an effective method to improve the sustainability of LIBs.

Introduction

The wider application of electrochemical energy storage devices, especially lithium-ion batteries (LIBs), is a critical component of strategies to reduce the global reliance on fossil fuels and slow global warming. However, several fossil-fuel-derived products are still

commonly used in fabricating most LIBs, including artificial graphite and carbon black, along with several other minor components. In addition to being derived from fossil fuels, producing these materials results in greenhouse gas emissions of up to 2.4 kg CO₂ equivalent per kg carbon black or up to 4.4 kg CO₂ equivalent per kg artificial graphite [2, 377]. In order to make LIBs more sustainable and less reliant on fossil-fuel-derived chemicals, the development of high-performance carbon materials from renewable feedstocks is needed.

A possible alternative to petroleum-derived graphite and carbon black is high-temperature biochar. Biochar is produced by the pyrolysis of biomass, resulting in a solid, carbonaceous powder (similar materials are also referred to as biocarbon, carbonized biomass, activated carbon, non-graphitized carbon, and char) [94, 102]. The physicochemical properties of biochar, and therefore the inherent electrical conductivity, vary depending on the feedstock and pyrolysis conditions used. With optimal processing conditions, biochar can be produced with comparable chemical composition and electrical properties to commercial carbon black [111, 114, 140, 143, 378, 379]. In particular, biochar produced from lignin feedstocks shows higher biochar yields than that produced from other biomass precursors [132, 143]. Recent studies have demonstrated lignin-derived biochar to have higher electrical conductivity than that produced from whole biomass at the same temperature [143]. Further, lignin is a well-known waste byproduct of the papermaking industry and biorefinery processes; upcycling waste lignin into a valuable product can improve the sustainability of these industries and advance the circular economy [380].

Biochar has previously been studied as an alternative active material to graphite in the anode of LIBs [20, 140, 172]. Like other synthetic disordered carbons (e.g., activated carbons), biochar can be produced that exhibits higher specific capacity than graphite via increased surface and edge adsorption in a “house of cards” type model of capacitive ion storage [170]. The performance of biochar as an active anode material is dependent on the electrical conductivity, graphitic structure, porosity, and chemical composition of the biochar

[132, 171]. Specifically for lignin-derived biochar, varying performance has been reported depending on the source of the lignin, pyrolysis conditions, and pre- and post-pyrolysis processing [132, 168, 381, 382, 383]. Despite strong interest in biochar as an active material, little attention has been given to biochar as an alternative conductive additive in the anode or cathode of LIBs, which typically account for up to 10% of the total mass of the electrode. In fact, all previous studies applying biomass-derived carbon as the active material in LIBs still use petroleum-derived carbon black as the conductive additive. The similar disordered graphitic structure and electrical conductivity of biochar to carbon black demonstrate its potential as an alternative to carbon black in electrode applications [111, 114, 143, 378].

Herein, we evaluate the use of high electrical conductivity biochar as both the conductive additive and active electrode material in typical liquid organic electrolyte-based LIBs. Biochar was produced by direct pyrolysis at 1100 °C from alkali lignin isolated from hybrid-poplar wood; the isolation and characterization of this lignin have been extensively detailed elsewhere [220]. This biochar was compared against a standard commercial carbon black (Super P) and high-performance graphite as the conductive additive and active material, respectively. Preliminary work was also carried out to determine the efficacy of the same biochar as a conductive additive within a standard LiFePO_4 (LFP) cathode. Based on its similar materials properties to Super P, we hypothesized that highly conductive lignin-derived biochar would be an effective and renewable alternative for carbon black as a conductive additive without needing to alter any of the processing conditions or other components of the LIB. The results shed insight into the role of particle size and shape, in addition to inherent materials properties as playing a crucial role in permitting the use of biochar as a conductive additive in LIBs.

Experimental methods

Methods

A benchmark, high-performance commercial graphite with extensively reported electrochemical properties [384] was obtained from Sigma-Aldrich (product #282863, 20 μm nominal particle size) as a standard active anode material. Two commercial carbon blacks were obtained for comparison to biochar: Super P (Timcal Ltd.) and Vulcan XC-72R (Cabot Corp.). A standard active cathode material, LiFePO_4 (LFP) was obtained from MTI Corp. (battery grade, median diameter: $3.5 \pm 1.0 \mu\text{m}$).

The following materials were used in the preparation of electrochemical cells: lithium hexafluorophosphate (LiPF_6 , battery grade, Gotion Inc.), ethylene carbonate (EC, battery grade, Gotion Inc.), ethylmethyl carbonate (EMC, battery grade, Gotion Inc.), fluoroethylene carbonate (FEC, battery grade, Gotion Inc.), lithium metal (chips, 99.9%, MTI Corp.), glass microfiber discs ($0.67 \times 257 \text{ mm}$, GF/D grade, catalog number 1823-257, Whatman), polyvinylidene fluoride (PVDF, 99.5%, MTI Corp.), N-methyl-2-pyrrolidone (NMP, 99.0%, Sigma-Aldrich), copper foil (thickness: 9 μm , MTI Corp.), and aluminum foil (thickness: 15 μm , MTI Corp.).

Biochar synthesis

Lignin was isolated from an NM-6 hybrid poplar genotype with an alkaline pre-extraction treatment at 95 $^\circ\text{C}$, as previously described [220]. To reduce moisture content, the so-isolated lignin was stored in a drying oven at 105 $^\circ\text{C}$ for at least 24 h prior to pyrolysis. Biochar was produced by the pyrolysis of 1 g of lignin in an alumina boat (100 mm $\times$ 20 mm $\times$ 13 mm) within a tube furnace fitted with an alumina work tube (Mini Mite, Lindberg/Blue M) under nitrogen atmosphere [99]. The heating zone was purged at 100 mL min^{-1} for 10 min prior to heating; the flow was reduced to 30 mL min^{-1} during pyrolysis. The furnace

temperature was ramped at $10\text{ }^{\circ}\text{C min}^{-1}$ to a maximum temperature of $1100\text{ }^{\circ}\text{C}$, held at the setpoint for 1 h, then allowed to cool to room temperature. After pyrolysis, the resulting biochar was triple washed with deionized water to dissolve sodium sulfate impurities and then dried at $105\text{ }^{\circ}\text{C}$. To reduce particle size, the biochar was then ball-milled (Mixer Mill 400, Retsch) at 30 Hz (1800 rpm) for 2.5 min with a 50 mL steel jar and a 25 mm steel ball, and then stored in a drying oven at $105\text{ }^{\circ}\text{C}$ until use.

Materials characterization

Fourier transform infrared spectroscopy (FTIR) was performed using a Thermo Fisher Nicolet iS10 FTIR spectrometer with a Smart iTX ATR accessory employing a diamond crystal. FTIR spectra were collected between $600\text{--}4000\text{ cm}^{-1}$ at a resolution of 4 cm^{-1} and with 64 scans per sample and analyzed using SpectraGryph software (v. 1.2.14, Friedrich Menges Software-Entwicklung). Raman spectroscopy was performed using a Horiba LabRam HR Evolution spectrometer outfitted with a confocal microscope. Raman spectra were collected using a $50\times$ long working distance objective, 1800 gr/mm grating, and by irradiation with a frequency-doubled Nd:YAG laser (532 nm) operated at 1-10 mW. The spectra were fitted and analyzed as described elsewhere [207]. X-ray diffraction (XRD) was measured using a Bruker D8 Advance powder X-ray diffractometer with $\text{Cu K}_{\alpha 1,2}$ radiation. XRD patterns were collected between $5\text{--}80^{\circ}$ in 2θ using a step size of 0.02° per step. Scanning electron microscopy (SEM) was performed using a Zeiss Supra 55VP field-emission SEM operated at 1 kV with an SE2 detector, with a working distance of approximately 7.5 mm. Energy-dispersive X-ray spectroscopy (EDX) was performed during SEM using an Oxford Xplore detector. EDX spectra were measured at $250\times$ magnification with a working distance of 8.4 mm. Biochar and carbon black particle size distributions were measured with $\sim 100\text{ mg}$ of material using a Malvern 3000 laser diffraction particle size analyzer with distilled water as a dispersant.

Direct current (DC) electrical conductivity was measured under compression using a guard electrode setup as described in detail elsewhere [221]. Typically, 150 mg of biochar or carbon black was placed in the sample holder, and resistivity measurements were performed every 0.0127 cm (0.005 in) upon compression from the lower current limit of the source meter (Keithly 2450) until further compression could not be applied. All electrical conductivity measurements were performed in triplicate.

Electrode and cell fabrication

Seven different permutations of electrode composition were prepared, employing either graphite, LFP, or biochar as the active material and Super P, biochar, or no material as the conductive additive, as shown in Table 10.1. First, slurries were prepared by hand-grinding the active material (80 wt.%) with conductive additive (10 wt.%) and polyvinylidene fluoride (PVDF) as a binder (10 wt.%) in NMP as the solvent. In slurries where no conductive additive was used, the weight of the conductive additive was replaced with the active material. Next, the so-obtained slurry was uniformly cast onto a metal foil current collector using the doctor blade technique, dried at 80 °C for 12 h, and then transferred to a vacuum oven at 100 °C for an additional 12 h to remove moisture and solvent. Copper foil was used for electrodes containing graphite or biochar as the active material, while aluminum foil was used for electrodes with LFP as the active material. The resulting electrode was cut into disks with a diameter of 10 mm, with uniform loadings of 2.5-3.0 mg cm⁻² (± 0.2 mg cm⁻²). Coin cells (316 stainless steel, 2032 format) were assembled in an argon-filled glove box in a two-electrode configuration with lithium metal serving as the counter and reference electrode, a glass microfiber disc as the separator, and a solution of 1.2 M LiPF₆ in EC/EMC (3:7, by weight) with 2 wt.% FEC as the electrolyte (125 μ L per cell).

Table 10.1: Cell compositions (by weight) in this study.

		Active Material		
		Graphite	Biochar	LFP
Conductive Additive	Super P	80% Graphite	80% Biochar	80% LFP
		10% Super P	10% Super P	10% Super P
	Biochar	80% Graphite	90% Biochar	80% LFP
		10% Biochar		10% Biochar
	None	90% Graphite	90% Biochar	N/A

Note: all cells contained 10% PVDF binder as the remaining portion by weight.

Electrochemical characterization

Galvanostatic charge and discharge (GCD) profiles were measured in half-cell configuration for all cells using a battery cycler (CT30001A, Landt Instruments) within an incubator oven held at a constant temperature of 25.0 °C. For graphite and biochar as the active material, the lithiation process (discharging) was measured using a two-step constant current constant voltage (CCCV) protocol, and the delithiation process (charging) was measured using a single-step constant current (CC) protocol, between 0.05-1.5 V vs. Li/Li+. A CC formation cycle was first performed at a current rate of 0.1 C (where the C rate is defined as 370 mA g⁻¹ for both graphite and biochar) and then allowed to rest for 5 min before further cycling. For LFP as the active material, lithiation (charging) was measured using a CCCV protocol, and delithiation (discharging) was measured using a CC protocol, between 2.0-4.0 V vs. Li/Li+. In all cases, five initial cycles were carried out at 0.2 C (for a total

of 5 h during CCCV discharge) to establish a robust electrode-electrolyte interphase. The rate capability of each electrode was evaluated at current rates of 2 C, 4 C, 6 C, 8 C, 10 C, 20 C, and 40 C. The CCCV lithiation of graphite and biochar was performed until the total discharging time was 30, 15, 10, 7.5, 6, 3, or 2 min, respectively. Electrochemical impedance spectroscopy (EIS) was measured both in situ (in newly formed cells) and ex situ (on bare electrodes never cycled within a coin cell). For ex situ measurements, spectra were collected using a four-point probe to reduce the impact of system resistance, system inductance, and contact resistance using a Gamry Reference 600 potentiostat from 0.1 Hz to 100 kHz with an applied voltage of 0.5 mV.

Results & Discussion

Biochar characterization

The biochar produced in this study (referred to in previous work as HL1100 [143]) shows comparable electrical conductivity ($9.1 \pm 0.89 \text{ S cm}^{-1}$) to the commercial carbon black powders commonly employed as the conductive additive in LIBs: Super P ($7.959 \pm 3.1 \text{ S cm}^{-1}$) and Vulcan XC-72R ($6.9 \pm 2.0 \text{ S cm}^{-1}$) (Figure 10.1a). The carbon structure contributing to this electrical conductivity was explored using Raman spectroscopy and XRD. All three materials show broad D (1340 cm^{-1}) and G (1580 cm^{-1}) peaks in their Raman spectra, indicating nanocrystalline graphitic structure with significant disorder. Importantly, all three materials exhibit a similar G peak width of 116 cm^{-1} at the half-maximum and a D:G intensity ratio of 1.0 (Figure 10.1b). Similarly, XRD patterns of all three materials show the presence of broad (002) and (10 l) reflections characteristic of turbostratic graphite (Figure 10.1c). In biochar and both carbon black materials, the (002) reflection is shifted to a lower angle than pristine graphite, indicating increased interlayer distance. Consistent with the Raman spectroscopy results, the biochar exhibits a more prominent (10 l) family of reflections than either of the carbon black materials, indicating higher in-plane ordering.

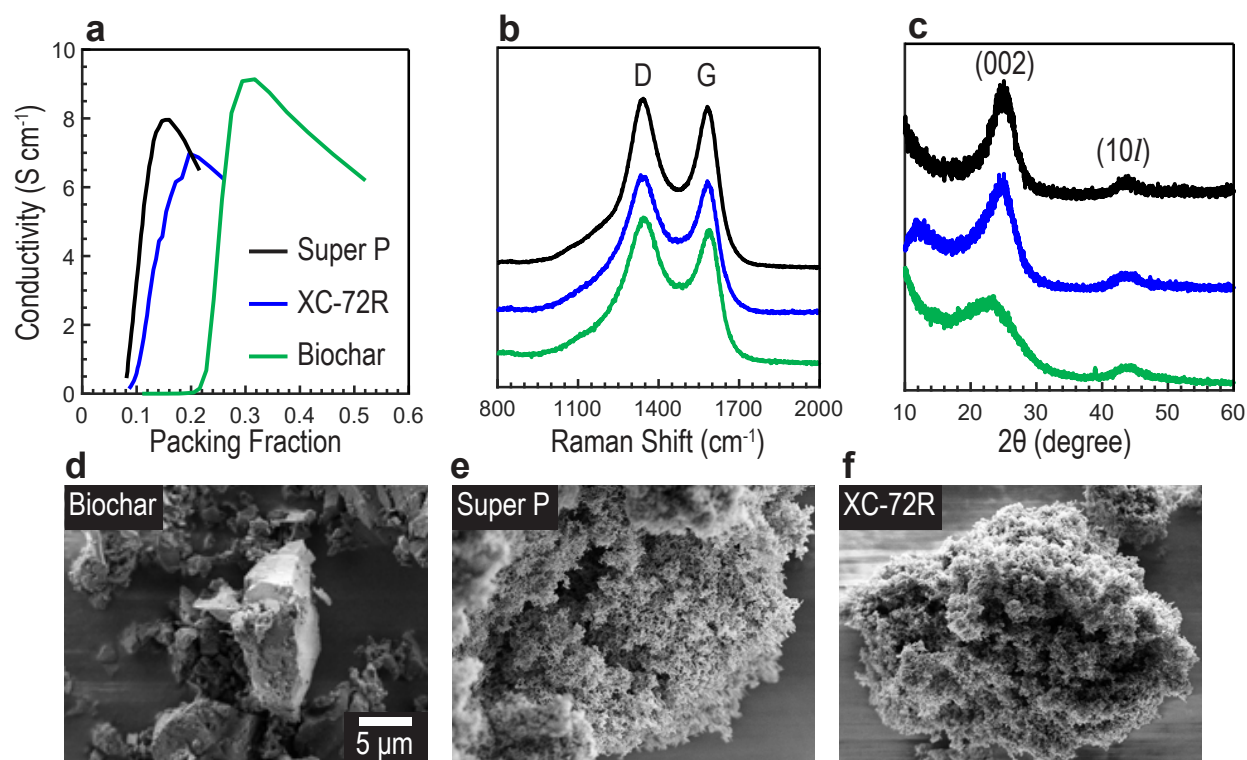


Figure 10.1: Materials properties of biochar compared to two commercial carbon black materials: Super P and Vulcan XC-72R. (a) Mean electrical conductivity as a function of packing fraction (the shaded region represents one standard deviation based on triplicate analysis). (b) Raman spectra as measured at an incident wavelength of 532 nm. (c) XRD patterns. (d-f) SEM micrographs at 6000 $\times$ magnification.

Hence, biochar's slightly higher electrical conductivity can be attributed to the existence of larger graphene domains than carbon black despite similar or perhaps poorer ordering along the stacking direction.

Despite similarities in electrical conductivity and graphitic structure, important differences in the particle morphology between biochar and the two carbon materials were observed upon electron microscopy investigation. A distinctively textured ("fluffy") surface structure was observed for Super P and Vulcan XC-72R. In contrast, biochar exhibits a more prismatic structure with smooth surfaces due to the ball-milling that was performed to reduce particle size (Figure 10.1d). Furthermore, biochar had a smaller median particle

size of 8.7 μm than either carbon black: 17.6 and 14.5 μm for Super P and Vulcan XC-72R, respectively (Figure G.2). As a result of these morphological differences, biochar has a higher unpacked bulk density than either carbon black, resulting in a higher electrical percolation threshold (Figure 10.1a). When considering chemical composition, EDX measurements indicate that biochar has higher oxygen content than either carbon black (Figure G.2). This oxygen content is directly proportional to defects within the graphitic carbon structure [102]. Before washing to remove inorganic impurities, sodium and sulfur were also observed in the biochar; FTIR and XRD reveal this as sodium sulfate (Na_2SO_4) (Figure G.2). Past studies have differed in their interpretation of the role that sodium sulfate plays during pyrolysis to produce biochar. Some studies hypothesize that sodium sulfate catalyzes the formation of graphitic structures, while other studies propose that sodium sulfate inhibits it [111, 112, 113]. After washing, limited sodium, and sulfur remain in the biochar, and no XRD peak corresponding to Na_2SO_4 is present (Figure G.2).

Electrochemical characterization

Electrochemical characterization of biochar compared to graphite within a half-cell configuration and using a standard LIB electrolyte is shown in Figure 10.2. At low current rates, the GCD profiles (Figure 10.2a) show that the typical staging features associated with the lithiation and delithiation of pristine graphite are lacking for the more disordered biochar. Most of the capacity in biochar is found within the sloped region of the GCD profile, which is consistent with a capacitive mechanism of charge storage typical of hard carbons [170]. At high current rates (using a CCCV lithiation protocol), the biochar displays nearly identical CCCV capacity to graphite (Figures 10.2b-d). For example, both biochar and graphite display capacities of ~ 160 and $\sim 120 \text{ mAh g}^{-1}$ at 4 C and 10 C rates, respectively. The similar capacity for both materials indicates that at high rates, charge storage at the electrode interface becomes dominant owing to limitations in ion mobility originating from higher

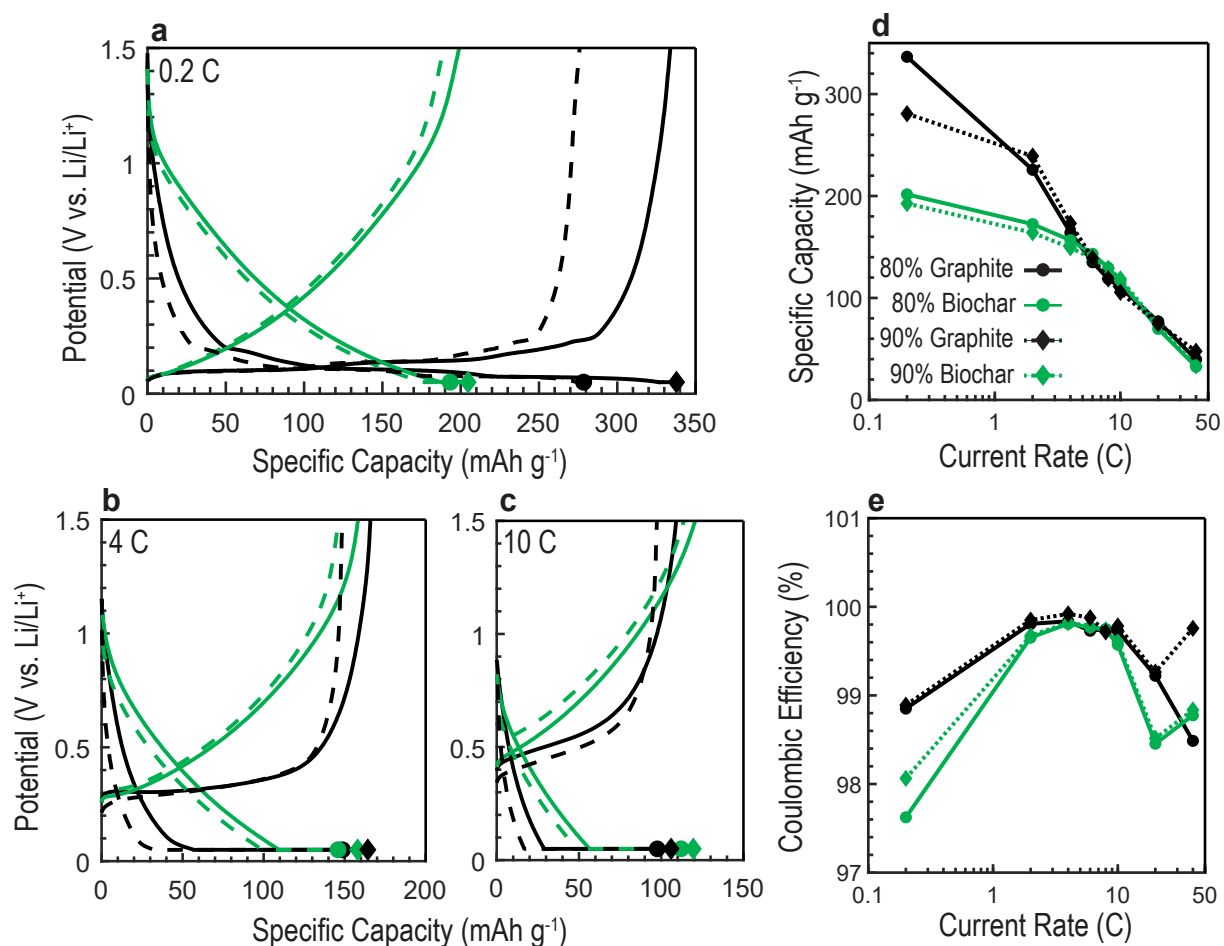


Figure 10.2: Comparison of biochar and artificial graphite as the active material in the anode of LIBs, with (80% active material) and without (90% active material) Super P conductive additive. Representative GCD profiles for graphite and biochar at charging rates of (a) 0.2 C, (b) 4 C, and (c) 10 C, with points indicating maximum discharge specific capacity prior to CCCV cutoff (additional measurements are shown in Figure G.3 and G.4). Rate capability measurements of graphite and biochar showing (d) capacity and (e) Coulombic efficiency for charging rates from 0.2 C to 40 C.

charge transfer resistance and solid-state diffusion within the graphite galleries. However, at low rates (0.2 and 2 C), graphite exhibits a much higher capacity than biochar as an active material (Figure 10.2a). This low-rate performance indicates that the biochar has a relatively low surface area accessible for ion adsorption compared to the inner “surface area” of the graphite galleries. There is no meaningful difference in Coulombic efficiency between

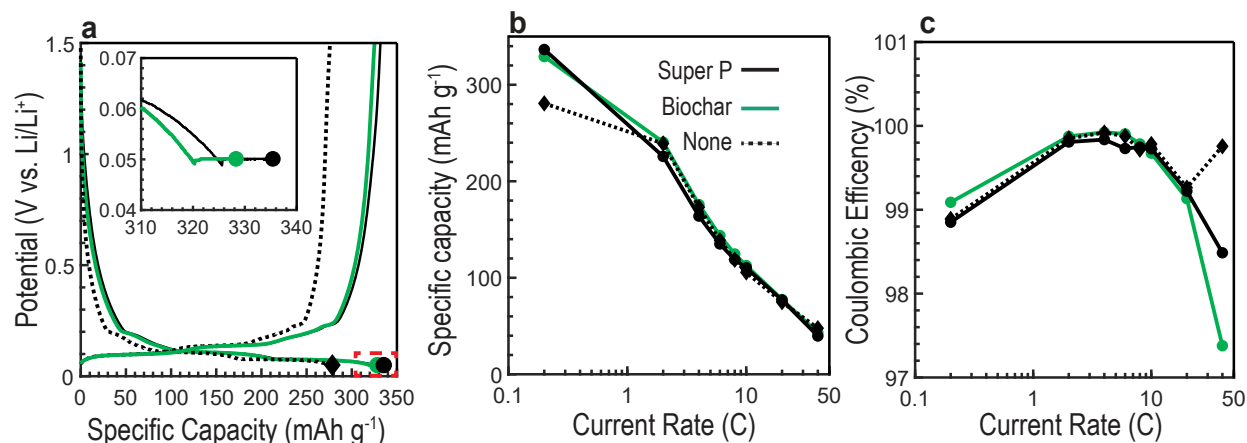


Figure 10.3: Comparison of Super P and biochar as the conductive additive in the anode of LIBs, with 80% graphite, 10% Super P or biochar, and 10% PVDF. (a) GCD profiles of graphite at 0.2 C. The inset highlights the region of maximum lithiation prior to CCCV cutoff (shown by the red box), with marked points indicating maximum discharge specific capacity prior to CCCV cutoff (additional measurements are shown in Figure G.5). Rate capability measurements of graphite showing (b) capacity and (c) Coulombic efficiency for charging rates from 0.2 C to 40 C.

graphite and biochar within this electrochemical protocol (Figure 10.2e).

Conductive additive in LIB anodes

Comparisons of biochar and super P as a conductive additive via GCD cycling and rate capability investigations show only minor differences between the two materials (Figure 10.3). There is no significant difference in the capacity of graphite measured at 0.2 C in the presence of either conductive additive (Figure 10.3a); the average specific capacity was 329.2 ± 1.4 mAh g⁻¹ for electrodes containing biochar and 336.5 ± 1.0 mAh g⁻¹ for electrodes containing Super P. This reduction in capacity can be observed in the discharge curve, where cells with biochar as the conductive additive reach the CC voltage cutoff (0.05 V) at a slightly lower capacity than Super P cells (Figure 10.3a, inset). The rate capability measurements at up to 40 C corroborate previous results [384] that the specific type of graphite chosen for this work exhibits excellent performance at extremely high current rates when combined

with a conductive additive. In the extremely high current rate regime, the capacity of graphite declines to $\sim 77 \text{ mAh g}^{-1}$ at 20 C and $\sim 40 \text{ mAh g}^{-1}$ at 40 C in the presence of both additives, though slightly higher with biochar than Super P. In the final measurements at 2 C, electrodes with biochar as the conductive additive exhibit a marginal increase in capacity ($237 \pm 16 \text{ mAh g}^{-1}$) relative to electrodes containing Super P ($209 \pm 20 \text{ mAh g}^{-1}$). All cells with either biochar or Super P as the conductive additive display a Coulombic efficiency of $\sim 100\%$ at current rates from 2-10 C (Figure 10.3c). Together, these results indicate that the biochar developed herein yields comparable performance as a standard conductive additive, Super P, commonly used in commercial LIBs.

The above results show that a 10 wt.% addition of biochar or Super P permits the full cycling of graphite at low current rates (0.2 C), where without any conductive additive, the performance of graphite is reduced by 17%. However, at higher rates, a similar capacity is found in cells with or without conductive additive. This difference can be attributed to a change in the primary charge storage mechanism at low and high current rates. At 0.2 C, the charge storage mechanism is primarily faradaic, and the electrical conductivity contributed by the conductive additive is needed to ensure connectivity of the entire electrode mass. At faster rates, the charge storage mechanism shifts to primarily capacitive. The similar performance at higher rates indicates that the electrode mass available for ion adsorption as opposed to intercalation is the same regardless of the presence of additive. Accordingly, cells with biochar as the active material exhibit a less significant decrease in low-current capacity in the absence of conductive additive than cells with graphite.

Conductive additive in LIB cathodes

In contrast to its effective application as a conductive additive in graphite-based LIB anodes, biochar was not found to be an effective additive within LFP-based cathodes in this work. Half-cells containing a standard commercial LFP powder as the active material

and biochar as the conductive additive in the working electrode exhibited no capacity. In contrast, control cells with Super P as the conductive additive exhibited a capacity of 218 mAh g⁻¹ at 0.2 C (normalized per mass of LFP). We hypothesize that this result is due to two major differences between biochar and Super P: the higher density of biochar and the fluffy morphology of Super P (a property it shares with other carbon blacks, such as Vulcan XC-72R). Together, these differences result in a higher electrical percolation threshold for biochar than Super P. This higher percolation threshold was observed in the packed powder electrical conductivity measurements presented herein (Figure 10.1a) and has also been previously observed for electrically conductive biochar in polymer composites [338]. This finding is further supported by ex situ four-point EIS measurements of the cathodes, which reveal that the impedance of the biochar-containing electrodes (>1.5 GΩ) is many orders of magnitude larger than that of Super P-containing electrodes (0.07 Ω). This limitation to the application of biochar as a universal conductive additive may highlight the importance of the fluffy particle structure of Super P. The texture of both Super P and Vulcan XC-72R is composed of small (<100 nm) nodules formed during spray pyrolysis, giving both materials a high void volume and low unpacked density [385]. When dispersed in the PVDF binder, this fluffy structure results in a reduced percolation threshold relative to the compact structure of biochar. Further investigation is necessary to understand how the biochar production process can be modified to combat this issue, whether by modifying the synthesis conditions or post-synthetic processing.

Environmental impact assessment

The production of an effective conductive additive for battery electrodes from lignin presents as a more sustainable alternative to the spray pyrolysis of fossil-fuel-derived chemicals. However, to date, no comprehensive study has been performed to determine the environmental impacts of biochar produced at temperatures higher than 900 °C. While

a comprehensive life cycle assessment is outside the scope of this study, the global warming potential of production of 1 kg of biochar is estimated. This estimate is based on the original carbon content of the lignin (56%), the biochar yield (27.2% or 3.7 kg lignin per kg biochar), and the carbon content of the resulting biochar (83.7%) [143] with the assumption that pyrolysis is net energy neutral [123, 124, 363] (more details are provided in the Supporting Information). This value should be compared to the greenhouse gas emissions required to produce 1 kg carbon black (2.4 kg CO₂ equivalent) [2] and that resulting from the atmospheric combustion of 3.7 kg lignin (7.7 kg CO₂ equivalent) which results in the additional production of 36.2 MJ of electricity [386]. The production of 1 kg of biochar results in net greenhouse gas emissions of 1.2 kg CO₂ equivalent, with additional emissions of 3.9 kg CO₂ equivalent produced to replace the energy that otherwise would be produced by combustion of the 3.7 kg lignin [362]. This results in a total estimated emission of 5.1 kg for the production of 1 kg of biochar, compared to 10.0 kg for the production of 1 kg of carbon black and the combustion of 3.7 kg of lignin. Therefore, the use of biochar rather than carbon black is estimated to reduce emissions by 4.9 kg CO₂ equivalent per kg of conductive additive used, a reduction of 49%. This decrease is primarily due to two factors: the production of biochar resulting in lower emissions (1.2 kg CO₂ equivalent) than the production of carbon black (2.4 kg CO₂ equivalent) and that energy produced by the combustion of lignin results in more emissions (0.209 kg CO₂ eq. MJ⁻¹) than the electricity grid (taken herein as the average emissions associated with the electrical grid in the United States in 2020: 0.108 kg CO₂ eq. MJ⁻¹) [362]. While no studies to date have examined the environmental impacts of high-temperature biochar, past studies have found the global warming potential of biochar production to increase linearly as temperature increases between 300-600 °C [387]. When this relationship is extrapolated to biochar produced at 1100 °C, a net global warming potential of -0.134 kg CO₂ equivalent per kg feedstock is estimated. This result is comparable to the estimate of -0.657 kg CO₂ equivalent per kg lignin derived herein, when not including

the avoided impacts of carbon black production. A complete life cycle assessment, including other environmental impact factors and the application and end-of-life stages of the material, is needed to fully compare the environmental impacts of biochar and carbon black as a conductive additive. Until this is performed, in the production phase, the use of biochar is estimated to reduce the global warming potential of the conductive additive for LIB electrodes relative to carbon black.

Discussion

As hypothesized, the pyrolysis of lignin at 1100 °C results in an electrically conductive biochar that is comparable to a standard carbon black (Super P) as the conductive additive in the graphite anode of LIBs. Slightly poorer capacity was exhibited by biochar-containing cells at low current rates, while slightly higher capacity was exhibited at high current rates, compared to Super P. These results indicate that biochar can be produced by a simple method as an acceptable replacement for carbon black in LIB anodes. However, the failure of the same biochar as a conductive additive in a standard LFP-based LIB cathode demonstrates the limitations of this material in replacing carbon black in all battery electrode compositions. Previous studies have successfully produced biochar with a “fluffy” morphology via spray pyrolysis [388]. Further investigations of similar approaches may result in a biochar material with a shape and density more similar to carbon black, while maintaining the strong electrical conductivity found in this study, to address the poor percolation behavior of the biochar produced by direct one-pot pyrolysis as investigated herein.

The biochar produced in this study exhibits a lower specific capacity as the active material than that reported for similar materials produced in past studies [132, 381, 382]. Such differences are likely owed to a difference in specific surface area (for capacitive-type charge storage) or in crystallinity (for intercalation-type charge storage), both of which can be widely varied by tuning the synthesis conditions. The biochar produced herein was

optimized with a focus on maximizing electrical conductivity rather than producing biochar with high surface area or a highly graphitic structure. Hence, the biochar in this study performs well as a conductive additive but foregoes a focus on the role of the additive in increasing the overall capacity of the electrode.

Conclusions

Biochar can be produced from lignin with limited processing and demonstrated to be comparable in terms of electrical conductivity and graphitic structure to standard commercial carbon blacks. The particle density and morphology achieved in this work serve biochar well as an effective replacement for carbon black as the conductive additive in the graphite-based anode of LIBs. However, the similar application of biochar in an LFP-based LIB cathode is ineffective, likely owing to its high percolation threshold relative to carbon black. This biochar was selected based on its high electrical conductivity rather than surface area or ordered graphitic structure that has been prioritized in past investigations of biochar as an active electrode material; as a result, this biochar exhibits lower capacity as an active material than materials specifically optimized as an active material in past studies. When combined with past research on bio-based active materials (e.g., highly graphitized biochar) [132, 171], this study reveals a path forward to LIBs with only bio-based carbon materials. Such a replacement is estimated to reduce the greenhouse gas emissions associated with the production of conductive additives for battery electrodes by 49% and reduce the reliance on fossil fuel-derived products, improving the sustainability of LIBs without any degradation of battery performance.

CONCLUSIONS

This work addresses three areas critical to the development of biochar as a renewable, electrically conductive additive in polymers:

1. Biochar with electrical conductivity comparable to carbon black was developed, and the feedstock factors that contribute to high variability in biochar electrical conductivity were examined, with sodium sulfate content, oxygen content, and particle size all playing a critical role. This biochar is demonstrated as a replacement for carbon black in lithium-ion battery electrodes.
2. The primary cause of the negative impact of biochar on the biodegradable plastics PLA and PHBV was determined to be due to the presence of sodium sulfate, and a simple water rinsing process was developed to remove these inorganics and produce bio-based composites of biochar and PLA/PHBV blends with high electrical conductivity and improved mechanical properties.
3. An environmental impact assessment found that the production of biochar-composites can create carbon-negative materials at biochar loadings while increasing the plastic's strength.

Comparison of past electrical conductivity measurements of powders between studies is limited by high variation between measurement techniques. Herein, a more repeatable and accurate method is developed for the measurement of the electrical conductivity of powders. This method uses a guard electrode fixture to allow for three-point measurements of powders and is comprised entirely of commonly available or 3D printable parts. This method was compared with conventional two-piston measurement techniques and agreed better with established electrical conductivity values for standard carbon powders. In addition, as this

test fixture comprises commonly available or 3D printable parts, measurements are expected to be more repeatable between studies.

This improved electrical conductivity method was then applied to characterize the electrical conductivity of biochar from various lignin feedstocks, along with cellulose and wheat stems, at pyrolysis temperatures of 900 and 1100 °C. The resulting biochars show a wide range of electrical conductivities from 0.002 to 18.5 S/cm, demonstrating that even when controlling for the electrical conductivity measurement method, there are significant differences in biochar electrical conductivity between feedstocks. This study's highest electrical conductivity biochars are comparable to commercial electrically conductive carbon black. Biochar oxygen content and particle size play critical roles in the electrical conductivity of the biochar; with low oxygen, small particle size in biochars having higher electrical conductivity.

The electrical conductivity of biochars produced from a wide variety of lignins at 1100 °C were examined to determine the role lignin properties play in the previously observed high variation in biochar electrical conductivity. Electrical conductivities were found to range from 0.19-18.9 S/cm. During pyrolysis, these lignins show varying thermal transitions, which result in three distinct biochar physical structures. No correlation was found between this pyrolysis behavior and electrical conductivity or between lignin isolation methods, feedstocks, or isolation temperatures and electrical conductivity. Sodium sulfate is identified to inhibit the formation of graphitic structures in lignin-derived biochar. Simple washing procedures can be applied to remove sodium sulfate from the lignin prior to pyrolysis. However, despite the observed increase in graphitization without sodium sulfate, these biochars decrease in electrical conductivity. This finding is proposed to be due to the high aspect ratio of graphitic crystallites in these biochars, reducing electrical conductivity through poorer packing of these crystallites in the biochar.

Next, various biochars are examined as filler materials in common biodegradable

plastics, PLA and PHBV, and recycled HDPE. First, biochar derived from post-consumer food waste is examined as a method to reuse this high-volume organic waste stream. Despite the inhomogeneous nature of post-consumer food waste, food-waste-derived biochar is found to have comparable electrical conductivity and graphitic structure to biochar produced from homogeneous biomass feedstocks. This biochar demonstrates pyrolysis as a promising alternative to composting or anaerobic digestion to upcycle food waste. When this biochar is added to PLA or HDPE, the two polymers show broad differences in impact from biochar. In recycled HDPE, biochar addition has minimal impact on the microstructure or mechanical properties of the polymer.

In contrast, adding food-waste-derived biochar to PLA reduces the thermal degradation temperature, melt viscosity, and thermal transitions of PLA, indicating a loss in polymer molecular weight. As a result, the mechanical properties are severely reduced. However, biochar addition increases the composting rate of PLA due to increased moisture adsorption. The differences between rHDPE and PLA highlight the challenges of using biochar as a filler in common biodegradable plastics. This finding is consistent with most studies examining biochar as a filler material in PLA and PHBV, which found significant decreases in thermal stability with biochar addition.

Prior studies had identified this loss in thermal stability with the addition of biochar as a critical gap in developing biochar composites. These studies proposed a wide variety of hypotheses for this decreased thermal stability. By examining the impacts of various biochars on the thermal degradation of PLA and PHBV, biochar alkali and alkaline earth metal content were found to play a critical role in reducing the thermal degradation temperature of both PLA and PHBV. These metals depolymerize the polymer backbone at the ester bond, reducing the molecular weight of these polymers even below the onset of thermal degradation. Biochar moisture content, which was previously hypothesized as a primary cause of thermal degradation of PLA by biochar, was found to have only a secondary impact.

A simple water washing procedure was then applied to remove sodium sulfate from highly electrically conductive lignin-derived biochar, to develop a viable biochar filler material for PLA and PHBV. Before this washing treatment, this biochar reduced the thermal degradation temperature of these polymers, but after the removal of the sodium sulfate, it increased the thermal degradation temperature of both polymers. This biochar had electrical conductivity similar to that of carbon black. However, when this biochar was applied in composites of PLA and PHBV to produce 3D printable, electrically conductive composite materials for use in sensing applications, the resulting composite electrical conductivity of biochar was found to be much lower than a composite of carbon black. This difference is hypothesized due to the blocky structure of biochar, resulting in poorer dispersion in the polymer than carbon black and increased distance between biochar particles.

In addition to material property benefits, biochar can reduce plastics' environmental impacts. In many plastics, biochar loadings of 40-50% result in a material that sequesters carbon with increased strength and stiffness relative to the neat polymer. This reduction in global warming potential is accompanied by reductions in fossil fuel depletion and, critically for biodegradable plastics, reductions in environmental impact categories such as acidification that are higher for bioplastics than petroleum-derived plastics. Furthermore, as biochar replaces a portion of the plastic at the end of life, this replacement also reduces the volume of plastic waste generated. However, in end-of-life scenarios where plastic may be recycled, biochar addition may prevent recycling with current systems. This environmental impact assessment examines commercial biochar, which is available at a lower cost than recycled or biobased plastics demonstrating the potential to reduce the costs of these plastics, to help meet consumer demand for alternatives to petroleum-derived plastics.

Finally, the highly electrically conductive biochar developed herein is applied as a conductive additive in the electrodes of a lithium-ion battery. In a graphite-based anode, biochar shows similar performance to carbon black, with slight improvements in capacity

observed at higher charging rates. However, in the anode, a drastic loss in capacity is observed with biochar relative to carbon black. This poor performance is attributed to the blocky structure of biochar relative to carbon black, similarly to what is observed in polymer composites. Biochar is found to have the potential to reduce the greenhouse gas emissions of this critical battery material by 49% relative to carbon black, improving the sustainability of this rapidly growing application.

Biochar morphology remains a critical challenge to the development of electrically conductive composite materials, as demonstrated by the reduced electrical conductivity of biochar-plastic composites and poor performance of cathodes with biochar conductive additive relative to carbon black. Spray pyrolysis of lignin looks to be a promising method to produce biochar with a nodule-aggregate structure more similar to carbon black. As lignin from pulping or cellulosic biofuel processes is in solution in isolation, this process may present an opportunity to avoid costly drying steps otherwise required to upcycle lignin. Future work should center around developing methods to reduce the particle size of lignin-derived biochar, to optimize the electrical performance across a broad range of applications. Further, research on further improvements in electrical conductivity of biochar should focus on the chemical structure-nanostructure-macrostructure-bulk powder interactions of biochar. This work should attempt to develop a comprehensive model to explain decreases in electrical conductivity observed in this work with increased graphitic crystallite size and tie this relationship to both individual particle electrical conductivity and bulk powder electrical conductivity. This work should aim to develop methods to better understand how changes in structure at each level of the material impact electrical performance in important applications.

This work develops biochar as a conductive additive in biodegradable plastic. The findings presented herein have expanded knowledge of how biochar electrical conductivity can be improved and helped to explain the high variation in biochar electrical conductivity

that has previously been observed in the literature. Lignin-derived biochar is developed with electrical conductivity comparable to carbon black. The harmful interactions with PLA and PHBV that have previously limited biochar application in these plastics are resolved by removing alkali and alkaline earth metal-containing compounds in this biochar. This new biochar allows a new class of biocomposites with unique properties to be created, with biochar providing benefits across the material life cycle. During production, biochar can reduce environmental impacts and costs. During the use life of the material, biochar can improve strength, act as a pigment, or increase the material's electrical conductivity. Finally, at the end-of-life of the material, biochar can improve composting rates of PLA and reduce plastic pollution while continuing to sequester carbon. Combined, this work demonstrates biochar biodegradable plastic composites as a promising class of material to aid in reducing our society's reliance on fossil fuels while expanding the potential applications of biodegradable plastics.

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APPENDICES

APPENDIX A

CODE FOR ANALYSIS OF RAMAN SPECTRA OF CARBON MATERIALS

This MATLAB code analyzes the Raman spectra of graphitic carbons to deconvolute them into their constituent peaks with the method described by Ferrari et al. [206] and McGlammary et al. [207], as discussed in Ch. 3. This code fits the D- (approx. 1340 cm^{-1}) and G-peaks (approx. 1582 cm^{-1}) with a Lorentzian and Breit-Wigner-Fano function respectively, and applies a baseline correction to the spectra. This analysis allows for calculation of the position of the D- and G-peaks, intensity ratio of the D and G peaks (I_{dg}), and widths-at-half-height of the D- and G- peaks. This code requires Matlab vers. 2020a or newer and the MATLAB *Curve Fitting Toolbox*. Example outputs are shown in Fig. C.4-C.7.

```
%% Raman Analysis Code.
```

```
%This code fits a Raman spectra of carbon to determine the intensity ,  
%position , and width of the D and G peaks. The D peak is positioned at  
%approx. 1340 cm-1 and is fit with a Lorentzian curve , while the G  
peak is  
%positioned at approx. 1582 cm-1 and is fit with a BWF curve. For a  
more  
%detailed view of this fitting method, see Ferrari 2000  
%(https://doi.org/10.1103/PhysRevB.61.14095) or Mcglamery 2020  
%(https://pubs.acs.org/doi/10.1021/acs.jpcc.0c06918.).
```

```
clear;clc;close all;  
%Input data as a 2 column (Raman shift and intensity) xlsx file here.  
%This code is written for separate data files , but could be modified to  
accommodate multicolumn data.  
%This code was written for data from 1000–1800 cm-1 but may work for  
other  
%domains  
Raman=readmatrix('Raman.xlsx','Sheet','Raman');  
DATA(:, :, 1)=Raman(:, 1:2);  
DATA(:, :, 2)=Raman(:, 3:4);  
DATA(:, :, 3)=Raman(:, 5:6);  
for i=1:size(DATA,3)%Loops over # of data files  
X=DATA(:, 1 , i);  
Y=DATA(:, 2 , i);  
%% Curve Fitting tool box output in this section  
[xData , yData] = prepareCurveData( X, Y );  
  
% Set up fittype and options.  
ft = fittype( 'I_d/(1+((x-w_d)/r_d)^2)+I_g*((1+2*(x-W_g)/(Q_g*r_g))^2)  
/(1+(2*(x-W_g)/r_g)^2)+m*x+b', 'independent', 'x', 'dependent', 'y'  
); %Defines equation.  
opts = fitoptions( 'Method', 'NonlinearLeastSquares' ); %Fit method
```

```

opts.Display = 'Off';
opts.Lower = [0 0 -Inf -Inf -Inf -Inf -Inf -Inf -Inf];
opts.StartPoint = [2648.25042760131 2535.7624477102 -4.3343
1597.39661269397 346.7633 0.163392290067867 89.1806023084366
103.432777856906 1337.32324816058];
opts.Upper = [Inf Inf 0 Inf Inf Inf 400 400 Inf];

% Fit model to data.
[fitresult , gof] = fit( xData , yData , ft , opts ); %Does the fit
coeffs(i,:) = coeffvalues(fitresult); %Saves coefficients

%% Plotting data
Yd_fit = coeffs(i,1) ./ (1 + ((X - coeffs(i,9)) ./ coeffs(i,7)).^2); %D peak
equation
Yg_fit = coeffs(i,2) .* ((1 + 2.* (X - coeffs(i,4)) ./ (coeffs(i,3) * coeffs(i,8))).^2) ./ (1 + (2.* (X - coeffs(i,4)) ./ coeffs(i,8)).^2); %G peak equation
[pk_g, loc_g, width_g] = findpeaks(Yg_fit(1:760), X(1:760), 'WidthReference',
'halfheight')
Yb_fit = coeffs(i,5) + coeffs(i,6) * X; %Base line correction equation
Y_fit(:, i) = Yd_fit + Yg_fit + Yb_fit; %Total curve fit equation
[V1450, Index1450] = min(abs(X - 1450));
Id = max(Y_fit(1:Index1450, i));
Ig = max(Y_fit(Index1450:end, i));
Idg(i) = Id / Ig;
figure(i);
hold on
f1 = scatter(X, Y, 5, 'k', 'o', 'filled'); %Scatter plots raman data
f1.MarkerFaceAlpha = 0.15; %Transparency of scatter plot data
plot(X, Yd_fit, '--k', 'LineWidth', 3) %Plots d peak
plot(X, Yg_fit, '-k', 'LineWidth', 3) %Plots g peak
plot(X, Yb_fit, ':k', 'LineWidth', 3) %plots baseline
plot(X, Y_fit(:, i), 'k', 'LineWidth', 1.5) %Plots final curve fit
ylabel('Intensity (A.U.)')
xlabel('Raman Shift (cm-1)')
text(1600, 100, sprintf('IDG=%.3f', Idg))
set(gca, 'LineWidth', 1)
set(gca, 'TickLength', [0.015, 0.01])
set(gcf, 'PaperUnits', 'inches');
set(gca, 'box', 'off')
set(gcf, 'units', 'inches', 'position', [0, 0, 2.25, 2.25])
set(gca, 'YTick', []);
exportgraphics(gcf, 'Raman.pdf')
Idg = 0;
end

```


APPENDIX B

SUPPLEMENTAL INFORMATION TO: IMPROVEMENTS IN METHODS FOR
MEASURING THE VOLUME CONDUCTIVITY OF ELECTRICALLY CONDUCTIVE
CARBON POWDERS

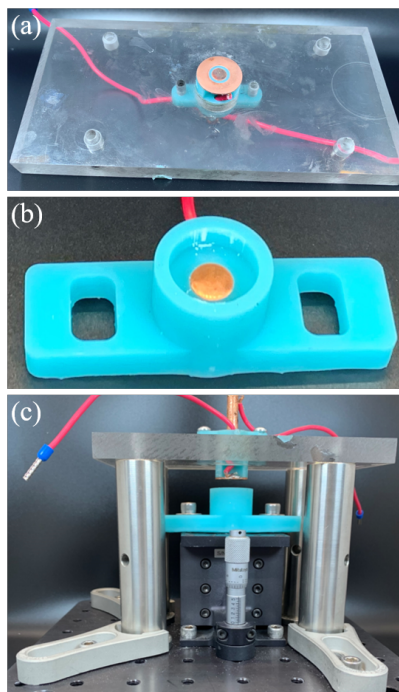


Figure B.1: Photographs of the experimental setup. (A) displays the upper portion of the fixture. (B) displays the lower portion of the fixture. (C) displays the assembled fixture.

This document has been compiled to support work comparing two-piston and guard-electrode methods of measuring electrical conductivity. It shows photos and CAD models of the test fixture (Figures S1 and S2). Additionally, it shows Nyquist plots of the impedance spectrum of conductivity measurements taken with both methods for copper (figure S3), cellulose (figure S4), graphite (figure S5), HL1100 biochar (figure S6) and VXC72R carbon black (figure S7) and Vulcan XC MAX22 carbon black (figure S8) and shows the change in these impedance spectra as the powder is compressed. Finally, it shows time dependent variance of DC conductivity of copper, graphite and Vulcan XC72R carbon blacks across a range of thicknesses, with additional focus on one points below, during and above percolation. All materials show low variance after 30 seconds, confirming that taking a measurement after 30 seconds produces a stable result. For additional information, see the full article.

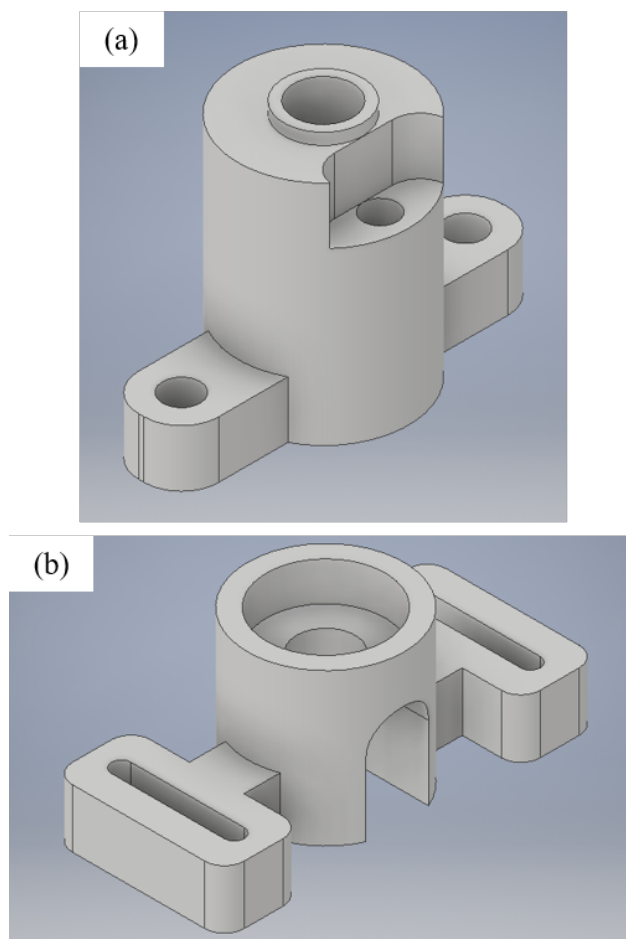


Figure B.2: Autodesk Inventor CAD models of the 3d printed parts. (A) displays the upper portion of the fixture. (B) displays the lower portion of the fixture.

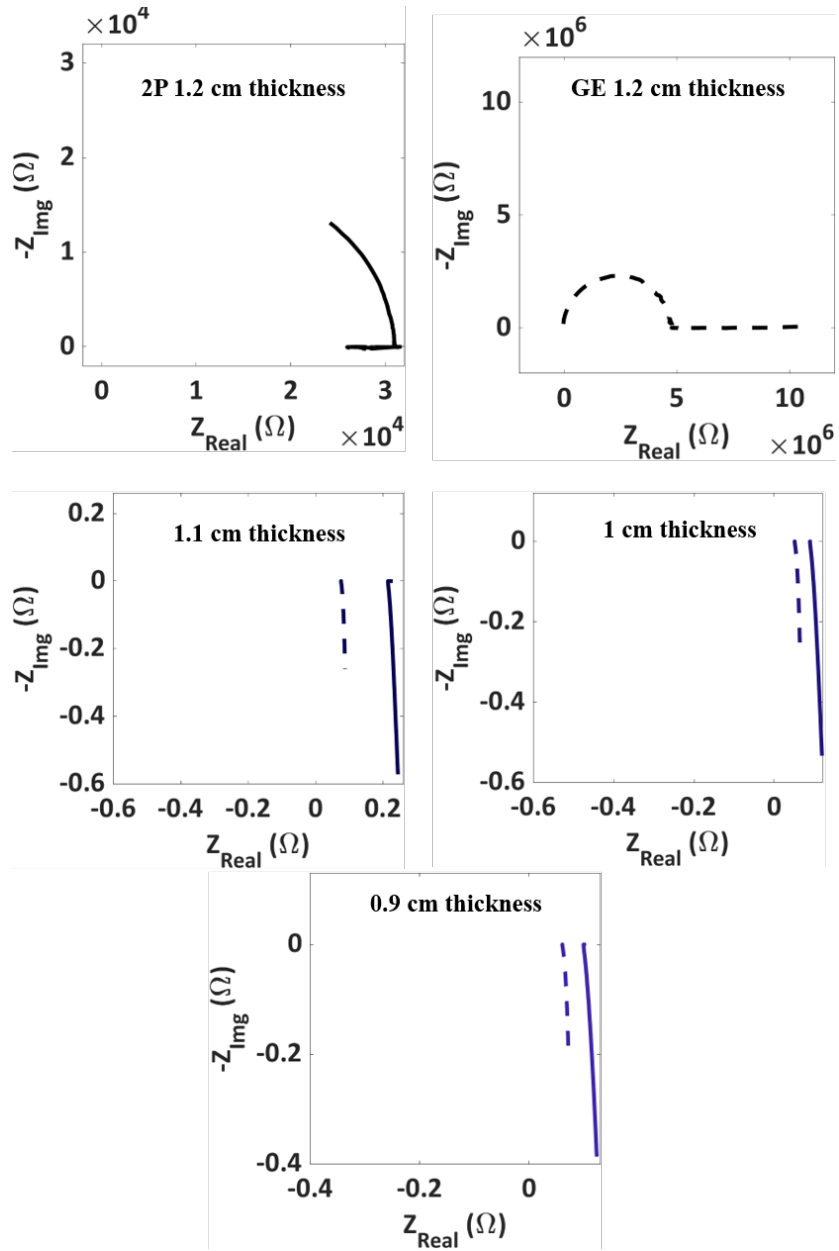


Figure B.3: Nyquist plots of the impedance spectrum for copper powder from 1.2 cm to 0.9 cm of sample thickness. Solid lines represent the two-piston method while dashed lines represent the guard electrode method.

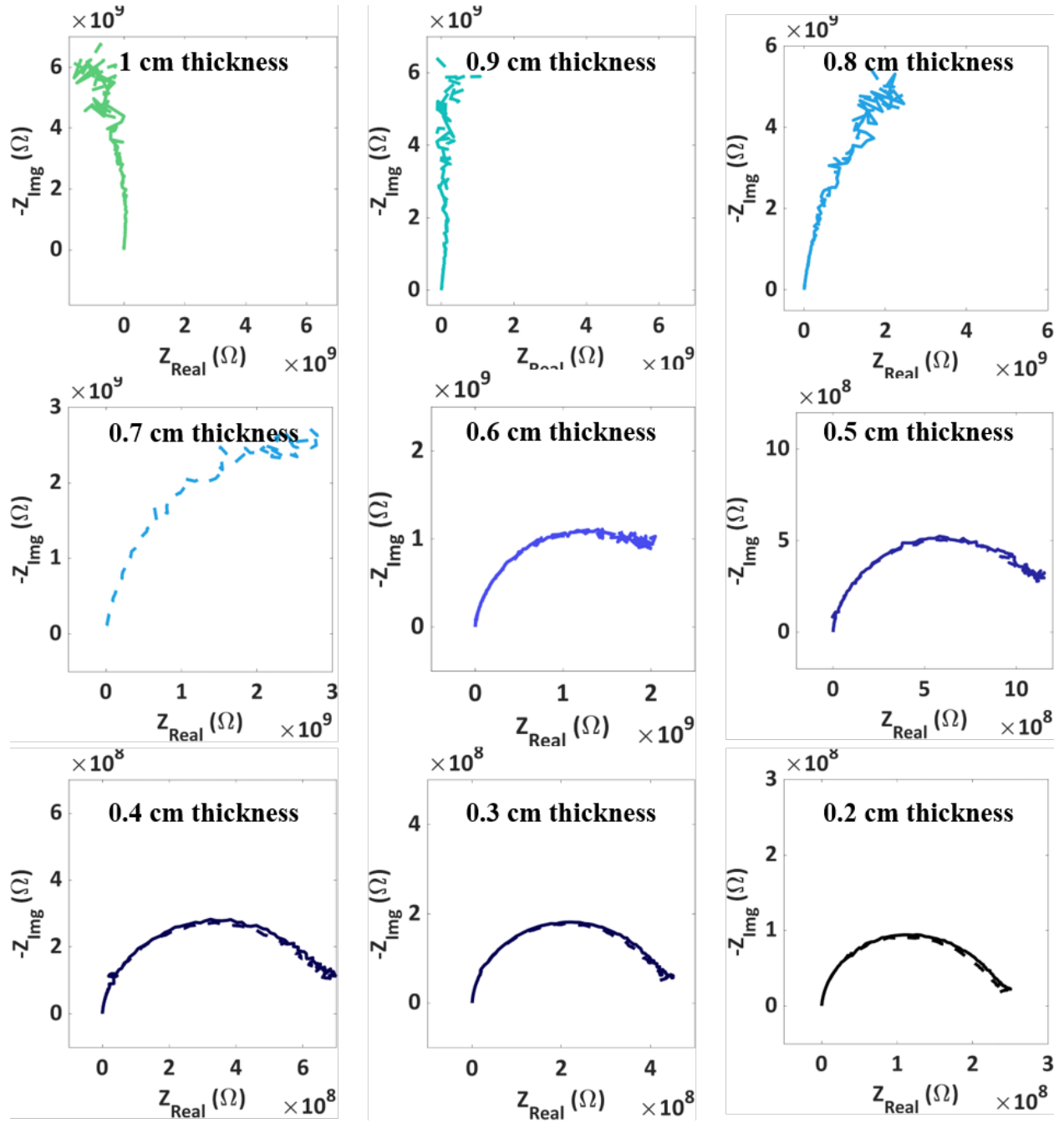


Figure B.4: Nyquist plots of the impedance spectrum for cellulose powder from 1 cm to 0.2 cm of sample thickness. Solid lines represent the two-piston method while dashed lines represent the guard electrode method.

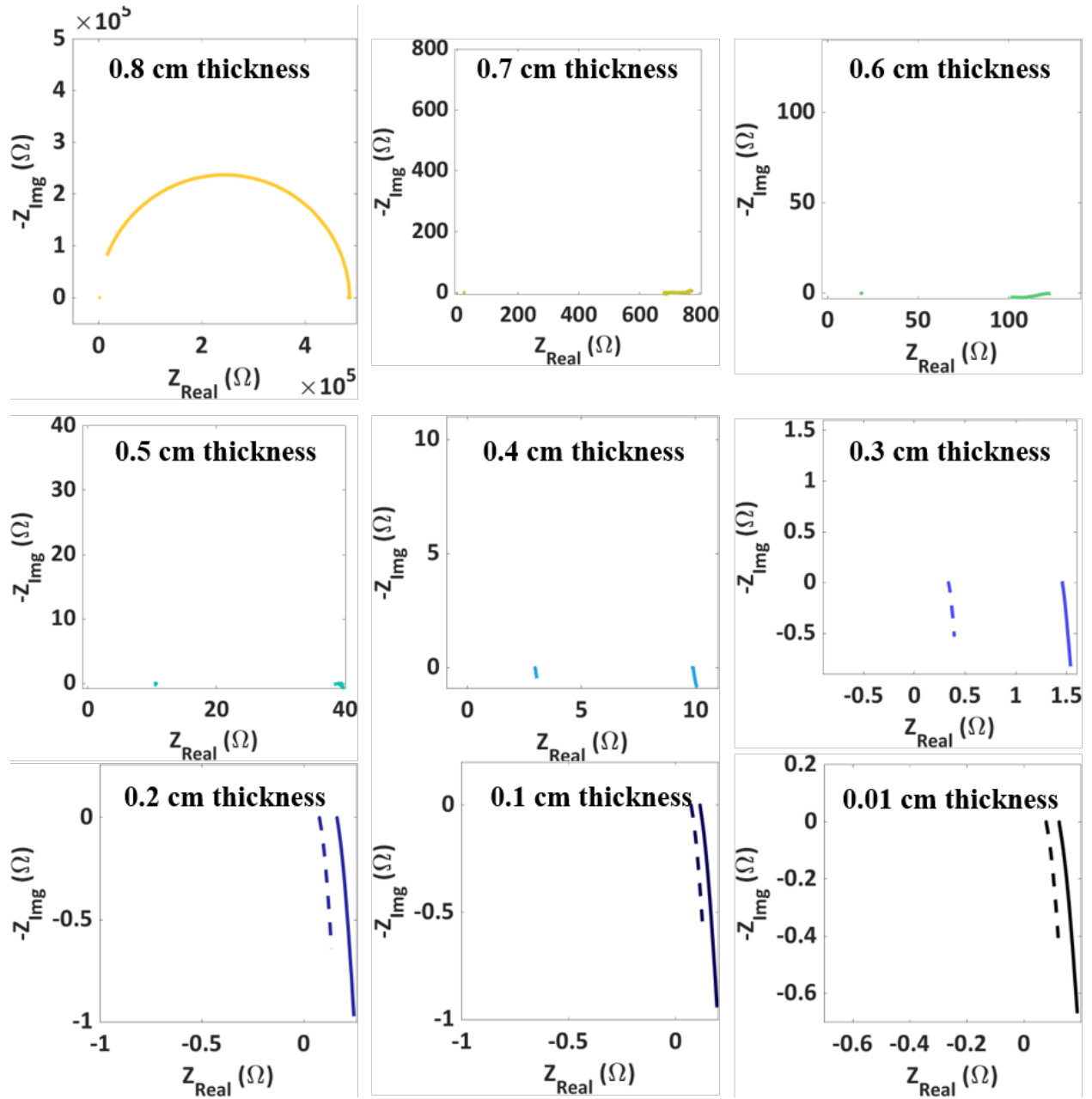


Figure B.5: Nyquist plots of the impedance spectrum for graphite from 0.8 to 0.01 cm of sample thickness. Solid lines represent the two-piston method while dashed lines represent the guard electrode method. Note that in some cases (0.7-0.5 cm thickness) the guard electrode method is much smaller than the two-piston method.

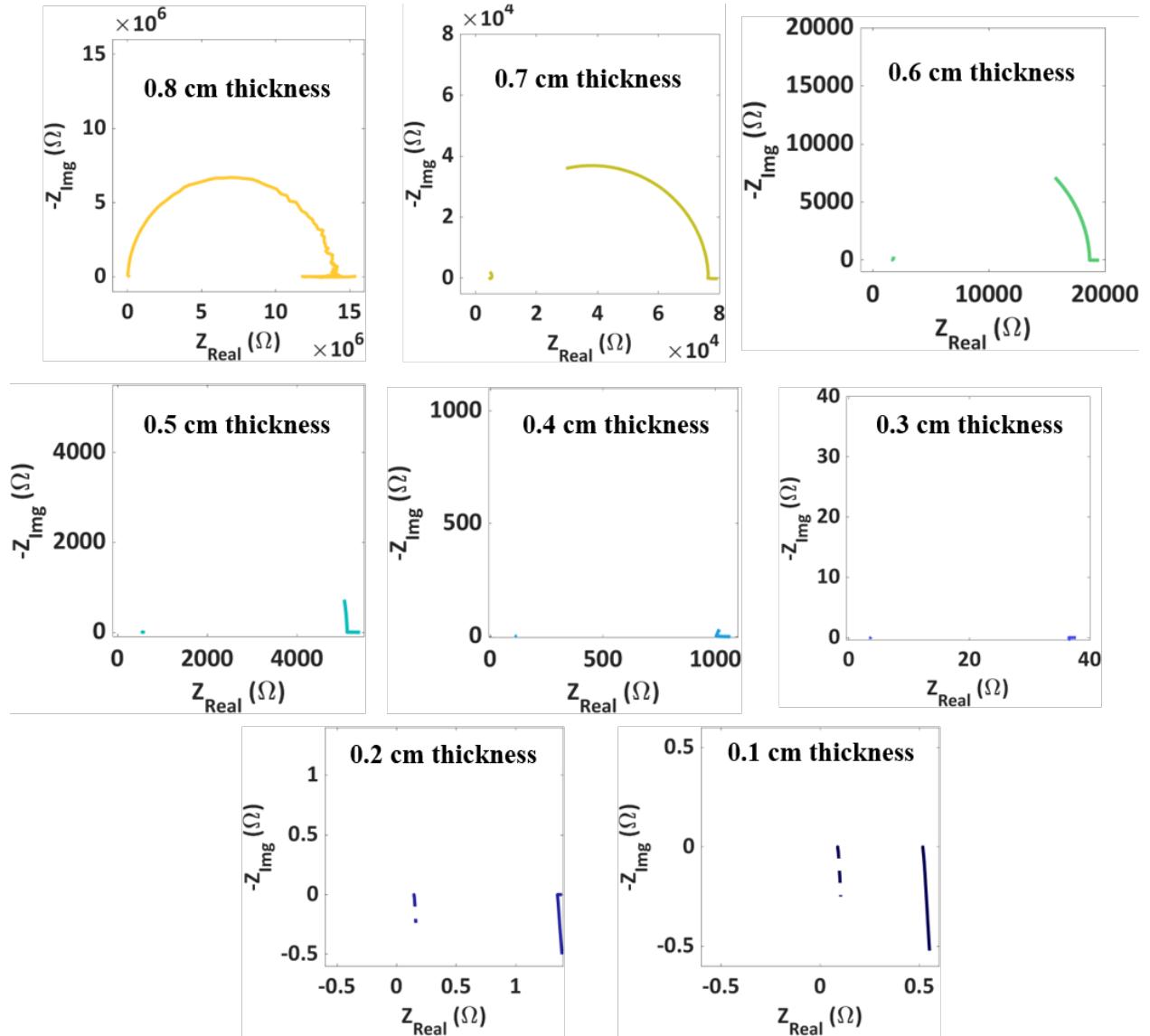


Figure B.6: Nyquist plots of the impedance spectrum for HL1100 biochar from 0.8 to 0.1 cm of sample thickness. Solid lines represent the two-piston method while dashed lines represent the guard electrode method. Note that in some cases (0.7-0.3 cm thickness) the guard electrode method is much smaller than the two-piston method.

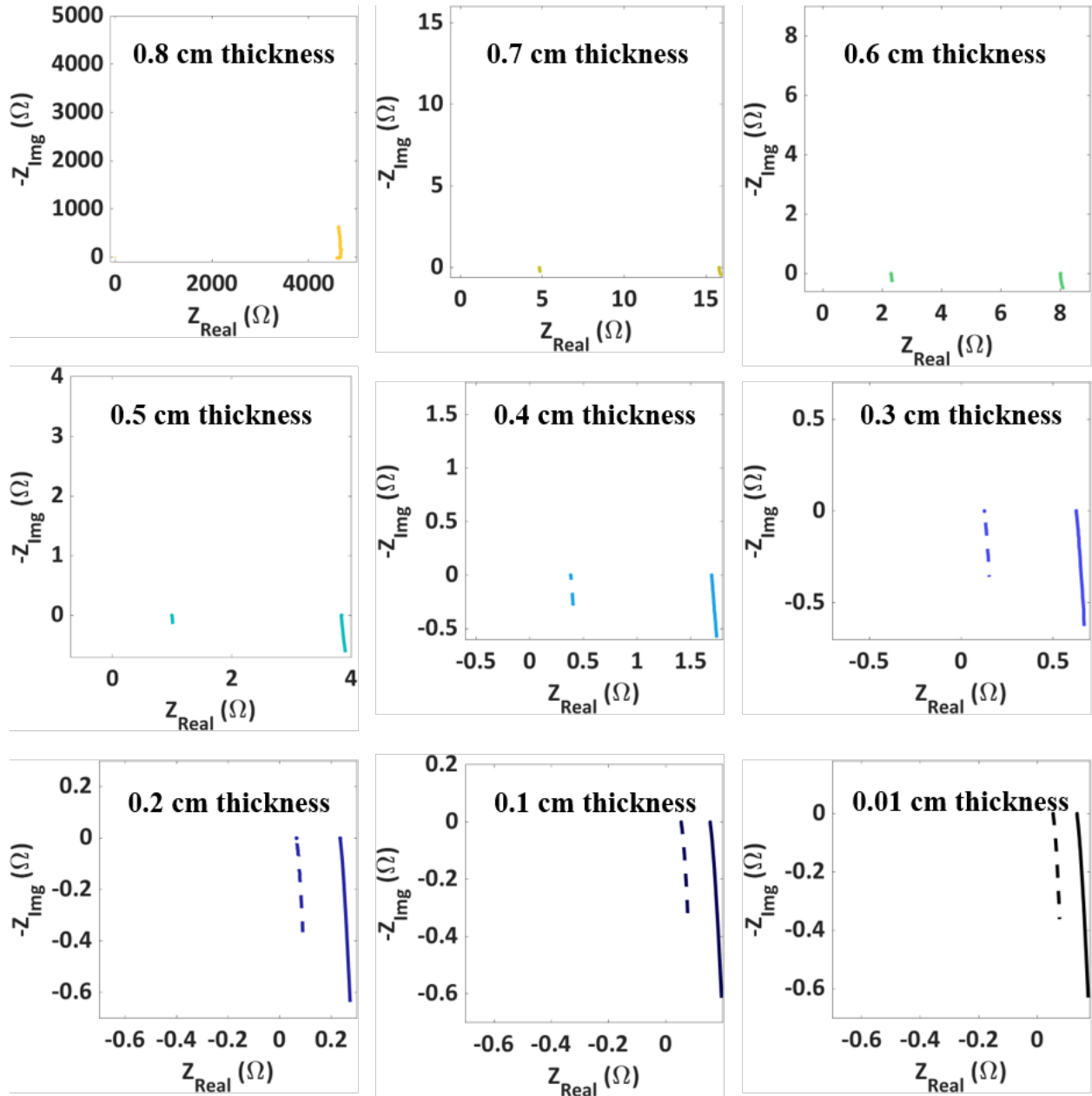


Figure B.7: Nyquist plots of the impedance spectrum for VXC72R carbon black from 0.8 to 0.01 cm of sample thickness. Solid lines represent the two-piston method while dashed lines represent the guard electrode method. Note that in some cases (0.8-0.5 cm thickness) the guard electrode method is much smaller than the two-piston method.

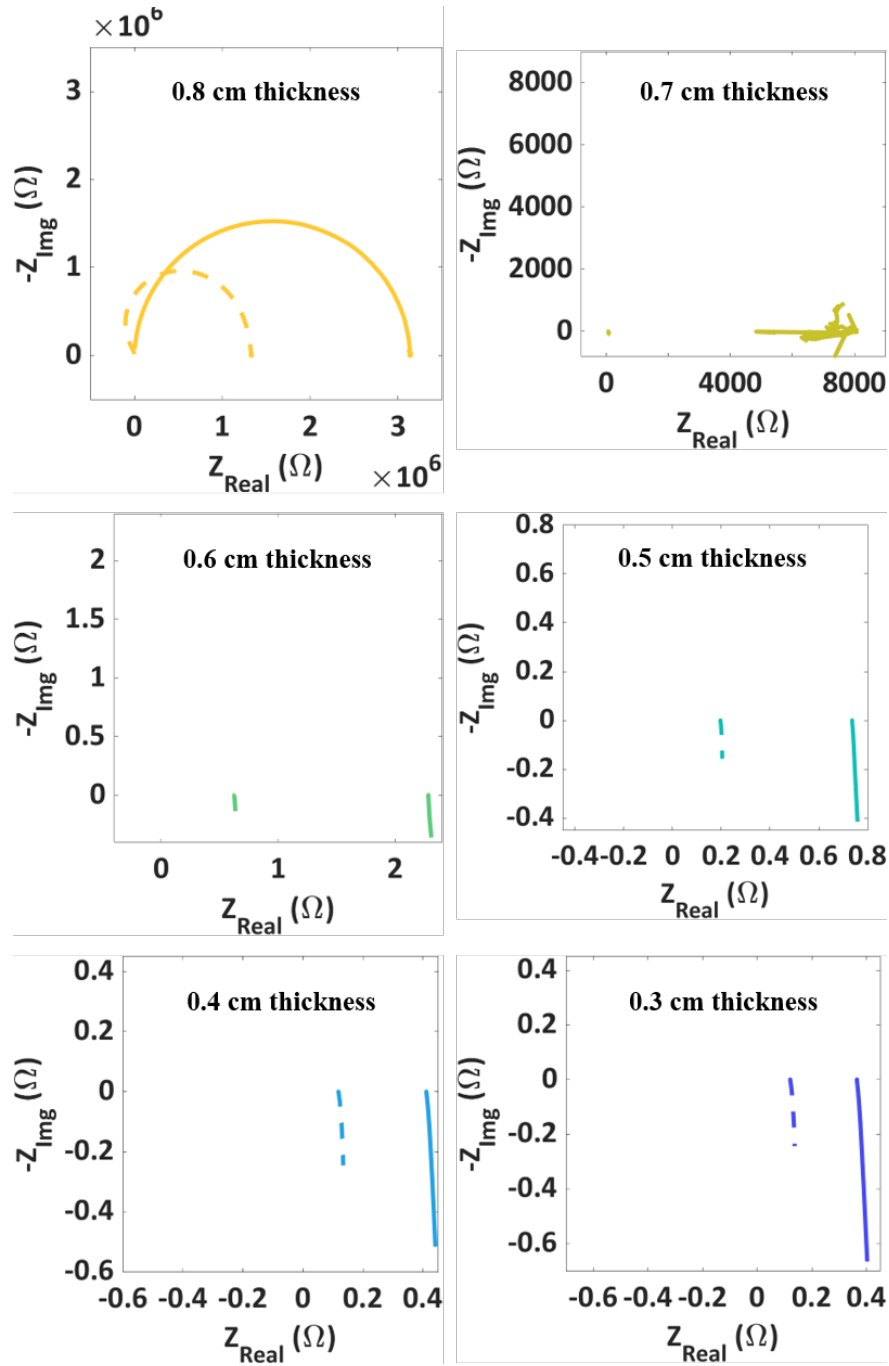


Figure B.8: Nyquist plots of the impedance spectrum for VXCM22 carbon black from 0.8 to 0.3 cm of sample thickness. Solid lines represent the two-piston method while dashed lines represent the guard electrode method. Note that in some cases (0.7 cm thickness) the guard electrode method is much smaller than the two-piston method.

Copper Guard-electrode method

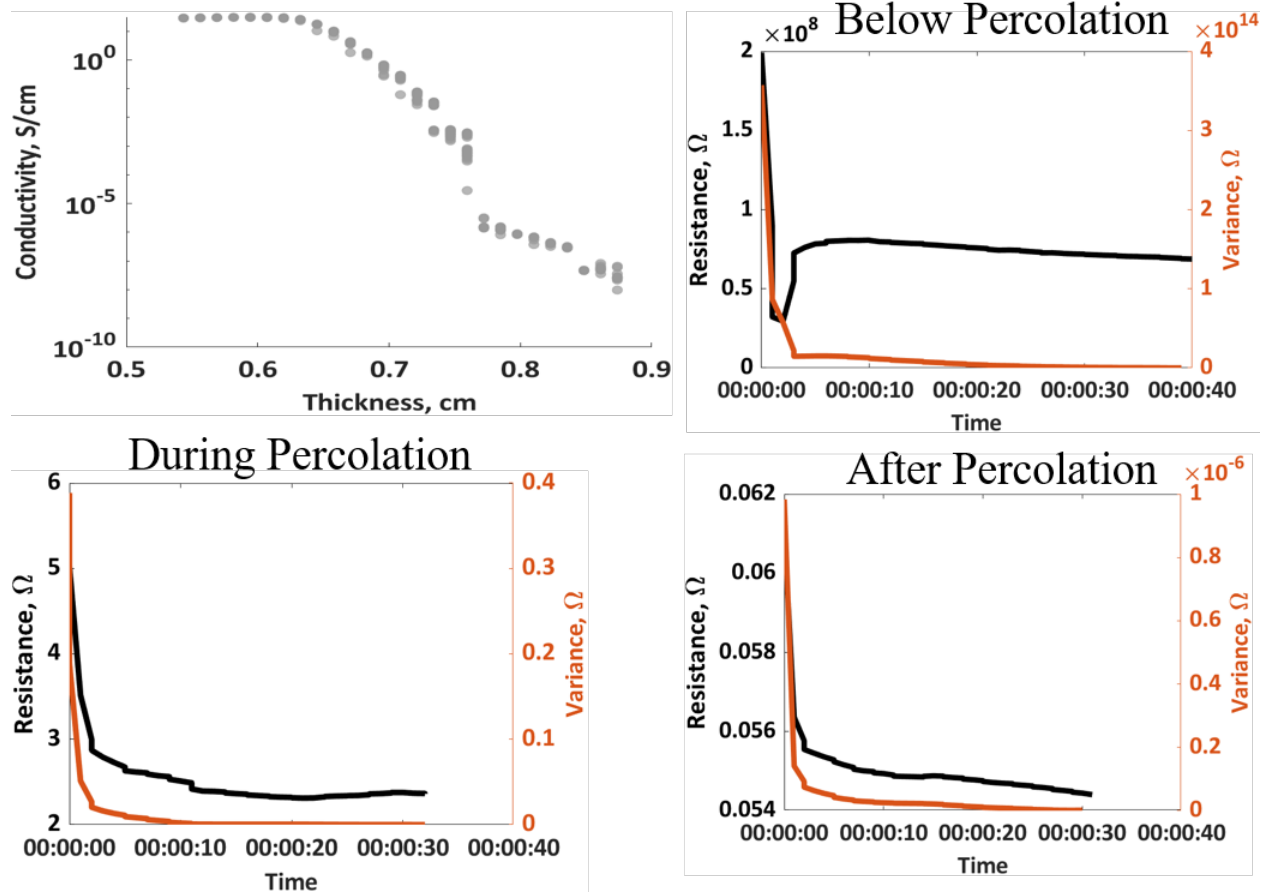


Figure B.9: Time dependent variation of conductivity of copper powder using the guard-electrode method. The top left figure shows all conductivity points, while the top right, bottom left and bottom right figures show a single compression point over time below, during and after percolation respectively.

Copper Two-piston method

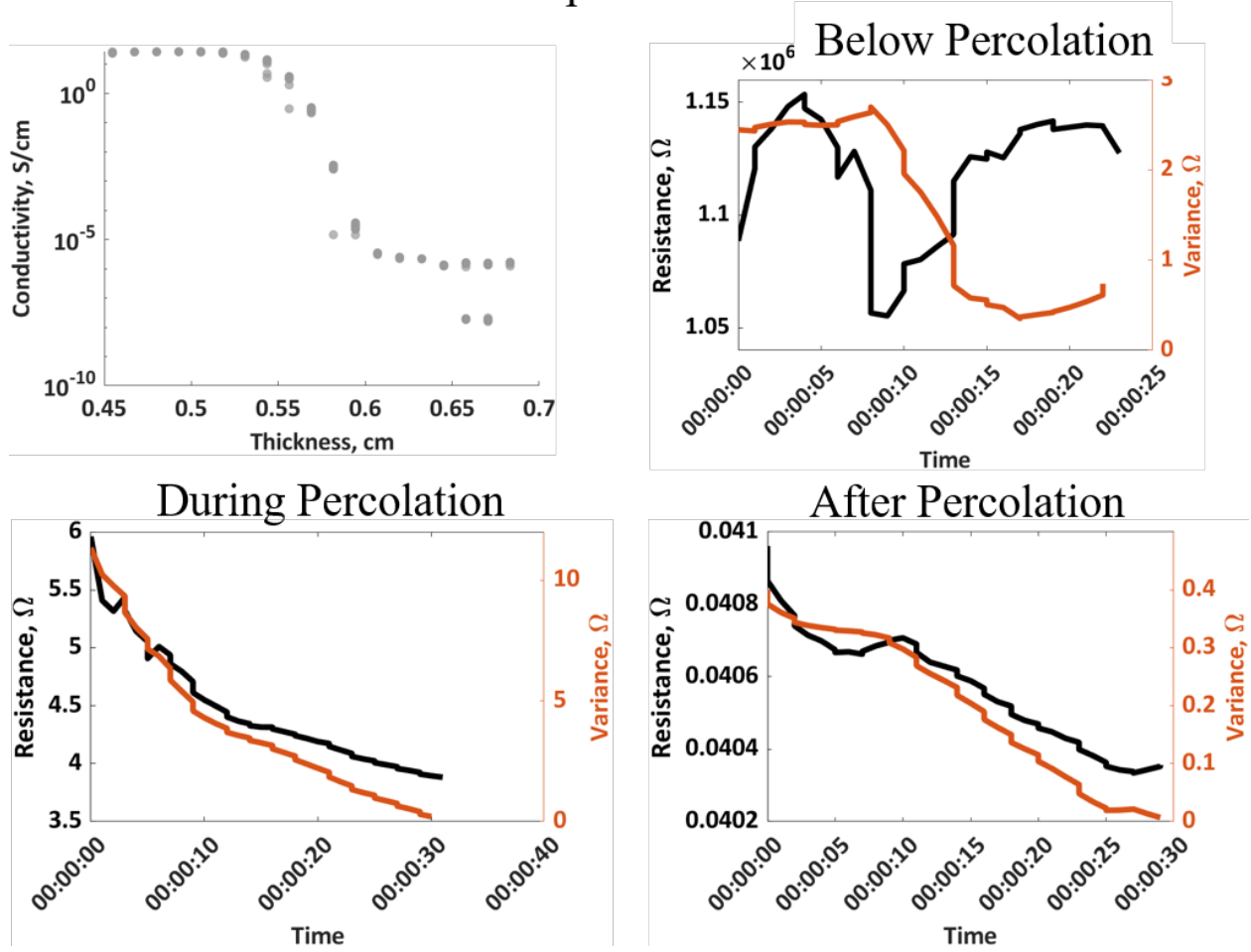


Figure B.10: Time dependent variation of conductivity of copper powder using the two-piston method. The top left figure shows all conductivity points, while the top right, bottom left and bottom right figures show a single compression point over time below, during and after percolation respectively.

Graphite Guard-electrode method

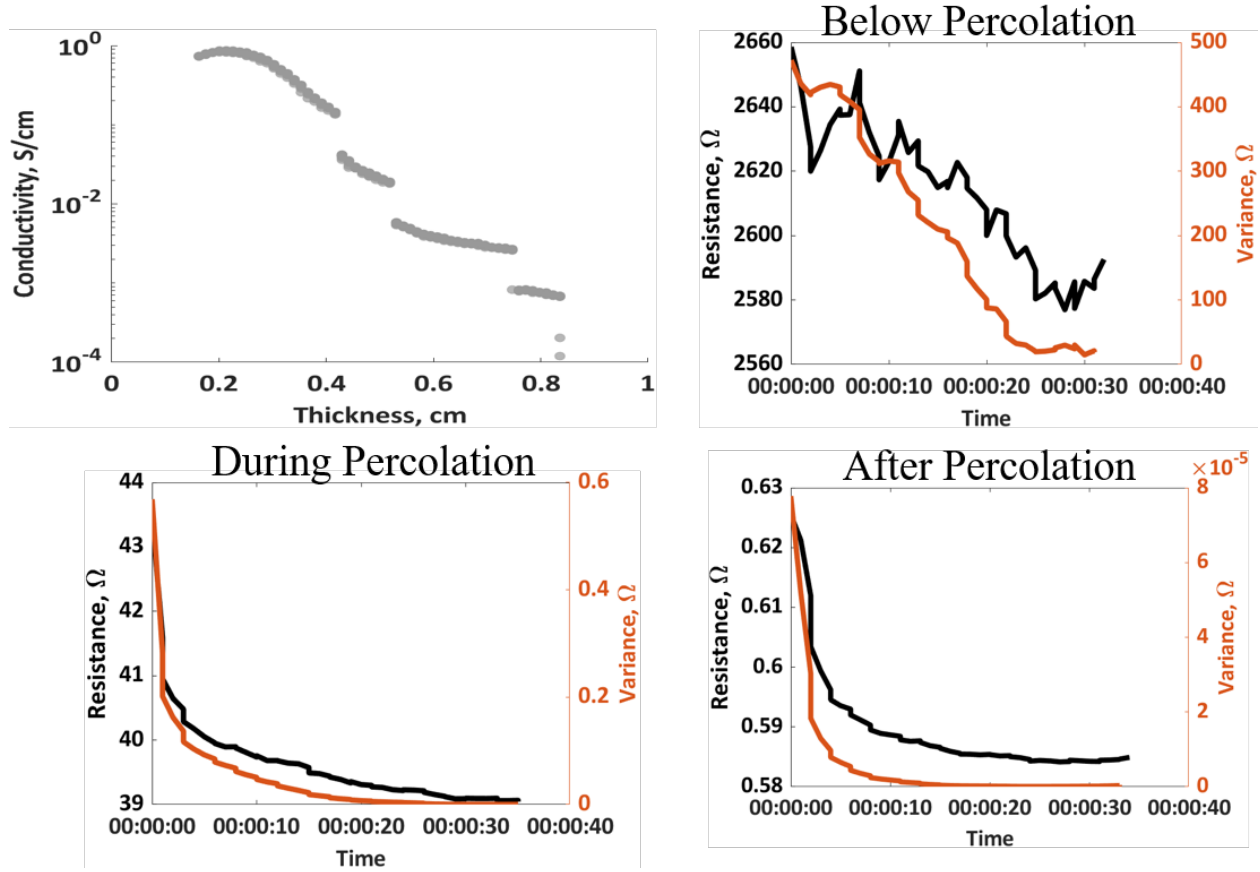


Figure B.11: Time dependent variation of conductivity of graphite powder using the guard-electrode method. The top left figure shows all conductivity points, while the top right, bottom left and bottom right figures show a single compression points over time below, during and after percolation respectively.

Graphite Two-piston method

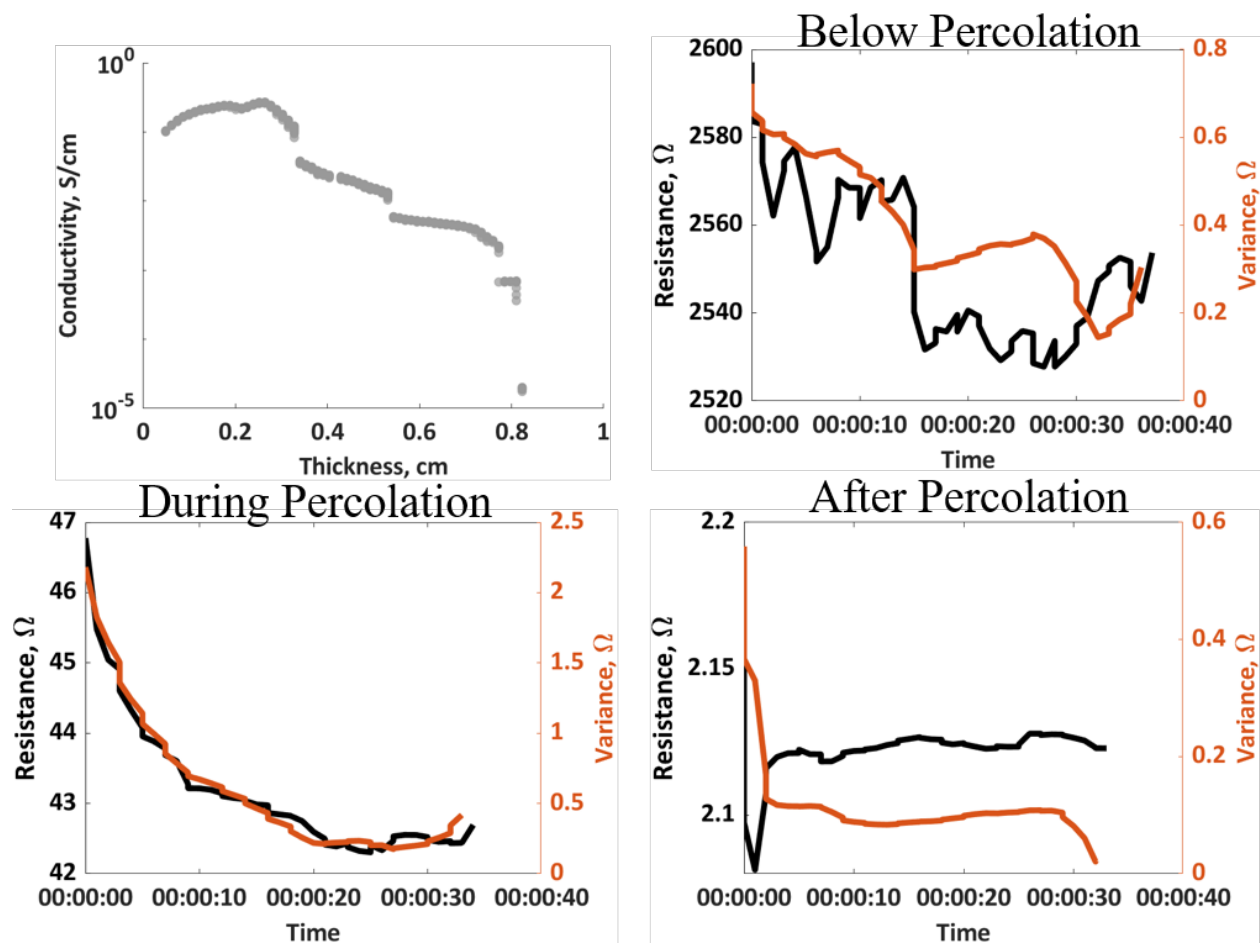


Figure B.12: Time dependent variation of conductivity of graphite powder using the two-piston method. The top left figure shows all conductivity points, while the top right, bottom left and bottom right figures show a single compression points over time below, during and after percolation respectively.

VXC72R CB Guard-electrode method

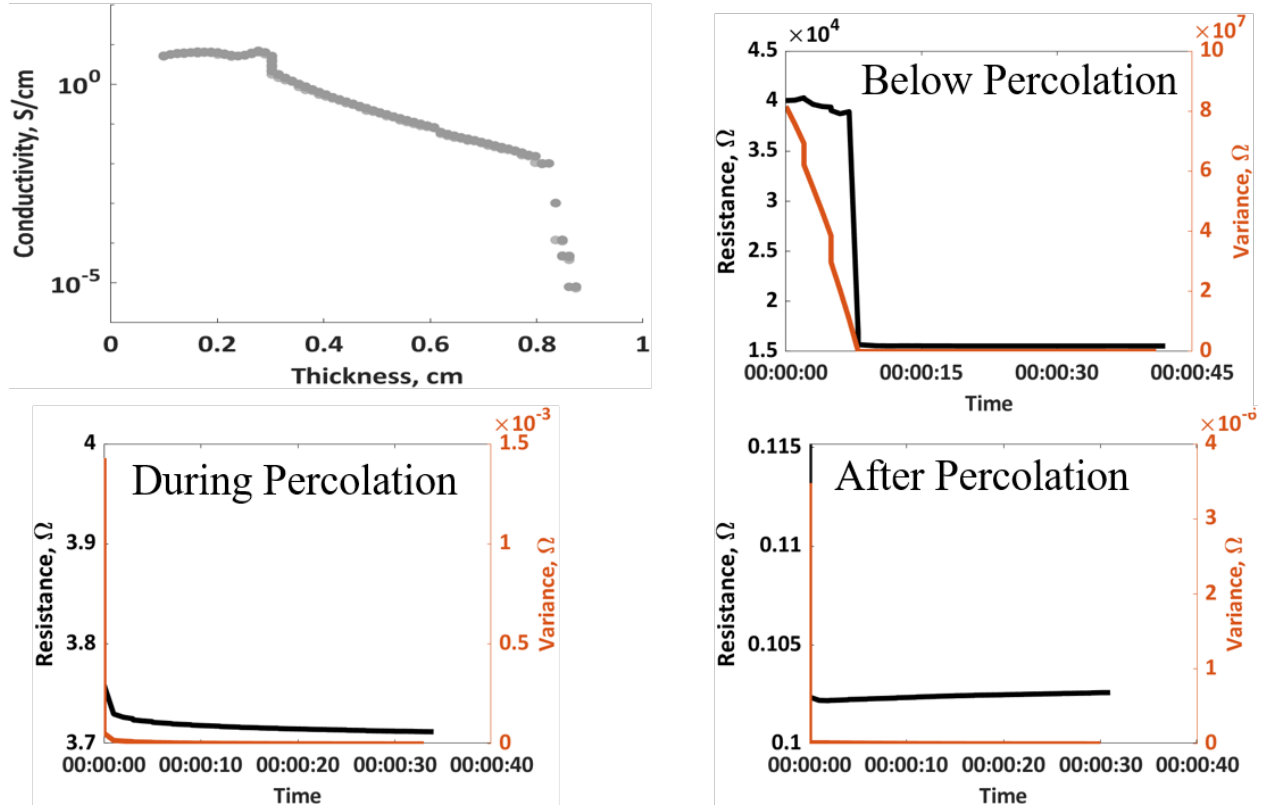


Figure B.13: Time dependent variation of conductivity of graphite powder using the guard-electrode method. The top left figure shows all conductivity points, while the top right, bottom left and bottom right figures show a single compression points over time below, during and after percolation respectively.

VXC72R CB

Two-piston method

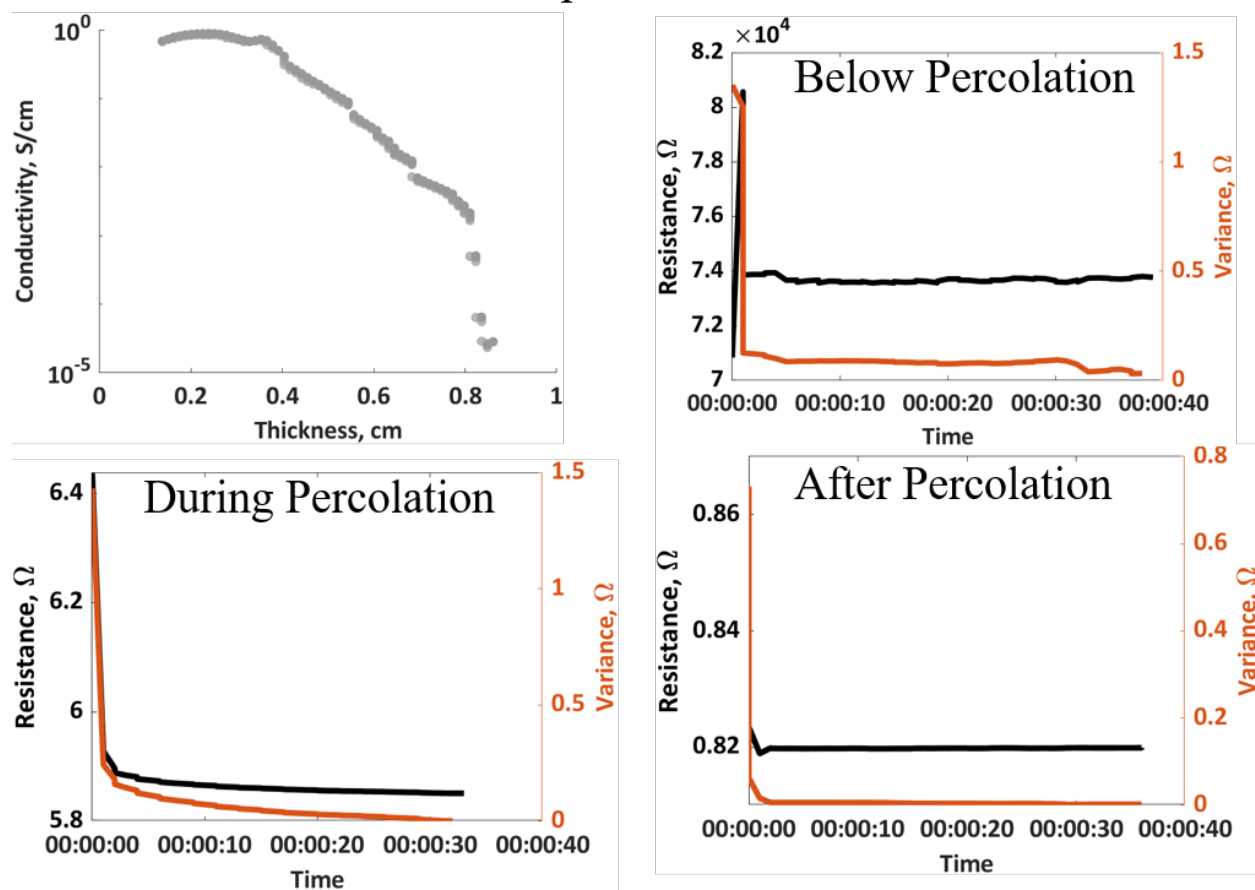


Figure B.14: Time dependent variation of conductivity of graphite powder using the two-piston method. The top left figure shows all conductivity points, while the top right, bottom left and bottom right figures show a single compression points over time below, during and after percolation respectively.

APPENDIX C

SUPPLEMENTAL INFORMATION TO: PHYSICAL AND CHEMICAL MECHANISMS
THAT INFLUENCE THE ELECTRICAL CONDUCTIVITY OF LIGNIN-DERIVED
BIOCHAR

The figures and text displayed here are shown in support of the article "Physical and chemical mechanisms that influence the electrical conductivity of lignin-derived biochar". Here we provide additional details on the literature review of biochar conductivity (Table C.1), the digestion of biochar samples for inductively coupled plasma optical emission spectroscopy (Section C.2), and statistical methods (Section C).

A more complete overview of the infrared spectroscopy results of thermogravimetric analysis gases is given (Figure 5). Nyquist plots for WS900, WS1100 and CELL900 biochars are shown in Figure C.2. FTIR spectra without baseline correction are shown in Figure C.3. Table C.3 and Figures C.4-C.7 show D positions, G positions, and I_{DG} ratios for all biochars, as well as the curve fitting process used to fit Raman spectra. Biochar pore size distributions and gas adsorption isotherms are shown in Figure C.8 and C.9 respectively. Biochar particle size distributions are shown in Figure C.10.

A more complete description of the results of the statistical analyses than is included in the main text is given in Section C.

Supplemental Methods

Biochar digestion

Biochar samples were diluted for inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis in the amounts shown in Table C.2.

Table C.1: A review of electrical conductivity of biochar in past literature. This table accompanies Figure 1 of the main text.

Feedstock	Pyrolysis Temperature °C	Conductivity S/cm	Measurement method
Sugar Maple [153]	950	3.99	Two piston
Lignin (with Ni catalyst) [240]	1100	0.57	Single particle
Hydrolysis lignin [114]	900	0.11	Two piston
Lignin [150]	1100	0.1	Single particle
Maple wood [149]	900	11.42	Four point
Microfibrillated cellulose/lignosulfonate [19]	1200	95	Four point
Microcrystalline cellulose [146]	2000	100	Four point
medium-density fiberboard [159]	1400	243	Four point
Oil palm/cotton cellulose [152]	1000	4.9	Four point
Coffee Chaff [99]	900	3.07E-3	Two piston
Sodium carbonate lignin [111]	900	1.5	Two piston
Miscanthus [103]	750	0.03	Two piston
Red wood cedar [157]	750	2	Two point
Coffee grounds [103]	1000	3	Two piston
Vineyard residues [156]	900	1.79	Two piston
Lignin [141]	1100	5.27	Guard electrode

Table C.2: Nitric acid dilution for ICP-OES measurements of biochar. Measurements were taken after the second dilution.

Biochar	Initial dilution mg/L	Final dilution mg/L
AL900	0.001599	0.000178
AL1100	0.001962	0.000223
CELL900	0.001829	0.000202
DAL900	0.001918	0.00021
DAL1100	0.001725	0.000189
HL900	0.001545	0.000171
HL1100	0.001812	0.000198
WS900	0.001959	0.000206
WS1100	0.001905	0.000204

Statistical methods

The linear mixed effects model shown in Equation C.1 was used to examine if differences existed in maximum conductivity between treatments.

$$Y_{ijk} = \mu + \tau_i + \delta_{j(i)} + \epsilon_{k(ij)} \quad (\text{C.1})$$

Where Y_{ijk} is the maximum conductivity of the k th time observation of the j th sample of the i th treatment, μ is the mean maximum conductivity for treatment AL1100, τ_i is the difference in mean maximum conductivity for treatment group i , with i pertaining to AL900, CELL900, DAL1100, DAL900, HL1100, HL900, WS1100, or WS900, $\delta_{j(i)}$ is the random effect for sample with $j = 1, 2 \dots 5$, with sample nested within treatment and assumed independently and identically distributed (iid) $\delta_{j(i)} \sim N(0, \sigma_\delta^2)$, and $\epsilon_{k(ij)}$ is the random effect for time observation with $k = 1, 2 \dots 7$, with time observation nested within sample and assumed iid $\epsilon_{k(ij)} \sim N(0, \sigma_\epsilon^2)$.

Relationships between biochar electrical conductivity and biochar physical and chemical properties were explored with the following theoretical additive, mixed effects model:

$$\sqrt{Y_{ijk}} = \beta_0 + \beta_1 \times \text{O:C}_i + \beta_2 \times \text{PS}_i^* + \beta_3 \times \text{PS}_i^{*2} + \alpha_i + \tau_{j(i)} + \epsilon_{k(ij)} \quad (\text{C.2})$$

where $\sqrt{Y_{ijk}}$ is the square root of the maximum conductivity of the k th time observation of the j th sample of the i th treatment, $i = \text{AL900, AL1100, DAL900, DAL1100, CELL900, HL900, HL1100, WS900, WS1100}$ is the treatment combination of temperature and feedstock, $j = 1, 2 \dots 5$ is the index for the sample in treatment, $k = 1, 2 \dots 7$ is the index for time observation in sample number in treatment, $\beta_0, \beta_1, \beta_2, \beta_3$ are parameters, O:C_i is the quantitative variable for the molar ratio of oxygen to carbon for each treatment i , PS_i^* is the orthogonal polynomial term to the first power for biochar particle size in each treatment

Table C.3: Raman average peak locations and I_{DG} ratio for all biochars. All reported values are an average of three measurements. The Raman spectra for a single measurement is shown in Figure 7 of the main text and the remainder are shown in the Figures C.4 - C.7.

Biochar	D (1320-1370 cm^{-1})	G (1530-1610 cm^{-1})	I_{DG}
AL900	1332	1599	1.01
AL1100	1329	1583	1.47
CELL900	1321	1596	1.18
DAL900	1335	1609	0.93
DAL1100	1337	1605	1.03
HL900	1334	1595	1.18
HL1100	1334	1596	0.98
WS900	1334	1605	0.91
WS1100	1335	1602	0.92

i , $(\text{PS}_i^*)^2$ is the orthogonal polynomial term to the second power for biochar particle size in each treatment i , α_i is the treatment random effect assumed iid $\alpha_i \sim N(0, \sigma_\alpha)$, $\tau_{j(i)}$ is the random effect of sample, with sample nested in treatment and assumed iid $\tau_{j(i)} \sim N(0, \sigma_\tau)$ and $\epsilon_{k(ij)}$ is the random effect of time observation, with time nested in sample, nested in treatment and assumed iid $\epsilon_{k(ij)} \sim N(0, \sigma_\epsilon)$.

Supplemental Results

Experimental Results

Statistical Results

The final estimated model for the relationship between electrical conductivity and biochar properties was defined as [250]:

$$\sqrt{\hat{\mu}_{ijk}} = 3.18 - 8.55(\text{O:C}_i) + 3.13(\text{PS}_i^*) + 7.14(\text{PS}_i^*)^2 \quad (\text{C.3})$$

where $\sqrt{\hat{\mu}_{ijk}}$ is the square root of the mean maximum conductivity of the k th time observation of the j th samples of the i th treatment, and is defined as $\sqrt{\hat{\sigma}_{\max,ijk}}$ in the main text of the paper for clarity, $i = \text{AL900, AL1100, DAL900, DAL1100, CELL900, HL900, HL1100, WS900, WS1100}$ is the treatment combination of temperature and feedstock, $j = 1, 2 \dots 5$ is the index for the sample, in treatment, $k = 1, 2 \dots 7$ is the index for time observation, in sample number in treatment, O:C_i is a quantitative variable for the molar ratio of oxygen to carbon in each treatment i , PS_i^* is the orthogonal polynomial term to the first power for particle size in each treatment i , and $(\text{PS}_i^*)^2$ is the orthogonal polynomial term to the second power for particle size in each treatment i .

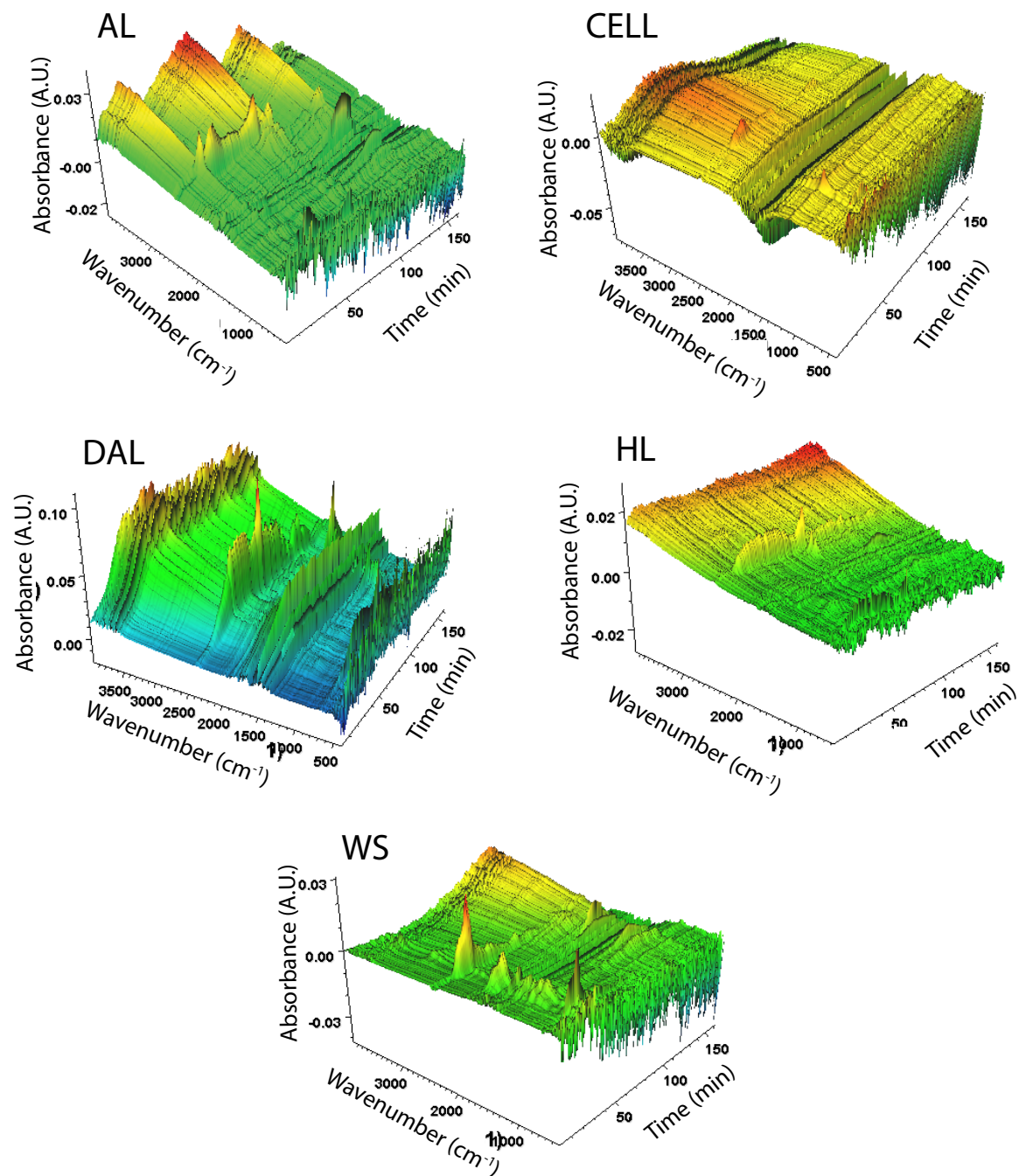


Figure C.1: Full 3D representations of TGA-IR data for all biochar feedstocks. See Figure 3 of the main text for accompanying TGA and Gram-Schmidt curves.

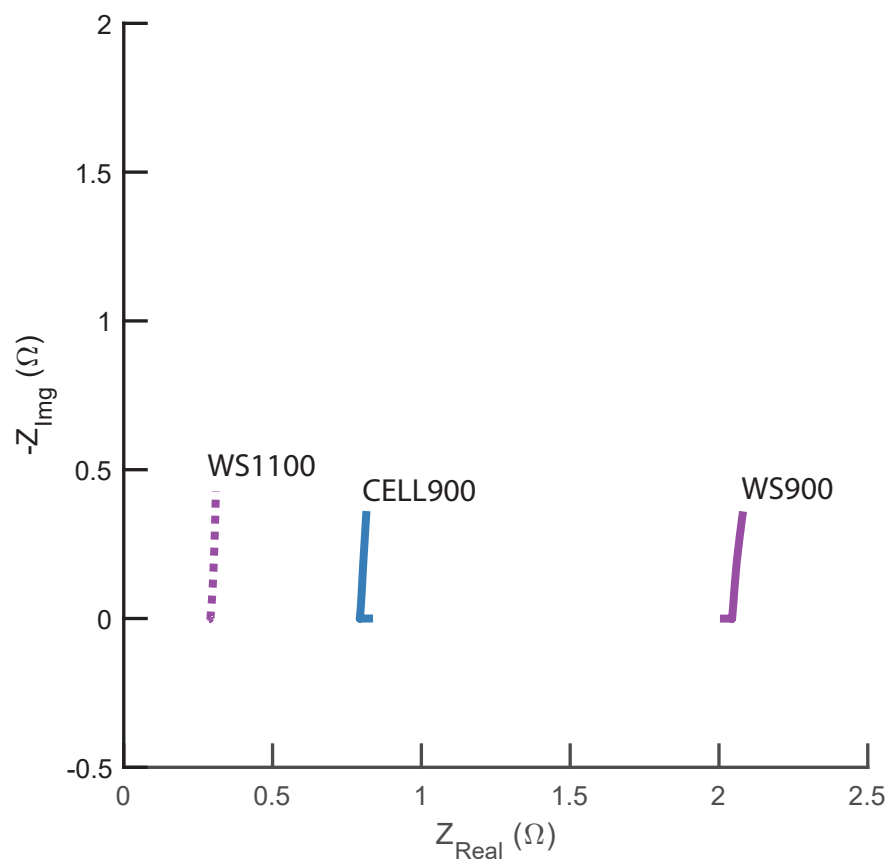


Figure C.2: Nyquist plot for WS900, WS1100 and CELL900 biochars. See Figure 5 of the main text for Nyquist plots of the other biochars.

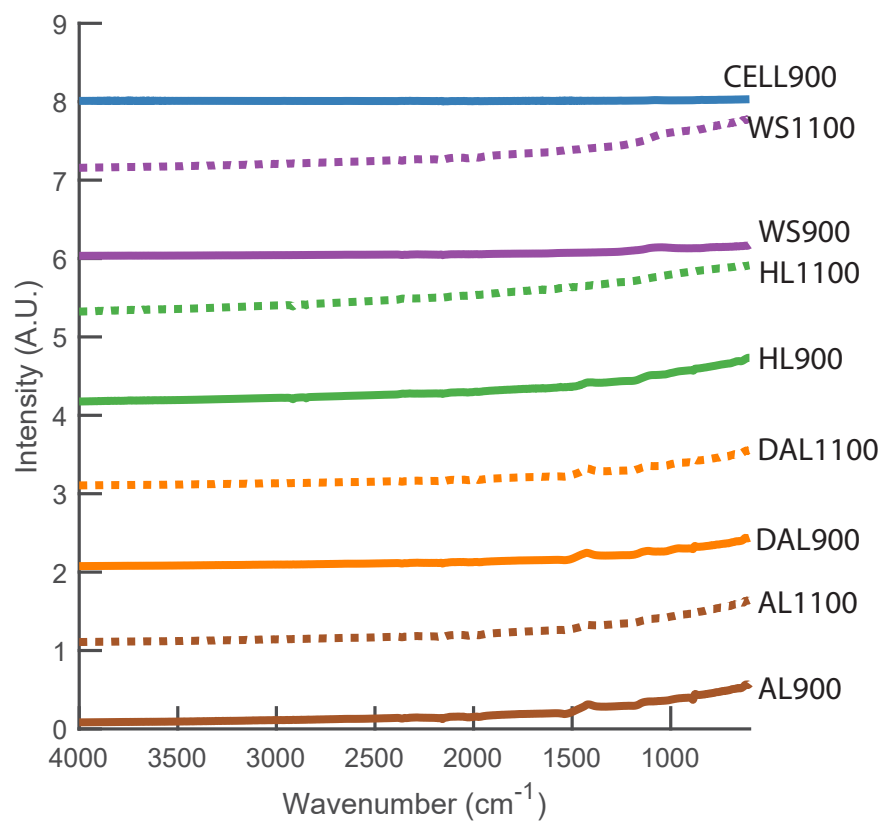


Figure C.3: Full spectra and non-baseline corrected FTIR curves for all biochar. See Figure 6 of the main text for baseline corrected FTIR spectra.

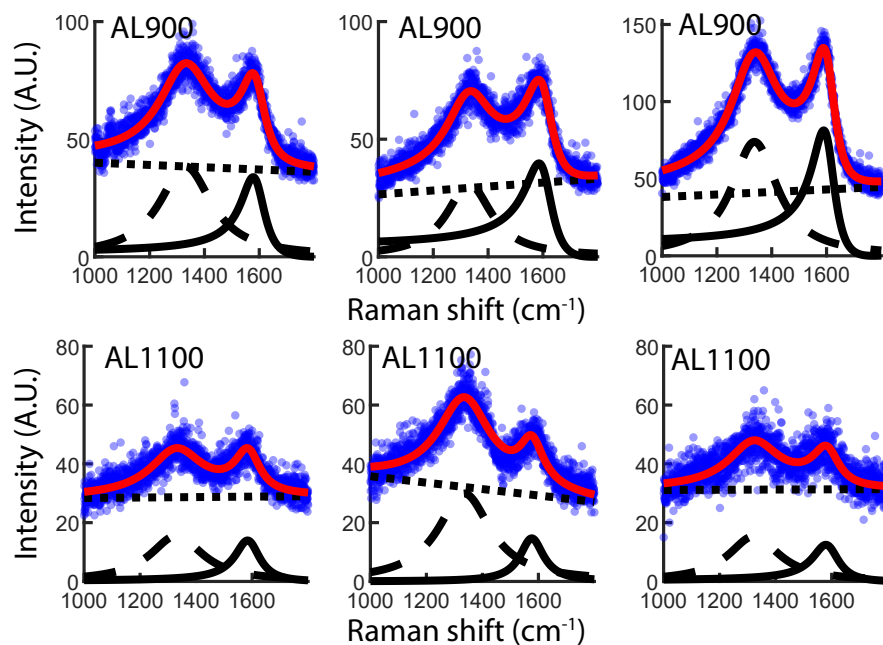


Figure C.4: Raman spectra and curve fitting for three replicates each of AL900 (top) and AL1100 (bottom) biochars. Red lines represent the final curve fit, blue dots represent the raw Raman data, solid black lines represent the fit for the G peak, long dashed black lines, the fit for the D peak and short dashed lines the baseline shift.

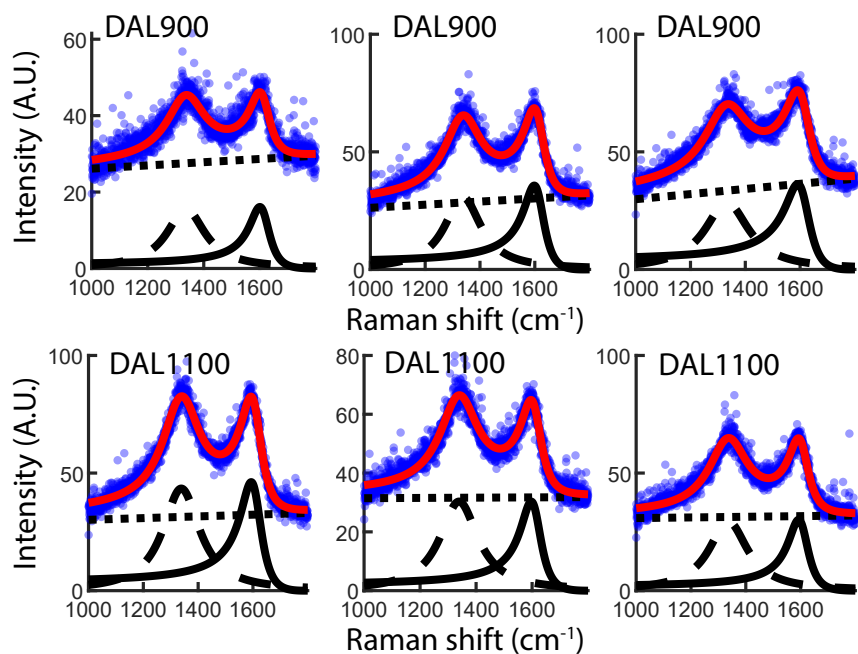


Figure C.5: Raman spectra and curve fitting for three replicates each of DAL900 (top) and DAL1100 (bottom) biochars. Red lines represent the final curve fit, blue dots represent the raw Raman data, solid black lines represent the fit for the G peak, long dashed black lines, the fit for the D peak and short dashed lines the baseline shift.

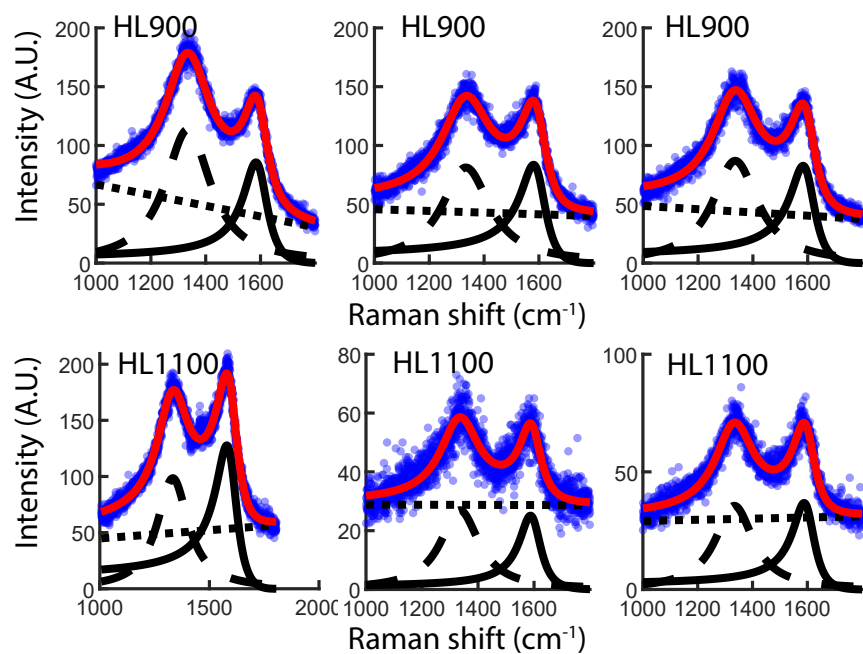


Figure C.6: Raman spectra and curve fitting for three replicates each of HL900 (top) and HL1100 (bottom) biochars. Red lines represent the final curve fit, blue dots represent the raw Raman data, solid black lines represent the fit for the G peak, long dashed black lines, the fit for the D peak and short dashed lines the baseline shift.

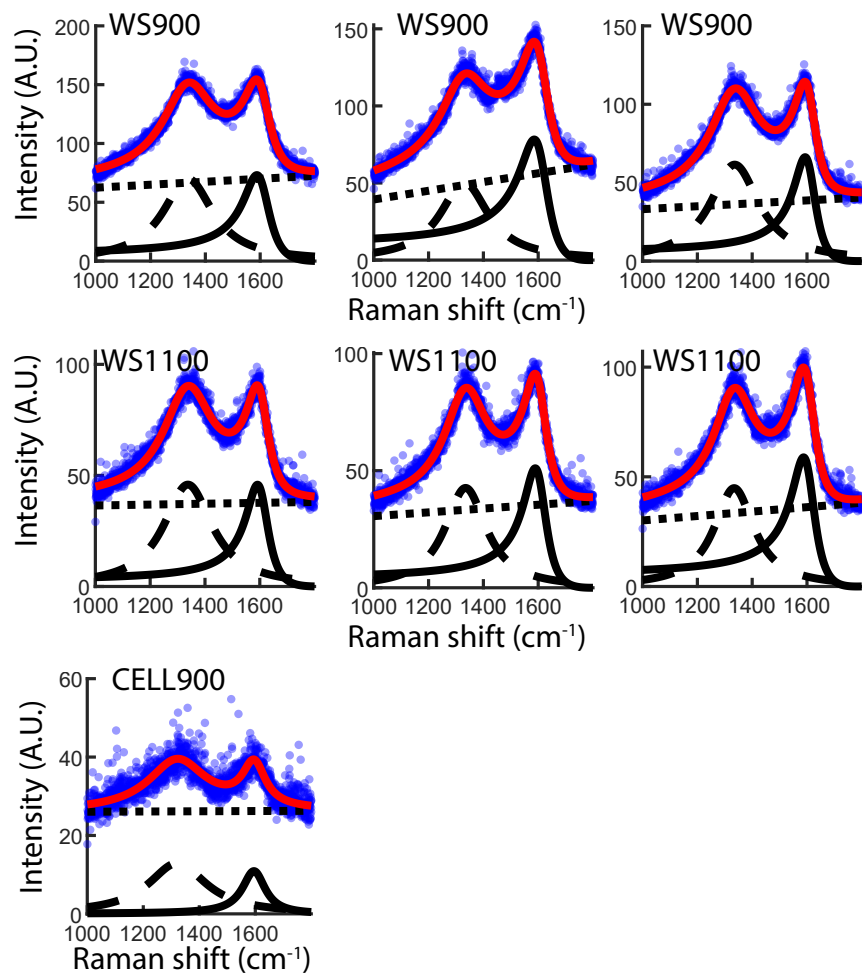


Figure C.7: Raman spectra and curve fitting for three replicates each of WS900 (top) and WS1100 (middle) biochars. (Bottom) single Raman spectra and curve fitting for CELL900 biochar, no additional replicates were ran due to issues with the laser used burning the biochar. Red lines represent the final curve fit, blue dots represent the raw Raman data, solid black lines represent the fit for the G peak, long dashed black lines, the fit for the D peak and short dashed lines the baseline shift.

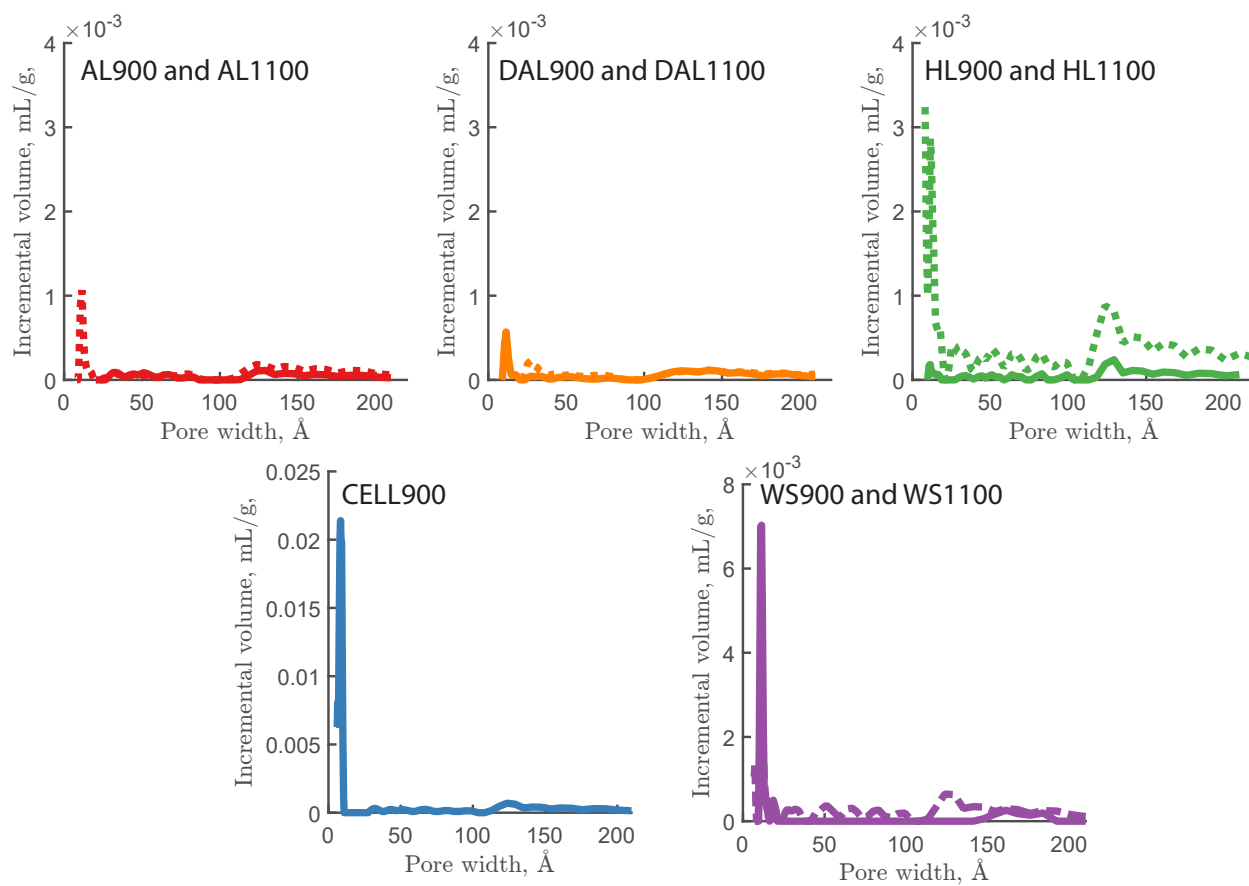


Figure C.8: Pore size distribution from gas adsorption measurements for all biochars. Solid lines indicate biochars produced at 900 °C while dashed lines indicate biochars produced at 1100 °C.

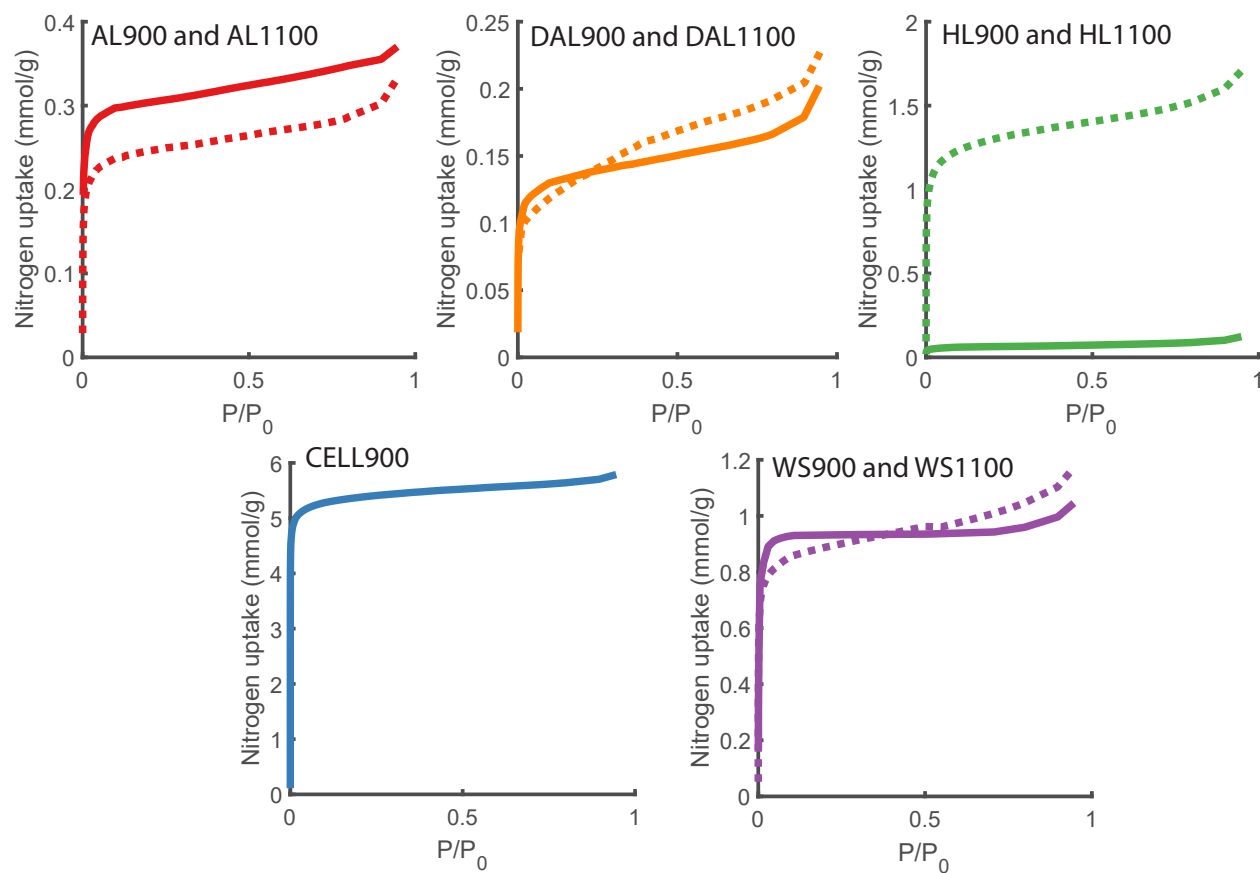


Figure C.9: Gas adsorption isotherms for all biochars. Solid lines indicate biochars produced at 900 °C while dashed lines indicate biochars produced at 1100 °C.

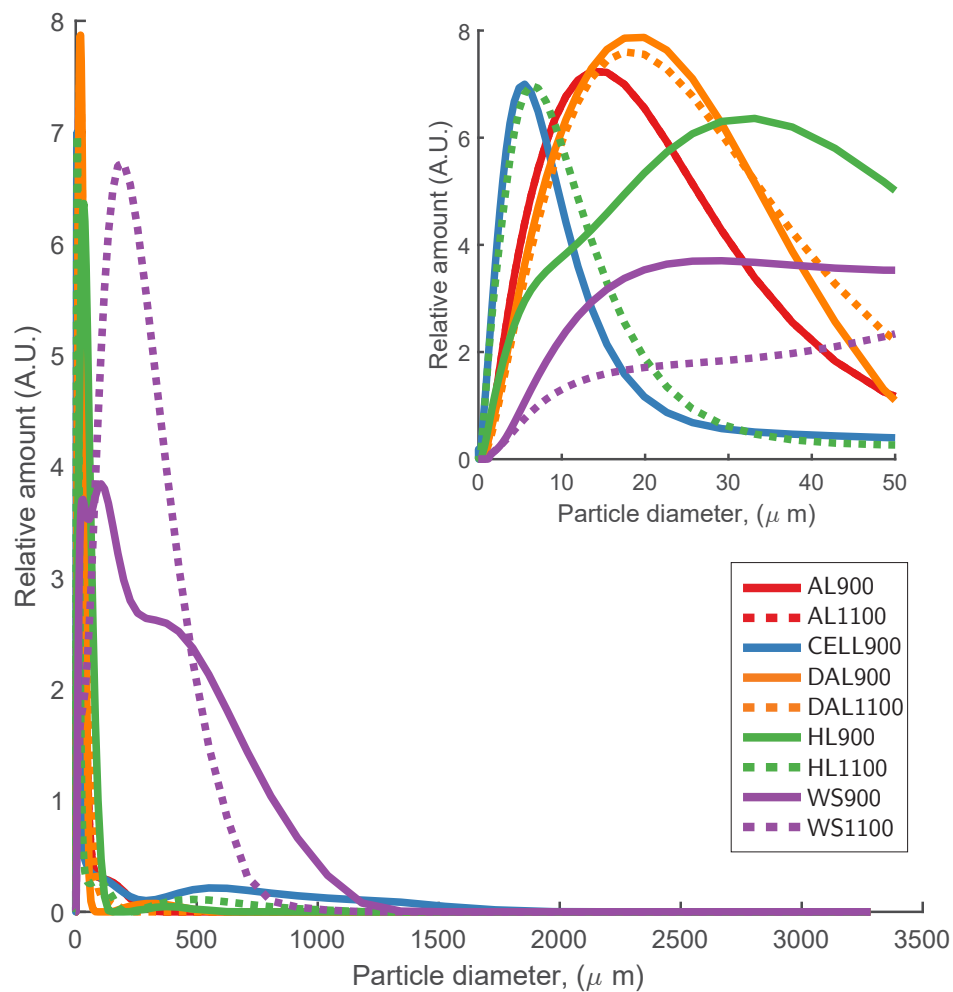


Figure C.10: Particle size distribution for all biochars. The inset shows the relative distribution between 0 and 50 μm in greater detail.

APPENDIX D

SUPPLEMENTAL INFORMATION TO: BIOCHAR FROM FOOD WASTE AS A
SUSTAINABLE REPLACEMENT FOR CARBON BLACK IN UPCYCLED AND
COMPOSTABLE COMPOSITES

This document is prepared in support of the article "Upcycled and compostable biocarbon-filled plastics: biochar from food waste as a sustainable replacement for carbon black." Figures and data displayed herein are intended to provide additional detail on the methods and results described in that article. For additional information, see the full article.

Supplemental Methods

Figure D.1 shows a photograph of the four-probe electrical conductivity setup used to measure the electrical conductivity of the composite samples. Spring-loaded needle electrodes are mounted in a polycarbonate plate, with a distance of 2 mm between the center of each needle and a needle diameter of 0.75 mm. Samples are placed on the below microscope stage and can be raised or lowered to apply pressure to the needles.

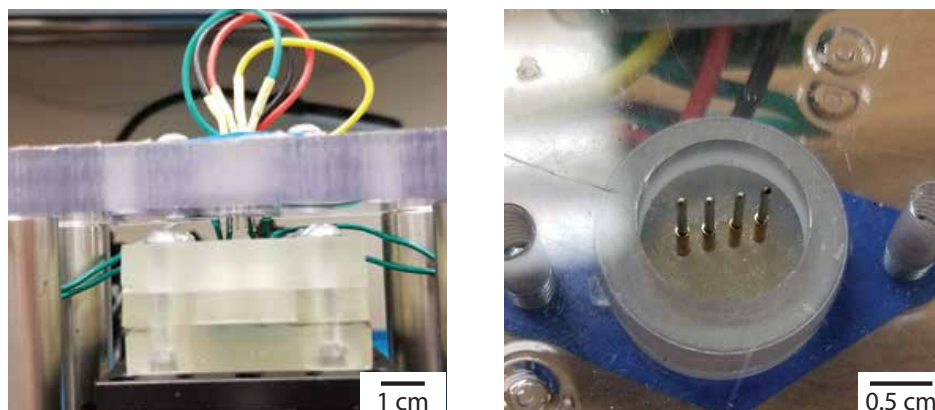


Figure D.1: Photograph of the four-point electrical conductivity method setup from the side (left) and below needles (right). The lower stage can be raised to apply pressure to the sample by the springloaded needles.

Figure D.2 shows photographs of the bagged composting samples (left) with a cellulose sample (top) and two PLA samples (middle and bottom). The 2L polycarbonate composting containers used (center) are shown, with the two vents added being the barbed hose attachments. The right photograph shows the bagged composting samples after 20 days of composting. Bacterial attachment to the samples can be observed.

Optical microscopy images of the composites were captured on a piece of flashing from injection molding to increase the light transmission through the sample. Images were capture on an Olympus BX41 Phase Contrast and Darkfield Microscope with an AmScope microscope digital camera. Samples were backlit, and images were captured at 20 $\times$ magnification for all samples.



Figure D.2: Photographs of the setup for PLA and FW900 biochar composting experiments. (left) Samples in mesh bags prior to composting. (center) 2L polycarbonate container with compost. (right) Samples in mesh bags after 20 days of composting.

Supplemental Results

In addition to the EDS spectra displayed in Figure 2a of the main text, EDS maps were captured over the displayed area shown in Figure 2b of the main text (Figure D.4). EDS maps show that most elements are evenly distributed throughout the biochar, with sodium and chlorine tending to be located in the same area, indicating NaCl salt's presence. Additionally, magnesium, calcium, and phosphorous show minor clumping. Thus, the relatively homogenous EDS results indicate that we can expect largely homogeneous properties of the biochar.

Figure D.5 provides the first DSC heating cycle as a comparison for the second cycle shown in Figure 4 of the main text. In PLA during the first heating cycle, only minor differences are observed between 0% FW900 and 20% FW900, with a slightly increased glass transition temperature in 0% FW900, reduced cold crystallization enthalpy in 20% FW900, and a minor shoulder on the melt peak of PLA in 20% FW900. In HDPE, an increase in melt enthalpy is observed in 0% HDPE. After correcting for the addition of biochar, HDPE and 20% FW900 are found to have higher crystallinity, following the trend observed in the second heating cycle.

FTIR spectra of the composites do not show any changes in spectra from neat PLA or HDPE with the addition of biochar (Figure D.6). This result is expected, as no major peaks were present in the FTIR spectra of the neat biochar before baseline correction.

For each sample type, three DMA three-point bending samples were run. A representative curve of each sample is shown in Figure 5 of the main text, while Figure D.7 shows the complete set of three replicates for each sample. Note that in these samples, data collected after PLA and 10% and 20% FW900 were observed to fail are shown, while

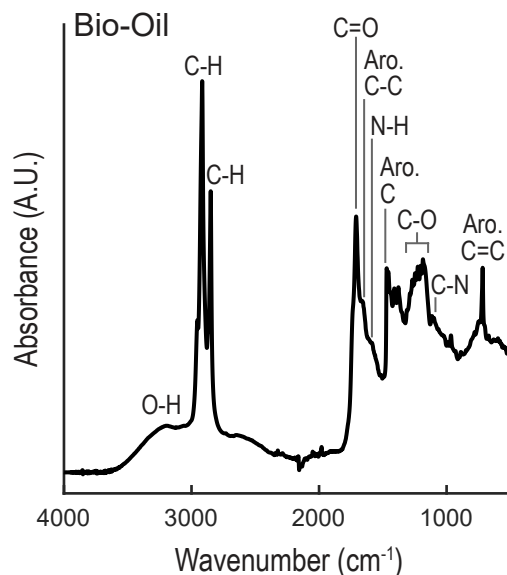


Figure D.3: FTIR spectra of bio-oil produced during pyrolysis of FW900. Primary peaks are identified as (from left to right): a broad peak from 3600-3100 cm^{-1} attributed to O-H bonds associated with water, strong peaks at 2914 and 2849 cm^{-1} attributed to aliphatic C-H bonds associated with fatty acids, a strong peak at 1709 cm^{-1} associated with C=O ester bonds in fatty acids, shoulders at 1660 and 1583 cm^{-1} associated with cyclic C-C bonds and N-H bonds respectively, a series of overlapping peaks from 1300-1185 cm^{-1} associated with C-O bonds in alcohols and esters, a weak shoulder at 1115 cm^{-1} associated with C-N amine bonds, and a strong peak at 717 cm^{-1} associated with aromatic C=C bonds.

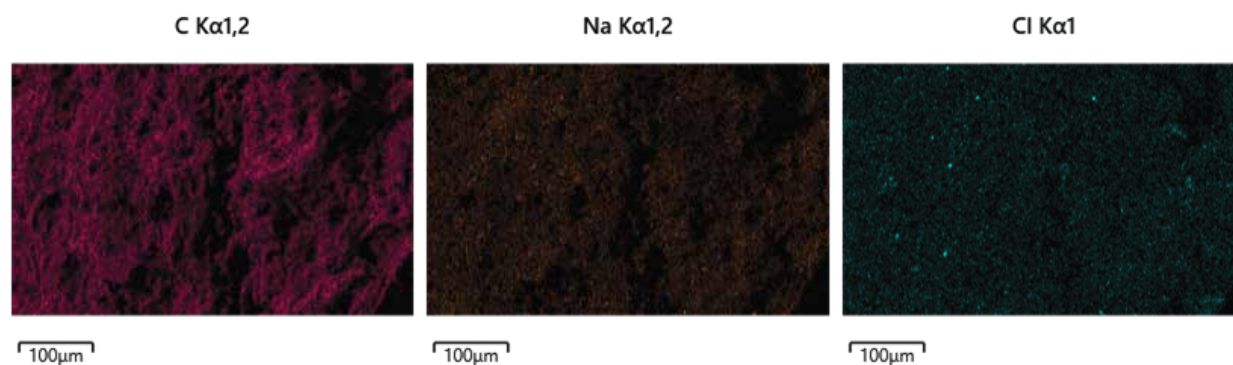


Figure D.4: EDS maps for (from top left to bottom right) carbon, sodium, and chlorine in FW900 biochar. Note the co-localization of sodium and chlorine.

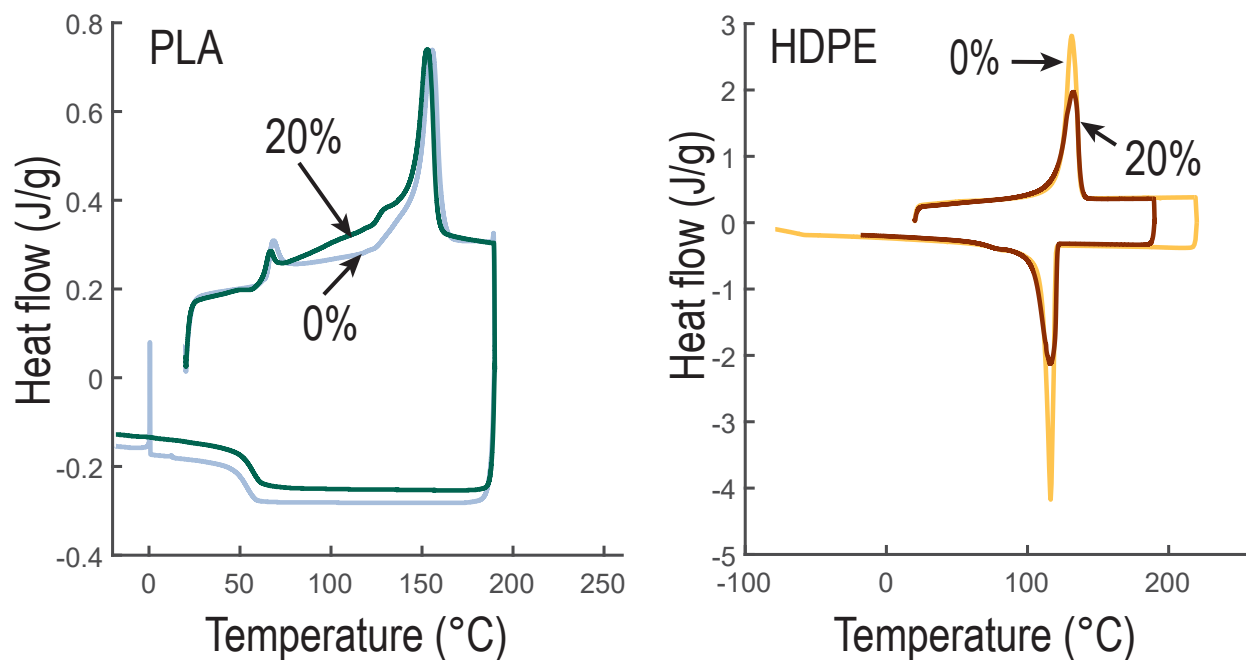


Figure D.5: First heating cycle DSC curves for non-extruded PLA with 0 and 20% FW900 (left), non-extruded HDPE with 0 and 20% FW900 (center), and injection molded PLA (right). All curves for HDPE showed no change in response between the first and second cycle (Figure 4). All curves are presented endothermic up.

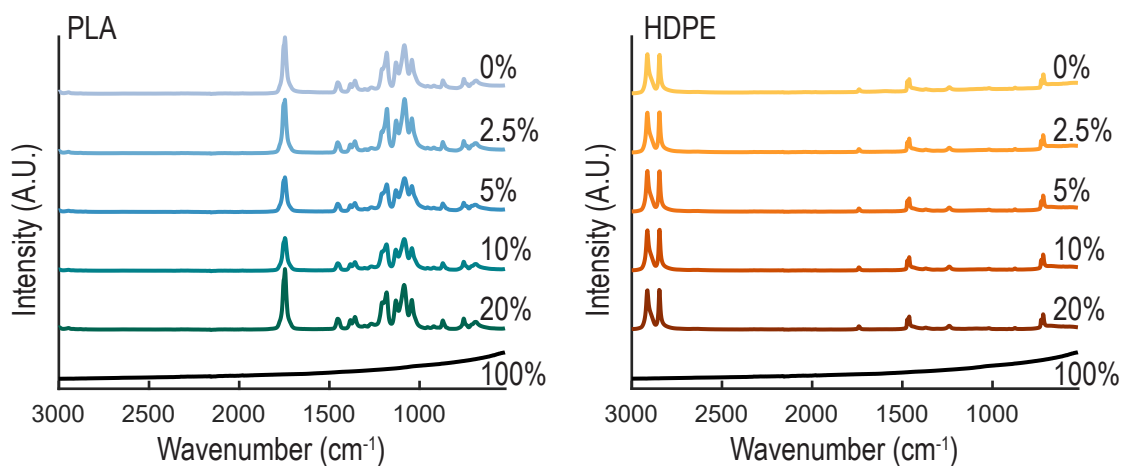


Figure D.6: Stacked FTIR spectra for PLA (left) and HDPE (right) for 0% to 100% biochar addition. No peaks were observed outside of the displayed region.

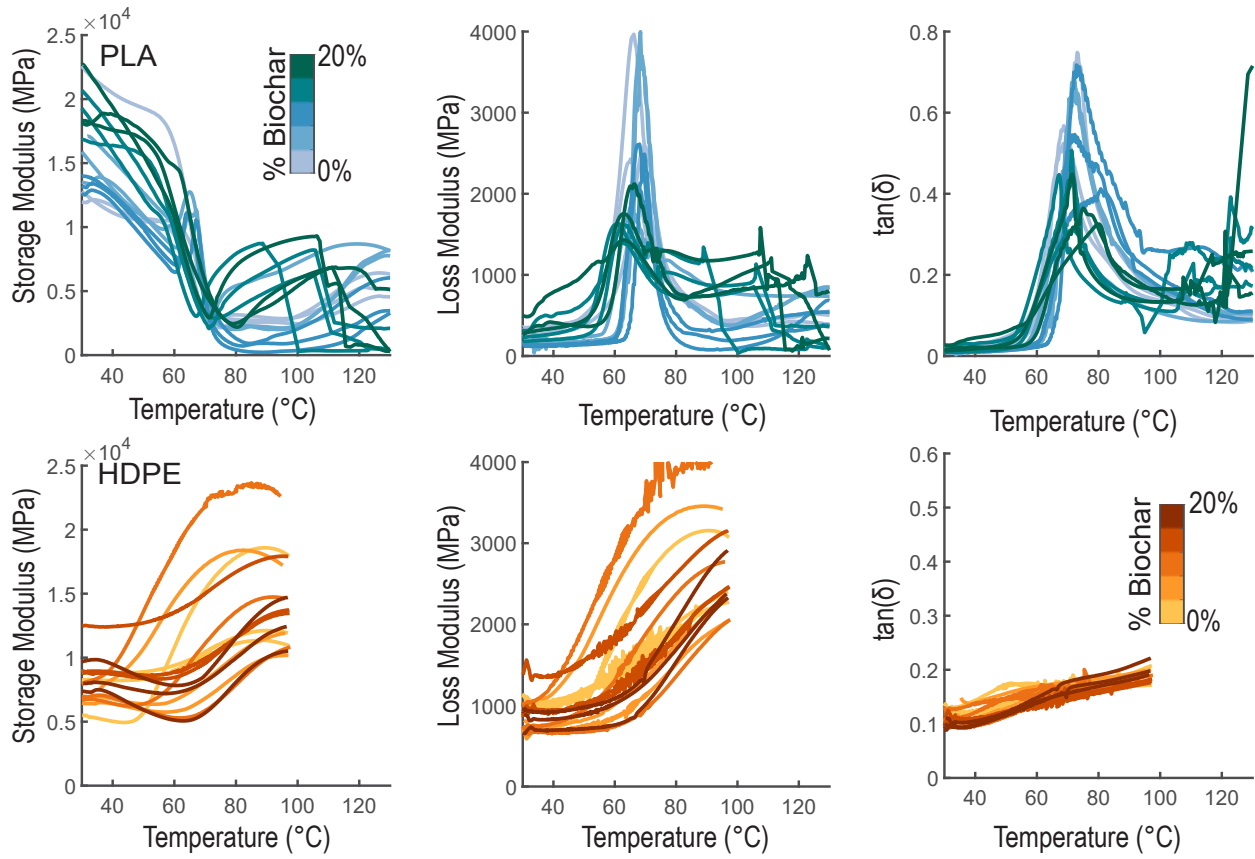


Figure D.7: All collected storage, loss and $\tan(\delta)$ curves for PLA (top) and HDPE (bottom) with FW900 biochar composites. Data collected after failure of the PLA and 10% and 20% FW900 samples is included. A single curve for each sample type are shown in Figure 5 of the main text.

Figure 5 of the main text truncates this data at failure.

Optical microscopy was performed on all PLA samples to examine the dispersion of FW900 particles in the PLA matrix (Figure D.8). Agglomeration is observed in 2.5%, 5%, and 20% FW900 samples, which may partially explain the low electrical conductivity observed in all 20% FW900 and PLA samples. However, FESEM images of 20% biochar addition to HDPE, for both original size and reduced size biochar do not show agglomeration.

In addition to the weight loss observed, composted PLA samples were visually observed to degrade (Figure D.9). After 20 days, neat PLA samples had fractured into several parts, and after 40 days, samples had degraded into powder. Note the color difference between neat PLA after 40 days (Figure D.9, right) and PLA with 20% FW900 after 40 days (Figure D.9, center).

Table D.1: Average glass transition temperatures from DMA loss modulus curves of PLA. Presented variations represent standard deviations from triplicate measurements.

% Biochar	0%	2.5%	5%	10%	20%
T_g (°C)	68.4 ± 1.9	65.3 ± 2.3	67.1 ± 1.4	62.2 ± 0.78	64.1 ± 1.9

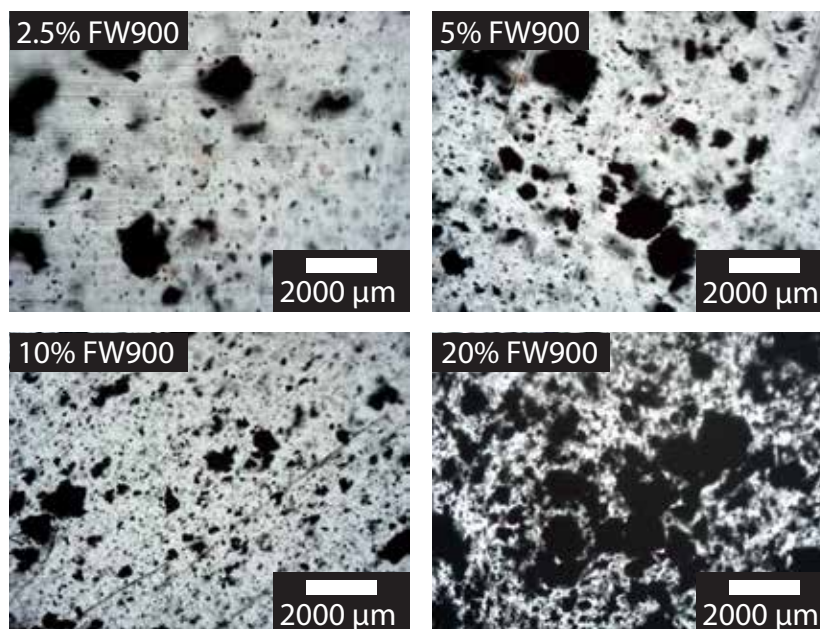


Figure D.8: Optical microscope images of PLA samples with 2.5%, 5%, 10% and 20% FW900 biochar at 20 $\times$ magnification. Images were not taken for HDPE composites as they were not optically clear.



Figure D.9: Composted PLA samples after 20 days (left), PLA with 20% FW900 after 40 days (center) and neat PLA after 40 days (right).

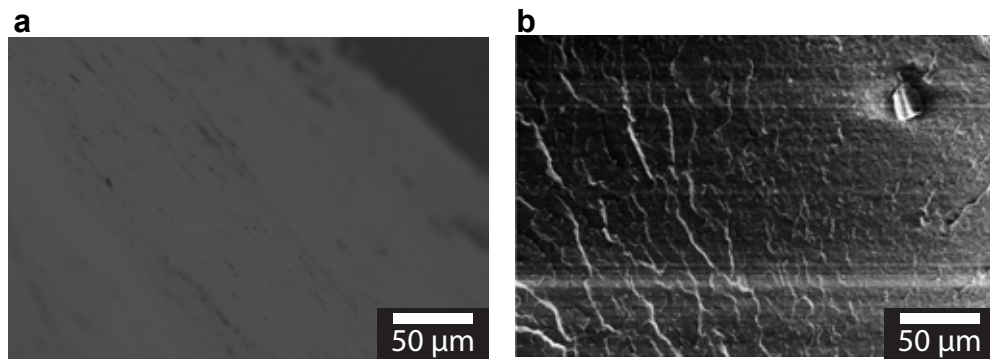


Figure D.10: FESEM micrographs for (a) neat PLA and (b) neat HDPE.

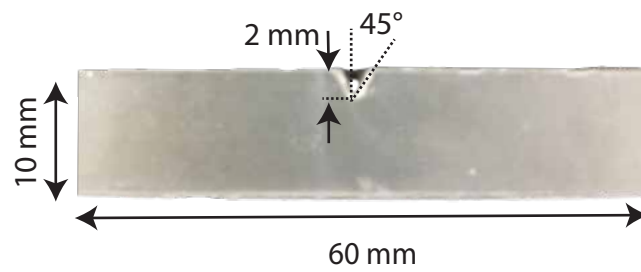


Figure D.11: Notch geometry of a Charpy impact sample shown in a neat PLA sample.

APPENDIX E

EXTENDED DATA TO: BIOCHAR-FILLED BIOPLASTICS: A NEW CLASS OF
BIOCOMPOSITES FOR ELECTRICAL APPLICATIONS AND BEYOND

Review of thermal degradation of PLA and PHBV with biochar

The properties of biochar and their impact on PLA are reviewed in Table E.1. Biochar from a variety of feedstocks, produced at a variety of pyrolysis temperatures all show reductions in thermal degradation temperature of PLA. PLA crystallinity shows more complex behavior with some highly crystalline PLAs showing reductions in crystallinity, while some highly amorphous PLAs instead increase in crystallinity.

Table E.1: A review of the thermo-mechanical degradation of PLA with the addition of biochar. T_{BioC} represents the highest treatment temperature of the biochar, d_{bioc} is the average particle diameter, W_{BioC} is the weight percentage of the biochar in the composite, ΔT_{deg} is the change in the onset temperature of thermal degradation relative to neat PLA, and $\Delta \chi_p$ is the change in crystallinity relative to neat PLA. For studies with multiple weight percentages of biochar added, the highest is examined. N/R refers to values that were not reported by the referenced study.

BioC Feedstock	T_{BioC} °C	d_{BioC} μm	W_{BioC} wt. %	ΔT_{deg} °C	$\Delta \chi_p$ % Cryst.
Switchgrasses[266]	500	< 600	20	Decrease	N/R
Miscanthus [181]	650	20-75	10	-22	+3
Miscanthus [181]	650	0.9	10	-43	+1.7
Miscanthus [182]	700	20-75	10	N/R	-1/+2
Bamboo [56]	N/R	10	7.50	- 16.3	-35.6
Bamboo [183]	N/R	9.52	≤ 40	-22.5	+20.97
Bamboo [184]	N/R	5.42	≤ 12.5	N/R	-26.9
Bamboo [185]	600	N/R	≤ 40	Decrease	+14.8
Bamboo [186, 327]	800	75-300	$\leq 35\%$	-72	-8.63
Chicken feathers [188]	600	N/R	20	-40.4	NR
Coffee grounds [189]	700	10	≤ 7.5	-46.7	+2.6

The washing procedure applied to remove sodium sulfate results in a complete loss of crystalline sodium sulfate peaks in HL1100 as measured via XRD (Figure E.1a). Similarly, EDX spectra of biochar after washing show a 85% reduction in sodium counts from before washing, relative to the carbon peak (Figure E.1b). EDS spectra of the residue collected after the first and second washing step show high sodium, sulfur, and oxygen content consistent with a majority sodium sulfate material.

Table E.2: Summary of biochar physical and chemical characterization, including all parameters included in the regression model [143].

Biochar	Moisture (wt. %)	Surface area (m ² /g)	Avg Particle Size (μ m)	C (wt. %)	H (wt. %)	N (wt. %)	S (wt. %)	Na (wt. %)	Mg (wt. %)	K (wt. %)	Ca (wt. %)	O (wt. %)	pH
AL900	0.02	27.00	13.10	64.00	0.70	0.8	3.00	9.82	0.05	0.15	0.16	21.29	10.7
AL1100	0.07	21.20	12.00	70.60	0.60	0.7	3.00	8.07	0.08	0.15	0.20	16.17	10.7
CELL900	0.01	480.16	4.90	92.20	0.60	0.0	0.00	0.01	0.01	0.15	0.01	7.09	7.6
CT	0.01	2.21	361.00	69.71	2.57	0.8	0.07	0.002	0.0009	0.0	0.0	26.85	6.0
DAL900	0.03	11.52	14.00	65.20	0.70	0.6	4.80	10.57	0.14	0.15	0.08	17.68	10.6
DAL1100	0.04	10.66	15.00	69.40	0.40	0.5	5.50	8.91	0.14	0.15	0.09	15.00	11.0
HL900	0.05	17.97	19.10	71.50	0.70	0.7	4.00	6.79	0.01	0.15	0.05	15.88	11.0
HL1100	0.02	109.10	5.53	83.70	0.70	0.7	2.50	2.47	0.01	0.21	0.06	9.81	10.5
WS900	0.02	86.80	62.00	60.80	1.00	1.0	0.20	0.01	0.44	2.86	0.71	13.57	10.9
WS1100	0.02	75.90	130.00	60.70	1.00	1.0	0.10	0.13	0.43	3.1	0.77	13.65	10.6

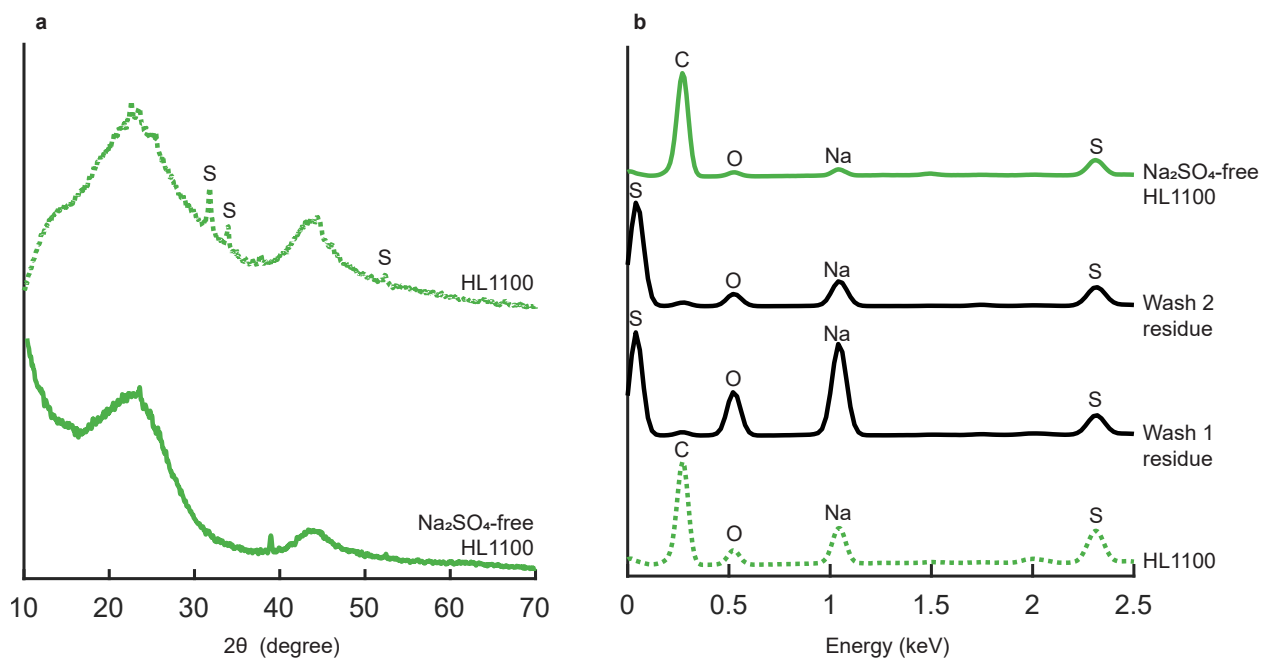


Figure E.1: Change in sodium sulfate content with washing as measured with (a) XRD and (b) EDS.

APPENDIX F

SUPPLEMENTAL DATA IN SUPPORT OF: REDUCING THE ENVIRONMENTAL
IMPACTS OF PLASTICS WHILE INCREASING STRENGTH: BIOCHAR FILLERS IN
BIODEGRADABLE, RECYCLED, AND FOSSIL-FUEL DERIVED PLASTICS



Figure F.1: Photographs of tensile samples with: (from left to right) 0%, 20%, and 40% biochar addition after testing and a flexural sample with 20% biochar addition.

Introduction

These data are presented in support of the article “Reducing the environmental impacts of plastics while increasing strength: biochar fillers in biodegradable, recycled, and fossil-fuel derived plastics” in Composites Part C: Open Access. The data herein provide additional characterization of the biochar, the biochar’s interaction with the plastics, and additional environmental impact assessment impact categories. For information related to the complete study, please refer to the main text of the article.

Supplemental Methods

To examine the relative chemical composition of the Pacific Biochar, energy dispersive X-ray spectra (EDX) were collected on a Zeiss SUPRA 55VP field emission scanning electron microscope with an Oxford energy dispersive X-ray detector. Prior to measurement samples were sputter coated with iridium. Measurements were taken over the entire displayed area at a magnification of $250\times$ and a working distance of 8.2 mm.

Supplemental Results

Addition of biochar to rHDPE increases the viscosity during extrusion, from 0.015 Pa-s at 0 wt.% biochar addition to 0.033 Pa-s at 40% biochar addition (Figure F.2). For both

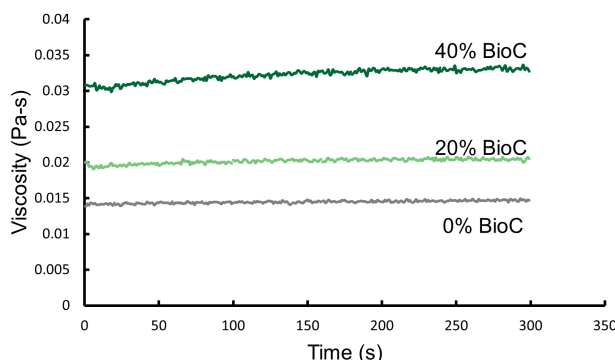


Figure F.2: Viscosity data collected during extrusion of rHDPE for samples with 0%, 20%, and 40% biochar.

Table F.1: Melt and crystallization temperatures (T_m and T_c and enthalpies (ΔH_m and ΔH_c) and % crystallization (χ_c) for rHDPE with 0%, 20%, and 40% biochar addition.

rHDPE with	T_m ($^{\circ}\text{C}$)	T_c ($^{\circ}\text{C}$)	ΔH_m (J/g)	ΔH_c (J/g)	χ_c (%)
0% biochar	132.4	118.9	158.8	172.3	54.18
20% biochar	131.8	118.4	138.1	143.3	48.9
40% biochar	133.2	119	142.1	155	80.8

20 wt.% and 40 wt.% biochar addition, stable viscosity measurements were reached before 5 min, indicating that 5 min was sufficient to fully mix the biochar into the plastic.

Other impact categories beyond what are shown in the main text were also determined from the environmental impact assessment (Figure F.4). These impact categories tend to follow similar trends to those of respiratory effects and acidification shown in the main text, with biochar resulting in larger reductions for PLA or PHB, where plastic production results in large impacts, and biochar addition resulting in smaller reductions or negligible increases for rHDPE and HDPE, where the effects of plastic production are much lower impact. Impacts not shown in the main text by constituent and processing steps are shown in Figure F.5. As for global warming potential, fossil fuel depletion, respiratory effects, and acidification, these impacts continue to be largely dominated by the effects of polymer production. As for the other impact categories, rHDPE is an exception, with limited impacts associated with its production. In general, PLA and PHB show higher impacts across all categories than rHDPE and HDPE.

EDX measurements confirm Pacific Biochar's reported carbon value for the biochar of 85% carbon. The remainder of the composition is oxygen (O) and metals, including potassium (K), calcium (Ca), and magnesium (Mg). These metals are expected to contribute to poor performance as a filler material in PHB and PLA by catalyzing the thermal

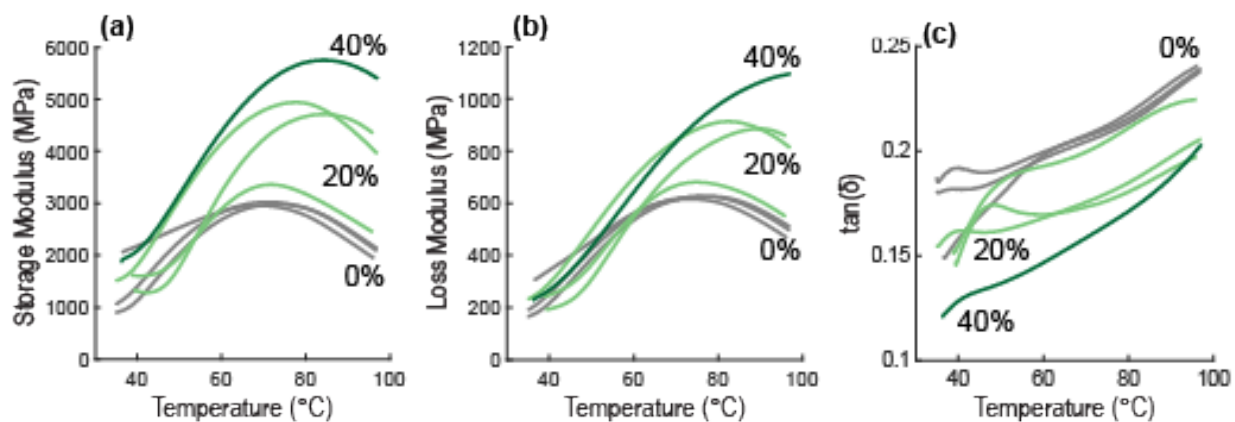


Figure F.3: Replicate DMA curves of composites of rHDPE with biochar showing (a) storage modulus (b) loss modulus and (c) $\tan \delta$. Only a single curve (single replicate) was collected for rHDPE and 40% biochar. A single representative curve for each sample type is shown in Figure 9.4.

degradation of these polymers, resulting in additional cleaning steps being required to remove these metals from the biochar.

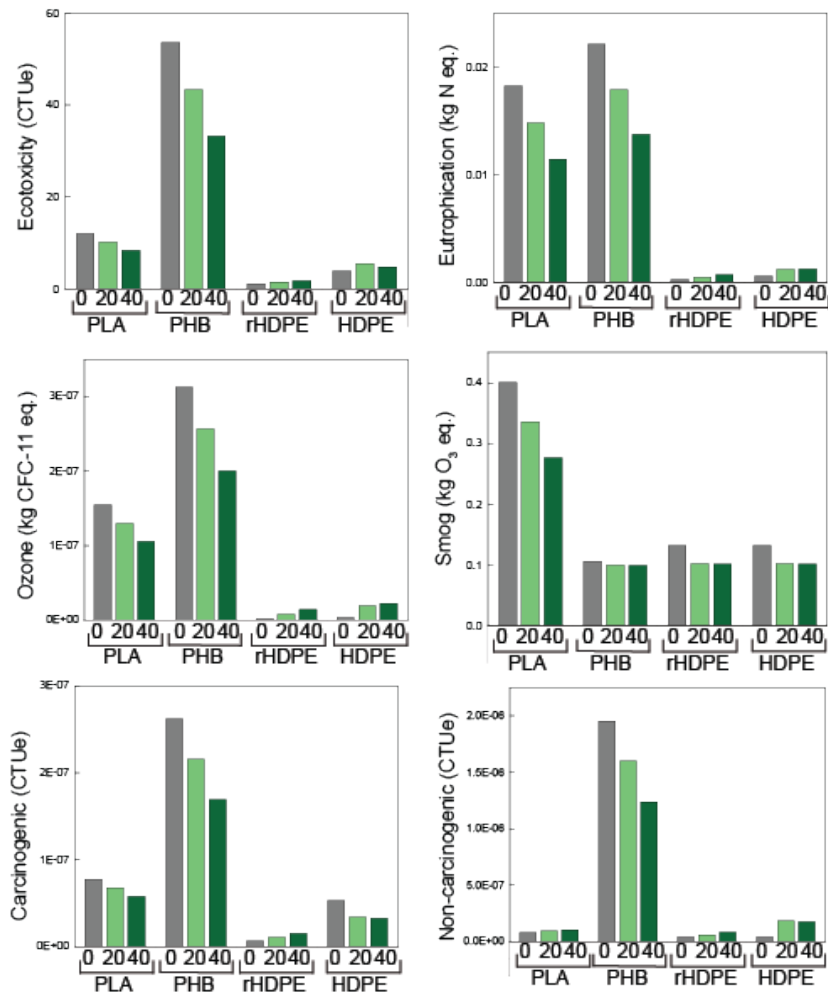


Figure F.4: Environmental impact assessment results for PLA, PHB, rHDPE, and HDPE for 0%, 20%, and 40% biochar addition. Impact indicators of (from top left to bottom right) ecotoxicity, eutrophication, ozone depletion, smog formation, human health cancer, and human health non-cancer are shown.

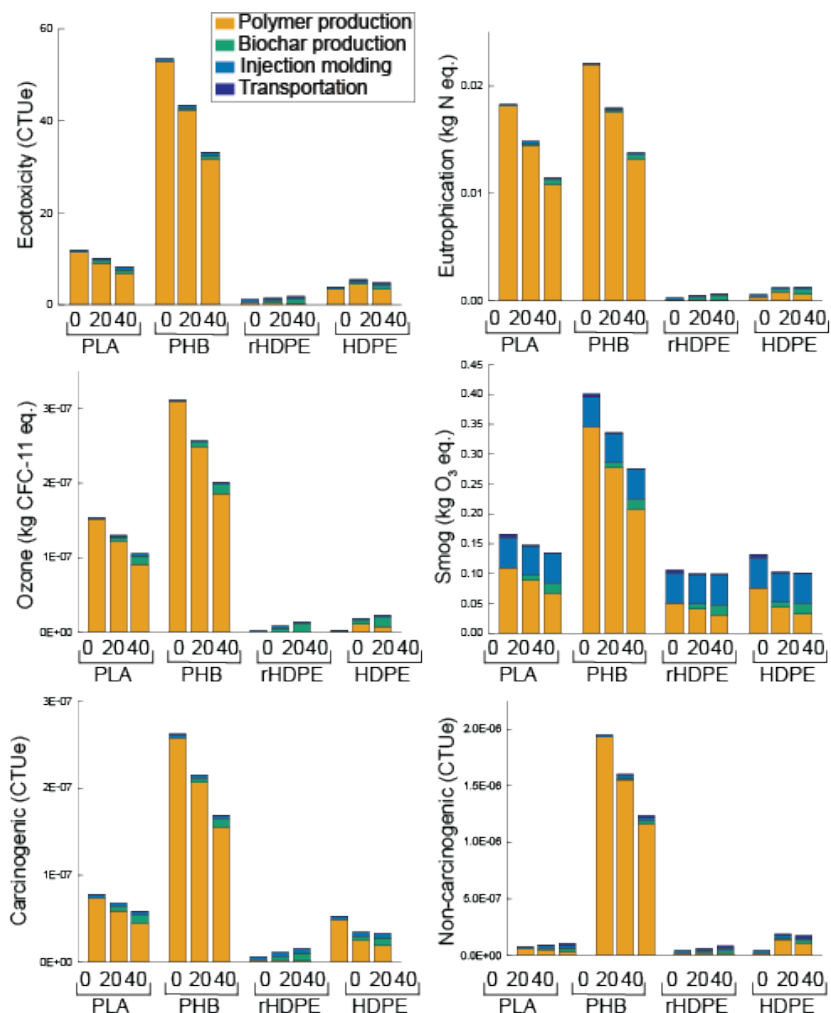


Figure F.5: Stacked bar plots of (from top left to bottom right) ecotoxicity, eutrophication, ozone depletion, smog formation, human health cancer, and human health non-cancer are shown by constituent and processing step for composites of 0%, 20%, and 40% biochar with HDPE, rHDPE, PLA and PHB.

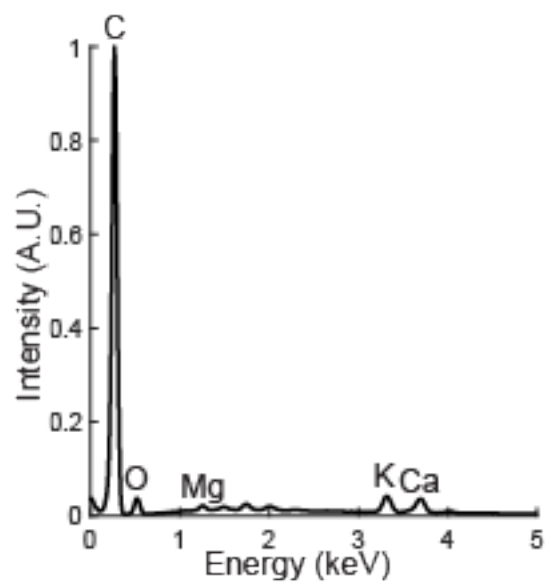


Figure F.6: EDX spectra for Pacific Biochar, with the elements that are detected, labeled.

APPENDIX G

SUPPORTING INFORMATION TO: BIOCHAR AS A RENEWABLE SUBSTITUTE
FOR CARBON BLACK IN LITHIUM-ION BATTERY ELECTRODES

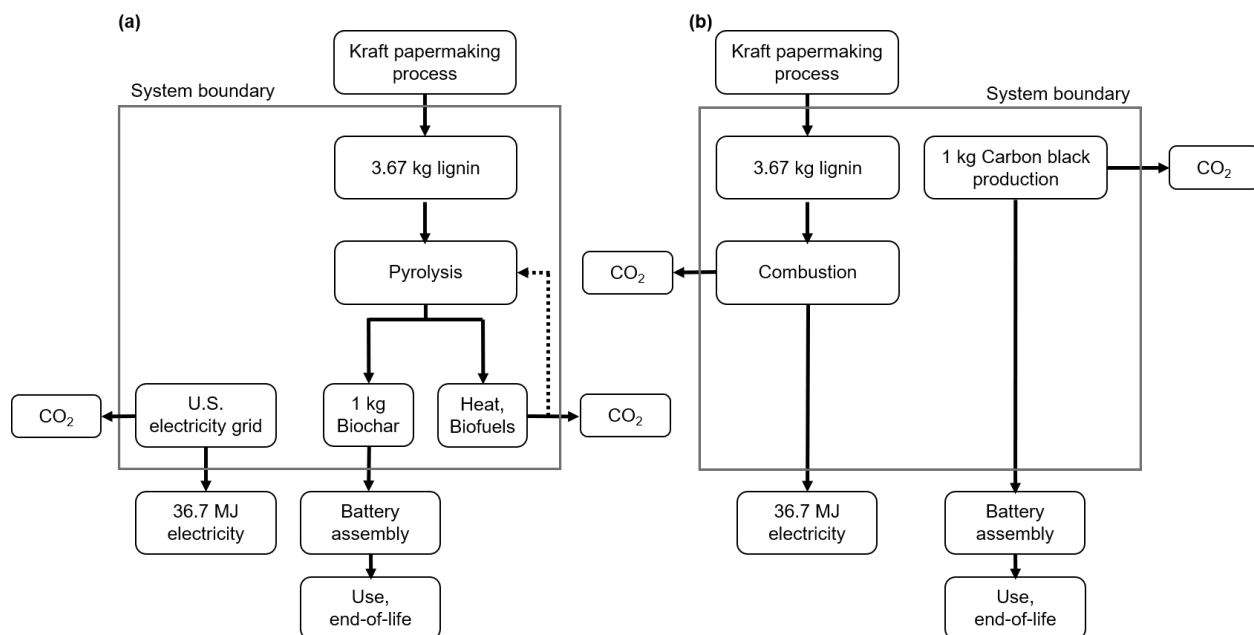


Figure G.1: System boundaries for the environmental impact assessment performed to compare the global warming potential of the production of (a) biochar and (b) carbon black.

Environmental Impact Assessment Methods

An environmental impact assessment was performed with the goal of estimating the global warming potential of the production of biochar as a conductive additive in lithium-ion batteries (LIBs) compared to commercially obtained carbon black. To this end, no environmental impact categories other than global warming potential were considered. We hypothesized that biochar would reduce the global warming potential associated with the production of a conductive additive relative to carbon black. This cradle-to-gate estimation was made with a functional unit of 1 kg conductive additive, comparing the production of biochar from lignin to the production of Vulcan XC-72R carbon black from petroleum (Figure G.1).

This estimation is made with the following assumptions: (1) that all carbon in the gas and liquid pyrolysis products is completely combusted to form CO₂, (2) that otherwise all carbon in the lignin would be completely combusted for energy, and (3) that lignin is a waste byproduct, and therefore all emissions associated with biomass production can be attributed to the other products of the kraft process. In the comparison scenario, 3.67 kg of lignin is combusted to generate 36.15 MJ of energy [386] was converted into biochar in the primary scenario. This combustion generates 36.15 MJ of energy; to avoid allocation, this is accounted for in the primary scenario by the addition of the production of energy at the 2020 U.S. electricity grid average [362]. It is assumed that the pyrolysis process is net energy neutral: i.e., that the heat generated from exothermic pyrolytic reactions and combustion of

the gas and liquid products is used to heat the pyrolysis process [123, 124, 363]. The fact that biochar pyrolysis produces surplus energy has been established and demonstrated to produce lower temperature biochars, and it is assumed herein that this also holds true at higher temperatures (no data for pyrolysis above 900 °C was found in the literature).

The battery production, application, and end-of-life phases of the material were outside the scope of this estimation. However, given the similar performance of biochar compared to carbon black as a conductive additive, it is a reasonable assumption that the substitution of carbon black with biochar would have minimal impact on these aspects of the assessment.

Further Material Characterization

In addition to the XRD patterns and Raman spectra presented in the main text, all conductive additive materials were characterized by EDX spectroscopy to determine the chemical composition (Figure G.1a). All of the materials were found to be mainly carbon (89-99 at. %), with some oxygen (0.7-7 at. %) and sulfur (0-2 at. %) also present. Biochar shows higher oxygen and sulfur content than carbon black, in addition to sodium. The sodium content in biochar can be attributed to the presence of sodium sulfate (Na_2SO_4) as confirmed by XRD and FTIR (Figures G.1b-c) and is significantly reduced by washing in copious water; hence, the washing procedure used herein is a simple and effective method to remove sodium sulfate.

All three conductive additive materials were also assessed in terms of particle size using optical methods (Figure G.1d). Biochar, XC-72, and Super P all show similar particle size distributions, with biochar having a slightly smaller median particle size than the agglomerates present in both carbon blacks, and with all three materials having a median particle size of $\sim 10\mu\text{m}$.

Further Active Material Electrochemical Characterization

For each set of electrochemical results presented in Figures 10.2 and 10.3 in the main text, at least three cells were fabricated to ensure reproducibility of the results. In some cases, many more cells and electrodes were tested. All of the replicate tests showed high consistency from cell to cell, as shown in Figures G.3-G.4. In all cases presented in the main text, the middle cell (or the cell nearest the mean) of any given series of replicates was used.

Further Anode Additive Characterization

As a conductive additive for LIB anodes (e.g., graphite), further electrochemical characterization of biochar, Super P, and Vulcan XC-72 was carried out to ensure reproducibility across multiple cells (Figure G.5) and to compare electrical conductivity of the prepared electrodes (Figure G.6).

Electrical impedance spectroscopy (EIS) of ex situ, never cycled electrodes containing either biochar or Super P as the conductive additive (10%). This result confirms that the

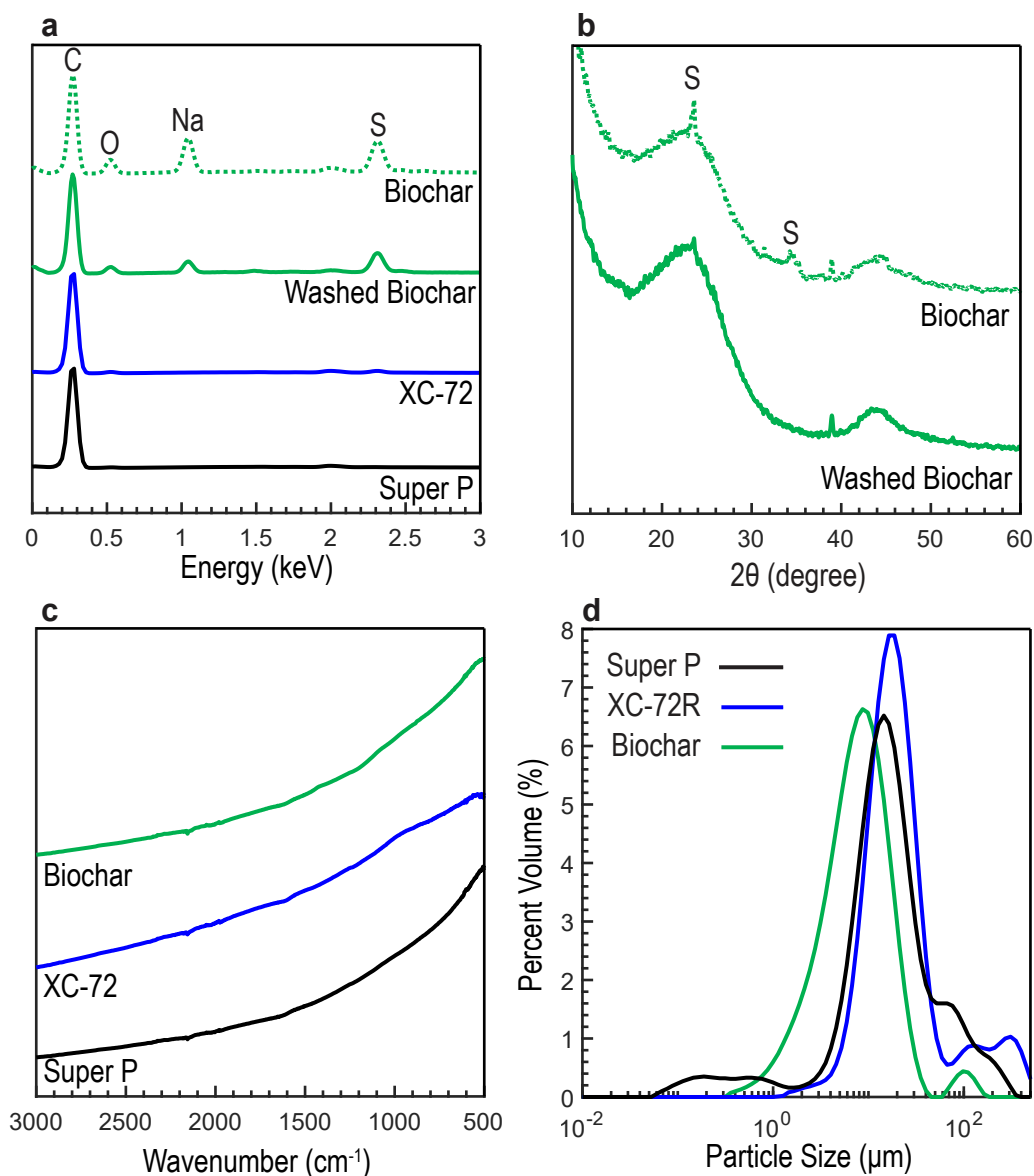


Figure G.2: Further materials characterization of Super P, Vulcan XC-72, and biochar (before and after washing with deionized water). (a) EDX spectra, (b) XRD patterns, (c) FTIR spectra, and (d) optical particle size distributions.

slight increase in electrical conductivity biochar compared to carbon black, as shown in Figure 10.1a in the main text, translates to increased electrical conductivity in the anode. Biochar is observed to exhibit higher average electrical conductivity than Super P; for ex situ anodes prepared with biochar or Super P as the conductive additive, Super P shows an average impedance (0.004Ω) approximately one order of magnitude higher than that of anodes prepared with biochar (0.0006Ω) at frequencies below 100 Hz. The impedance behavior for

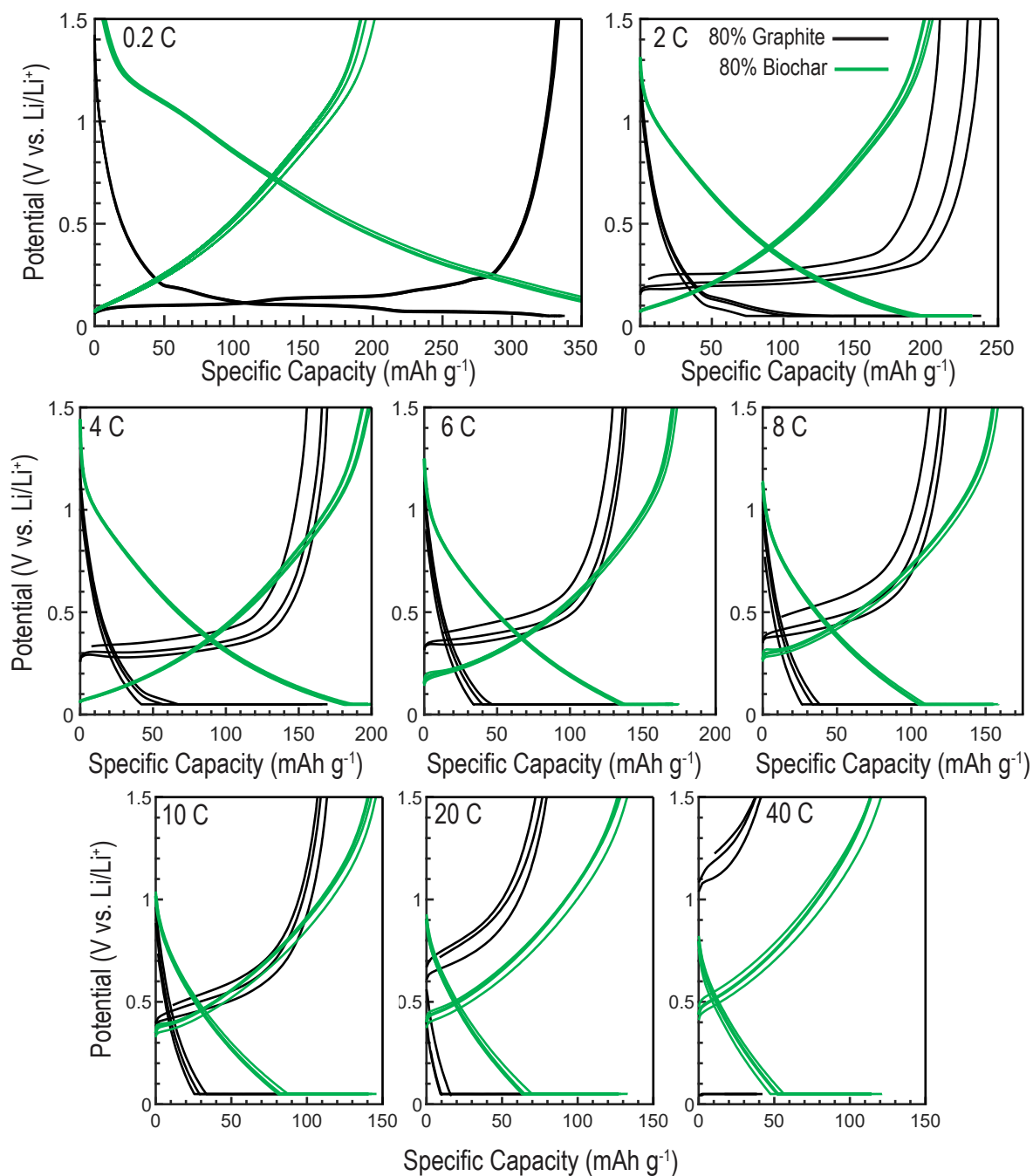


Figure G.3: Replicate electrochemical characterization of electrodes containing 80% biochar or graphite as the active material, between 0.2 C (top left) and 40 C (bottom right).

both anodes is largely resistive, with inductive behavior seen at higher frequencies (>1000 Hz), which is attributable to experimental measurement conditions [141].

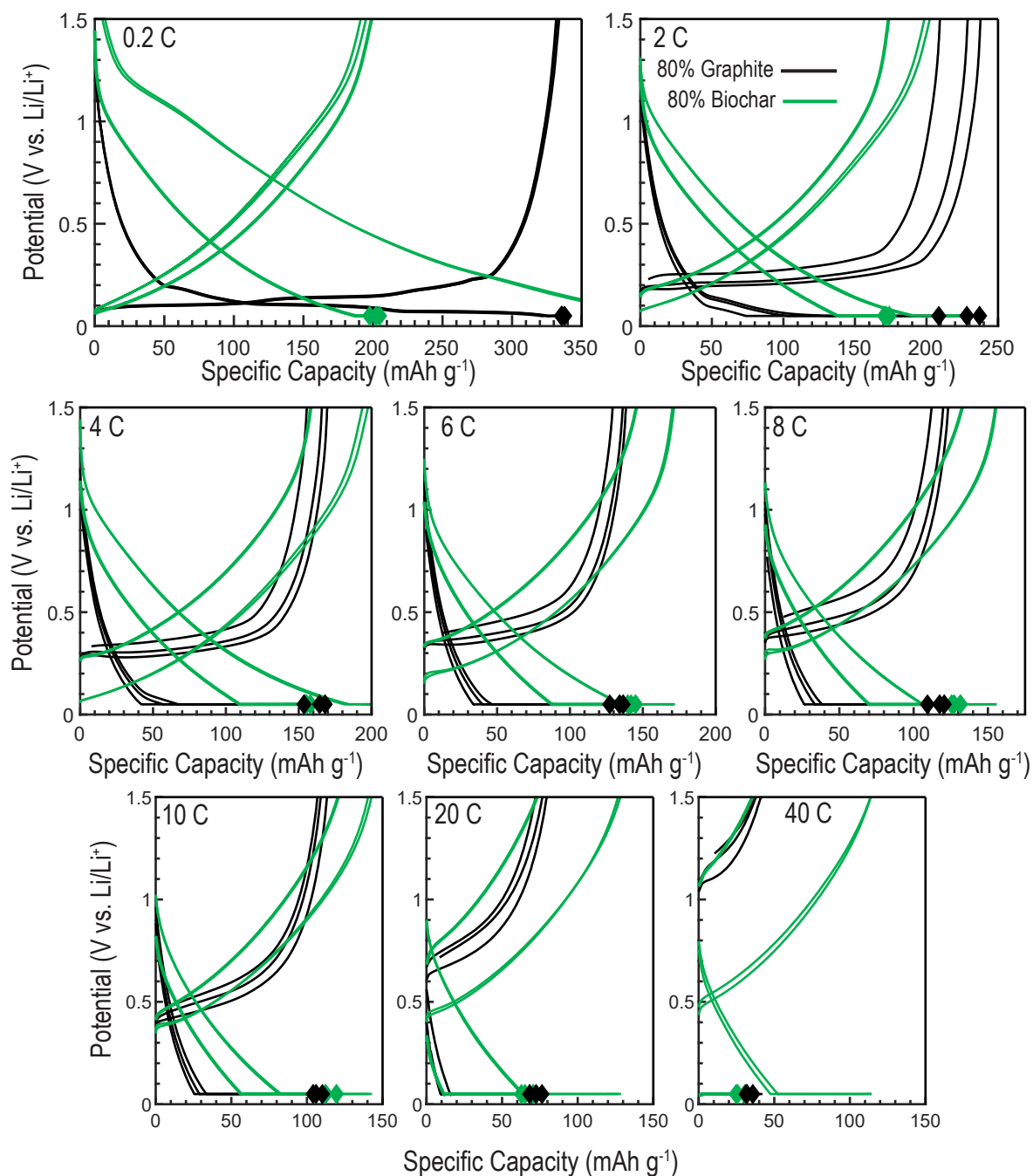


Figure G.4: Replicate electrochemical characterization of electrodes containing 90% biochar and graphite (no conductive additive) compared to electrodes containing 80% graphite and 10% Super P between 0.2 C (top left) and 40 C (bottom right).

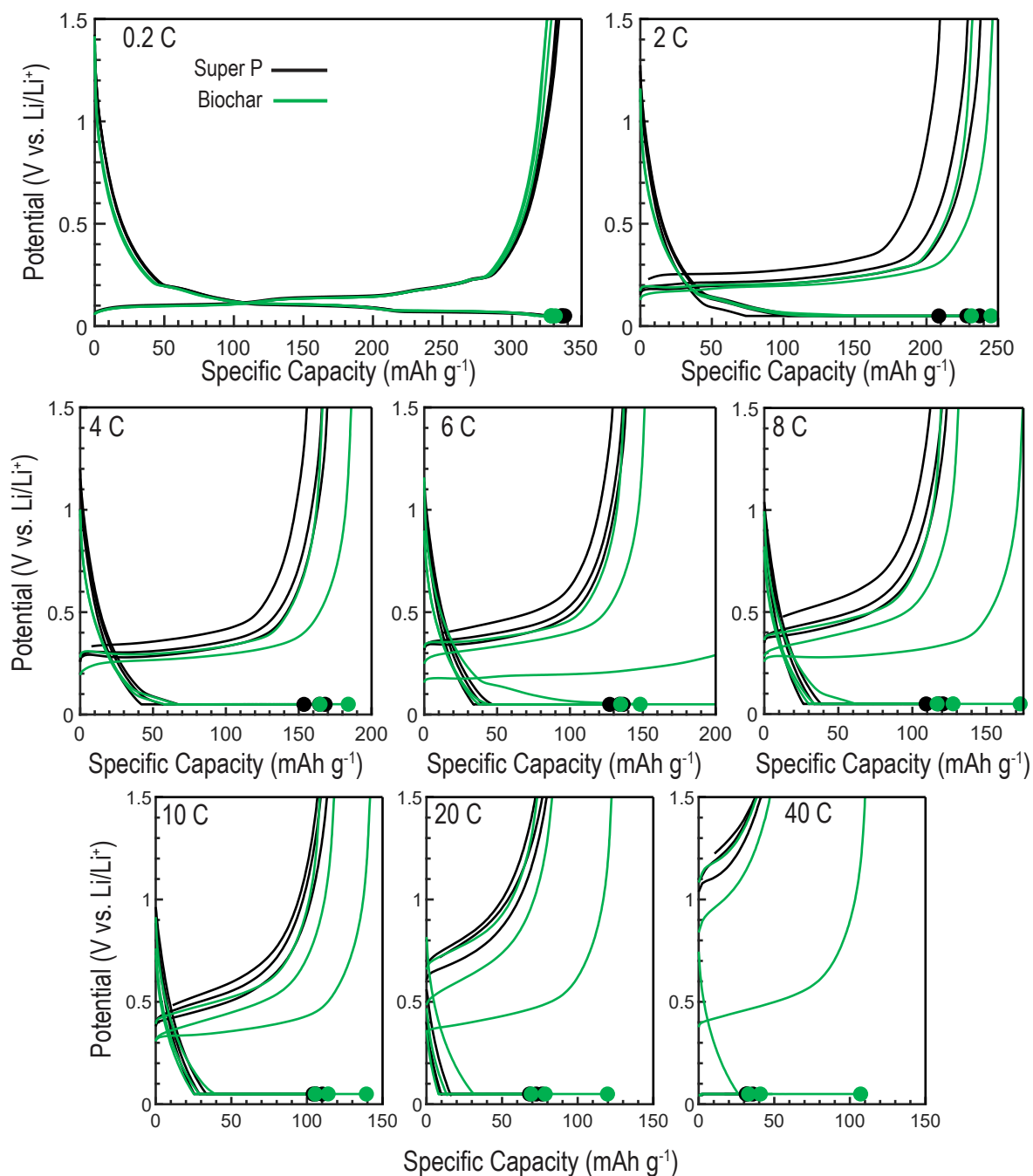


Figure G.5: Replicate electrochemical characterization of electrodes containing biochar or Super P as the conductive additive (10%), between 0.2 C (top left) and 40 C (bottom right).

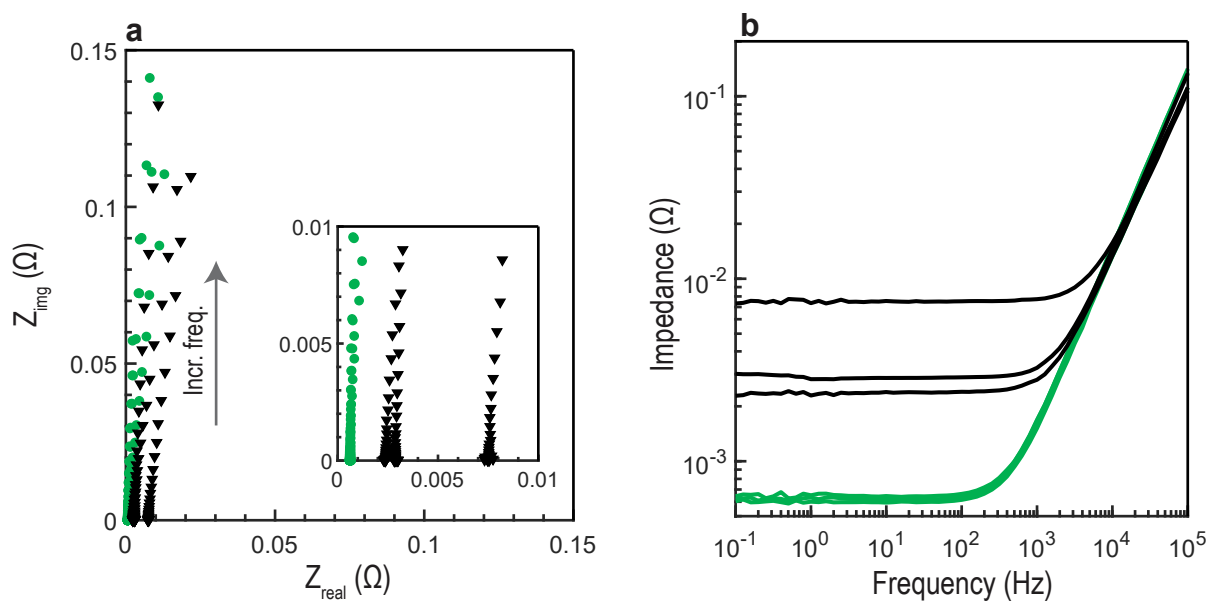


Figure G.6: Replicate EIS spectra of electrodes containing biochar or Super P as the conductive additive (10%): (a) Nyquist plot, with inset highlighting the low impedance region and (b) Bode plot.

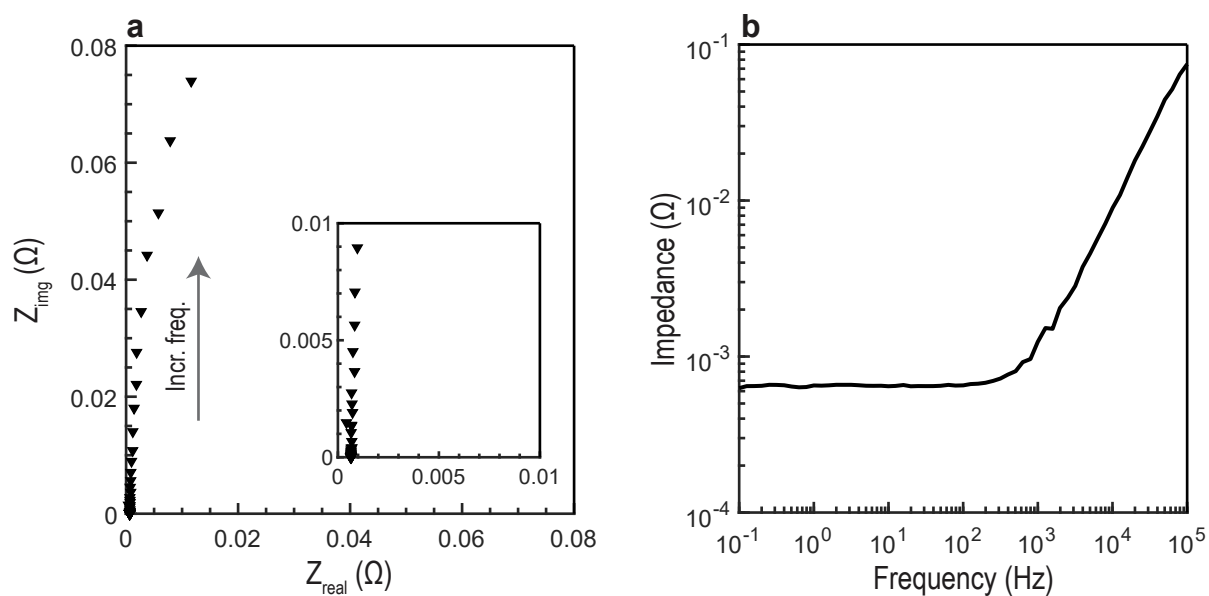


Figure G.7: Electrochemical characterization of NMC811 cathodes containing carbon black as the conductive additive from 0.1 C to 40 C. Data for NMC811 electrodes containing biochar as a conductive additive were not shown, as cells could not be successfully cycled.

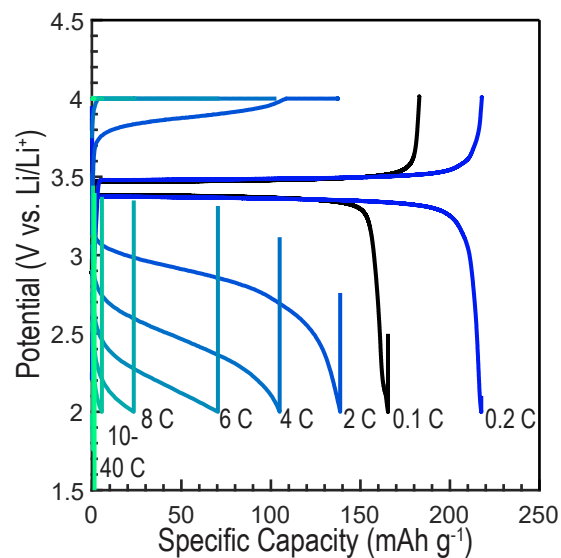


Figure G.8: EIS spectra of a NMC cathode with Super P as the conductive additive: (a) Nyquist plot, with the inset showing the low impedance region in detail and (b) Bode plot. Cells with biochar as the conductive additive are not shown, as the impedance was above the upper limit of the instrument ($>1.5 \text{ G}\Omega$).