Journal of
Composites Science

Article

Silica-Milled *Paulownia* Biochar as Partial Replacement of Carbon Black Filler in Natural Rubber

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Received: 25 September 2019; Accepted: 11 December 2019; Published: 13 December 2019

Abstract: Carbon black (CB) has been the dominant filler in the tire industry for decades. The demand for this petroleum byproduct is ever increasing, although petroleum markets can be volatile due to geopolitical issues. Finding sustainable, renewable substitutes for CB reduces the dependence on petroleum. Biochar is a renewable source of carbon that was studied as a potential CB replacement filler in styrene–butadiene rubber (SBR) composites, but little has been done in terms of natural rubber (NR). In this work, biochar made from fast-growing *Paulownia elongata* was co-milled with small amounts of silica in order to reduce the larger particle size typical with biochar respective to CB. The resulting silica-milled *Paulownia* biochar (PB) was then used to replace CB in natural rubber (NR) composites. By using this method to make natural rubber composites with 30% total filler, half of the CB was fully replaced with silica-milled biochar with very little loss (<6%) of tensile strength, and equal or better elongation and toughness compared to the 100% CB-filled control composite.

Keywords: *Paulownia*; biochar; carbon black; natural rubber; silica

1. Introduction

Natural rubber (NR) is an organic, elastic substance obtained from the sap of trees, and it is the precursor to modern synthetic rubber products. Although synthetic rubber composites have a larger market share than NR in most industrial applications today, NR is still a crucial and necessary material used in tire, hose, medical tubing, and barrier applications (NR is an excellent pathogen barrier). NR typically disperses heat better than synthetic rubber when strained and has better tear resistance at higher temperatures, making it advantageous for heavy-vehicle tires such as trucks and buses [1].

For roughly a century, the dominant filler used to strengthen NR has been carbon black (CB), a material manufactured from petroleum, because of its superior purity as a form of carbon along with its excellent reinforcement properties [2]. However, fossil fuel-based materials are not sustainable; thus, renewable substitutes for CB need to be explored to prepare for a time when fossil fuels become scarce. Biochar is a material that has great potential to replace CB since it is a solid source of carbon produced from the thermochemical treatment of biomass in the absence of oxygen [3]. Past studies showed that biochars made from wood-based feedstocks have a higher carbon content and lower ash content than other types of low-value renewable feedstocks such as grasses, corncobs, or manures [4,5]; hence, wood-based feedstocks would be a logical candidate if biochar mimicking carbon black is the desired outcome.

Paulownia elongata is a fast-growing hardwood tree that generated interest as a bioenergy crop due to its growth rate and ability to be coppiced (wood cut from the main stump is harvested and the regrowth from that stump can be re-harvested periodically) [6]. *Paulownia* plantations in Georgia with 1680 trees per hectare are expected to yield 100 tons of biomass after three years [7], and another study reported that 2000 trees per hectare produced 300 tons of hardwood annually beginning six years after planting [8]. *Paulownia* is a robust tree that can grow well in hardiness zones 6–11 [9], which means it could grow over virtually the entire southeastern United States from the Carolinas to Texas. It is currently used as a filler for wood–plastic composites [10], and biochar made from it was studied as a horticultural amendment to soil [11].

Biochars made from hardwood were previously tested as filler for styrene–butadiene rubber [12,13], but they were not successful mainly because of two significant differences regarding purity and particle size. Because biochar is usually made from a "top-down" method of pyrolyzing the biomass and then grinding the solid carbonaceous product, it is difficult to match both the nano-sized particulates of CB and the monodispersity of the CB structures using cost-effective milling methods. Previously milled biochars would have a certain population of particles with diameters of 10–100 μm. This is problematic in rubber composite samples because even a small amount of these larger biochar particles will cause localized stresses to develop and significantly weaken the composite in terms of tensile strength via fracture, tearing, or other types of defects. To improve this, recent work (using SBR as the rubber matrix) was done utilizing silica co-milling of biochar in which a very small amount of silica was added to the ball milling process in order to help reduce the particle size of biochar [14]. Because silica is very hard (hardness of ~6–7 GPa) and an excellent rubber reinforcing material on its own, it does an excellent job of shearing apart larger biochar agglomerates and does not need to be removed from the biochar post-milling. Thus, silica co-milling with biochar is much more efficient and significantly reduces the number of biochar agglomerates >10 μm. This increases the maximum packing fraction [15] of the biochar filler and should allow a higher amount of CB to be replaced with biochar.

In this work, biochar created from *Paulownia elongata* hardwood feedstock that was co-milled with silica in order to reduce the particle size was substituted for CB in composites using NR as the rubber matrix. The tensile strength, elongation, and toughness of these composites were compared with a 100% CB-filled control composite to determine to what extent CB could be replaced with *Paulownia* biochar (PB) while still retaining the same desirable tensile properties as the control.

2. Materials and Methods

2.1. Materials Used

Biochar made from *Paulownia elongata* using a proprietary method was supplied by Biochar Options (Whitewater, WI, USA). The CB control used was Vulcan M brand N-339 produced by the Cabot Corporation (Alpharetta, GA, USA). Technically specified grade natural rubber was supplied by Michelin (Greenville, SC, USA) and used as provided. The silica used in this work was Agilon performance silica 400GD supplied by PPG Industries (Pittsburgh, PA, USA) and used without further modification.

2.2. Chemical and Physical Material Properties

Elemental analysis of carbon (C) and hydrogen (H) was carried out using a Perkin Elmer 2400 CHNS/O series II analyzer (Norwalk, CT, USA) using cysteine as a standard. Each measurement used approximately 2 mg of PB and was done in triplicate. Ash content was determined using a TA Instruments Q2950 thermogravimetric analyzer (New Castle, DE, USA) by heating to 1000 °C at a heating rate of 10 $°C \cdot min^{-1}$ in an air atmosphere. Ash content was determined to be the weight percentage remaining, and oxygen (O) was determined by difference from the original dried sample and the sum of C, H, and ash. PB absolute density was measured as detailed in a previous manuscript [13].

Fourier-transform infrared (FTIR) spectra of PB and CB were collected using a Thermo Nicolet iS10 (Waltham, MA, USA) with a SensIR Technologies Durascope dATR attachment. Peaks were determined manually after obtaining the average absorbance values from 128 scans per sample.

Resistivity measurements were conducted using an Electro-Tech Systems Inc. (Glenside, PA, USA) Autoranging Resistance Indicator Model 880. Measurements in the conductive range ($<5 \times 10^5$) were made at 10 V while all other measurements were made at 100 V. Accuracy was ±10% with changeover points of one half-decade on a log scale.

X-ray diffractograms of PB and CB were obtained by using a Bruker D2 Phaser (Billerica, MA, USA) using θ/θ geometry and Cu-Kα radiation generated at a current of 10 mA and 30 kV. Scans were run over a 2θ range of 5°–90° with a step size of 0.02° and a time per step of 0.2 s. Initial divergence slit size was 0.6 mm, and a 1-mm air scatter screen was used above the sample. The sample stage was rotated at 10 rpm during the scan. A Lynxeye$^{\text{TM}}$ detector was used in conjunction with a 2.5° Soller slit and an Ni-Kα filter.

SEM images for CB and PB were collected on separate systems at different times; the PB images were more recent and used an updated SEM. The CB image was obtained by mounting CB onto aluminum stubs with conductive carbon tape and then sputter-coating them with Au–Pd. The CB was then examined with a JEOL 6400 V (JEOL USA, Inc., Peabody, MA, USA) scanning electron microscope. PB images were obtained in a similar fashion; PB was sputter-coated with Au and then examined using a JEOL JSM-6020LA analytical scanning electron microscope.

2.3. Formation of Rubber Composites and Tensile Testing

PB was milled with silica to reduce larger-sized particles as detailed in a previous manuscript [16]. Rubber composites were formulated using a C.W. Brabender Intelli-Torque Plasti-Corder torque rheometer (South Hackensack, NJ, USA), using a 75-mL three-piece mixer equipped with Banbury blades. The mixer was loaded to the recommended 70% volume of approximately 53 g, depending on composite density, which was calculated for each sample. Initial mixing was at 60 rpm and 120 °C. Then, NR was added, the loading ram chute was mounted, and then 2,2,4-trimethyl-1,2-dihydroquinone, *N*-1,3-dimethylbutyl-*N*-phenyl-*p*-phenylene diamine, CB and/or PB filler, zinc oxide, and stearic acid were added. Silica-milled biochar dispersed well and did not agglomerate. The piston was then stabilized by a 5.0-kg weight placed on top and allowed to continue mixing at 120 °C for a total of 10 min. The sample was then removed and sheeted out using an MTI HR01 hot rolling machine (Richmond, CA, USA) with a nip setting of 2 mm and a roller temperature of 25 °C. The mixer was then set to 100 °C, and the sheeted sample, sulfur, and *N*-cyclohexyl-2-benzothiazolesulfenamide were added and mixed for an additional 3 min. The gram amounts of each of these ingredients for the various rubber composite samples tested in this work are shown in Table 1. The finished composite was then sheeted an additional time in the hot rolling machine with the same settings as the first pass. Approximately 20 g of the sheeted composite was loaded into a 102 × 102 × 2 mm window-type mold and placed in a Carver press preheated to 160 °C, where it was then compressed at 89 kN for 20 min, after which the press was cooled for 25 min under pressure, and then the sample was removed.

Composite sample bars were cut using an ISO 37-2 cutting die. Samples were conditioned at 23 ± 1 °C and 50% ± 10% relative humidity for at least 24 h after molding. Testing was performed on an Instron 55R1123C5420 (Instron, Inc., Norwood, MA, USA) using Bluehill Software version 3.61. Tensile tests were run using a crosshead speed of 500 mm/min and a 1-kN load cell, as specified by ASTM D412. Tensile tests directly measured the stress and strain of each rubber composite sample, and toughness was calculated as the area under the stress/strain curve by the software.

Small-strain oscillation sweeps were made on a TA Instruments (New Castle, DE, USA) ARES G2 controlled-strain rheometer using 8-mm cross-hatched plates at 25 °C. Each sample was placed under a 0.1% strain (within the linear region) with a frequency of 1 Hz and cycled 1000 times, while the storage modulus (G′) was recorded for each cycle.

Table 1. 30% Total Filler Control and Composite Formulations (g).

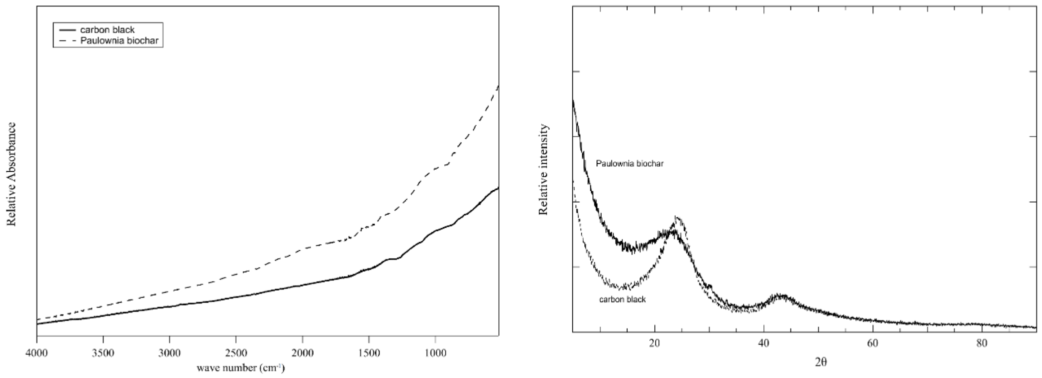
Filler Composition	NR	TMQ	6PPD	CB	PB	Stearic Acid	ZnO	Sulfur	CBTS
unfilled NR	46.66	0.23	0.23	0	0	0.93	2.33	1.17	0.47
100% CB	39.19	0.20	0.20	16.79	0	0.78	1.96	0.98	0.39
0% silica/100% PB	38.43	0.19	0.19	0	16.47	0.77	1.92	0.96	0.38
0.5% silica/100% PB	38.43	0.19	0.19	0	16.47	0.77	1.92	0.96	0.38
1% silica/100% PB	38.43	0.19	0.19	0	16.47	0.77	1.92	0.96	0.38
2% silica/100% PB	38.43	0.19	0.19	0	16.47	0.77	1.92	0.96	0.38
1% silica-75/25% PB/CB	38.62	0.19	0.19	4.14	12.41	0.77	1.93	0.97	0.39
1% silica-50/50% PB/CB	38.81	0.19	0.19	8.31	8.31	0.78	1.94	0.97	0.39

NR: natural rubber; TMQ: 2,2,4-trimethyl-1,2-dihydroquinone; 6PPD: *N*-1,3-dimethylbutyl-*N*-phenyl-*p*-phenylene diamine; CB: carbon black; PB: Paulownia biochar; ZnO: zinc oxide; CBTS: *N*-cyclohexyl-2-benzothiazolesulfenamide.

3. Results

3.1. Biochar Characterization

CB is a very pure form of carbon (>99%), with less than 1% hydrogen, oxygen, and ash, and a density of 1.7–1.9 g/cm^3 (data supplied by the manufacturer). The PB used in this study had a density of 1.75 g/cm^3 and an ash content of 2.90%. Elemental composition of the PB was 92.68% ± 0.57% carbon, 0.94% ± 0.05% hydrogen, and 3.48% oxygen (by difference). Similar to a previous study [16], the FTIR spectrum of PB was devoid of any functional group peaks, as would be expected from a nearly pure carbon material. The FTIR spectra of the PB and the CB used in this study can be seen in Figure 1, along with the X-ray diffraction spectra of both CB and PB. Both materials showed the characteristic carbon black graphitic *d*-spacing peaks at approximately 24° and 43° 2θ [17]. Neither sample showed any strong and/or sharp peaks that would indicate a significant amount of crystalline impurities, which was corroborated by both samples having >92% carbon content.



(a) (b)

Figure 1. (**a**) Fourier-transform infrared (FTIR) spectra of carbon black (CB) and *Paulownia* biochar (PB). No sharp functional groups peaks are evident; (**b**) X-ray diffraction spectra of carbon black and *Paulownia* biochar. Both traces show the characteristic CB graphitic *d*-spacing peaks at 24° and 43° 2θ.

Figure 2 shows SEM images of PB, both pre (a) and post (b) silica milling. These images illustrate the effective particle size reduction effect of milling biochar with silica. Images (c) and (d) show CB and post-silica-milled PB, respectively, at higher magnification. The typical aggregate and agglomerate structures of CB are seen in image (c); CB aggregates are typically 50–500 nm in size and can be seen in the image as the smaller spheres that make up the three primary larger agglomerates in the picture, each of which was several microns in diameter. Even though CB agglomerates and PB particles are not terribly different in size (both on the order of microns), CB agglomerates break down rather easily into the aforementioned CB aggregates with shearing forces that are commonly attained during rubber mixing/compounding. PB particles are more polydisperse and do not break down as easily; thus, if larger PB particles are present, they can cause local stresses in the rubber composite matrix that translate into lower tensile strength.

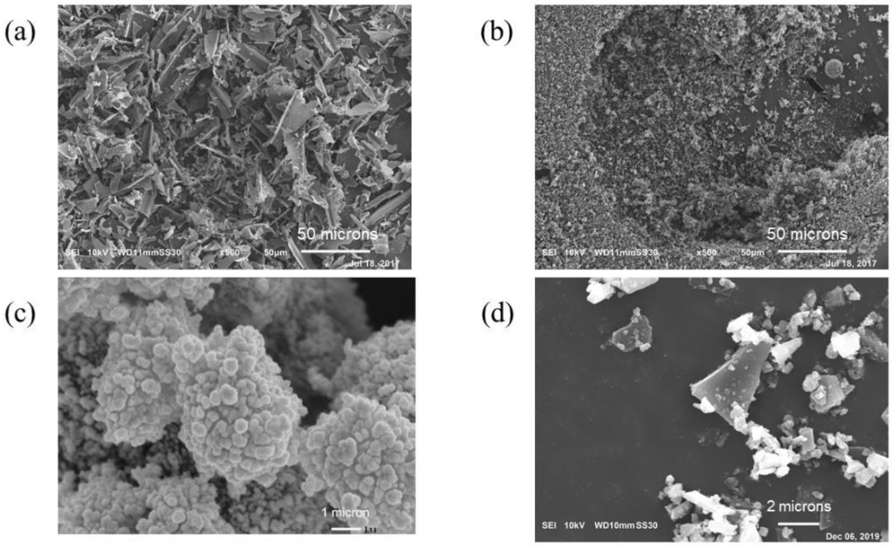


Figure 2. (**a**) SEM image of PB before silica milling and (**b**) after silica milling. For (**a**,**b**), the magnification is only 500×, and the white bar in the lower right corner represents 50 microns. (**c**) SEM image of CB structure at 10,000× magnification; the white bar in the lower right corner represents one micron; (**d**) SEM image of PB post silica milling at 7500× magnification to compare with CB; note the slight scale change where the white bar represents two microns.

3.2. Composite Properties

All composite samples were measured for their electrical resistivity, but only the CB control sample registered a resistance of 10^5 Ω, which is classified as conductive (10^3–10^5 Ω). All of the other samples containing PB at any concentration registered the same resistance of 10^{12} Ω, classified as insulative. Unfilled NR had a resistance of 10^{11} Ω, classified as static dissipative [18].

In this work, PB was milled with 0.5, 1, or 2 wt.% silica. Previous work in our lab showed us that milling with greater than 10 wt.% silica was detrimental to strength and toughness properties of the final composites. For previous SBR composites, 1% silica was optimal for biochar particle size reduction and favorable tensile properties; thus, that dictated our range in this study. Tensile properties for the NR composites are shown in Table 2. NR is a very soft rubber that needs to be reinforced for most real-world applications; this is illustrated in the tensile results for unfilled NR vs. the 100% CB-filled control. The CB-filled control had over twice the tensile strength and toughness, although this added strength did reduce the elongation at break.

Table 2. Tensile properties of NR composites with 30 wt.% total filler. N/A—not applicable.

Filler	Silica (%)	*n*	CB Replaced (%)	Tensile Strength (MPa)	Elongation (%)	Toughness (MPa)	Young's Modulus (MPa)
Unfilled NR	0	6	N/A	11.9 ± 1.2	626 ± 9	19.4 ± 1.6	1.2 ± 0.1
100% CB	0	6	0	25.7 ± 0.6	476 ± 8	51.7 ± 2.3	3.9 ± 0.4
100% PB	0	9	100	15.3 ± 1.6	522 ± 21	32.2 ± 4.7	1.9 ± 0.3
100% PB	0.5	5	100	18.9 ± 0.7	516 ± 10	39.3 ± 2.2	2.2 ± 0.3
100% PB	1	6	100	19.3 ± 0.9	519 ± 8	40.1 ± 2.3	2.2 ± 0.3
100% PB	2	9	100	17.3 ± 1.2	469 ± 20	32.4 ± 3.9	2.3 ± 0.4
75/25% PB/CB	1	6	75	21.0 ± 0.9	524 ± 11	43.9 ± 2.6	2.2 ± 0.2
50/50% PB/CB	1	6	50	24.3 ± 0.4	527 ± 12	52.3 ± 1.4	2.8 ± 0.3

The next four rows show NR with 100% PB filler replacing the CB, with varying silica concentration. In terms of tensile strength and toughness, 0.5% and 1% silica provided the best results, at roughly 19 and 40 MPa, respectively; however, these data are significantly lower than the CB control. Elongation was improved in each of these samples except for the one with 2% silica. The CB-filled control was a stiffer composite compared to the biochar-substituted composites; this was reflected in both the increased elongation behavior and decreased Young's modulus behavior. To see if the tensile properties of PB-filled NR composites could be improved, PB milled with 1% silica was blended with CB at ratios of 75/25 and 50/50 PB/CB. The results for these composites are shown as the final two rows of Table 2. Tensile strength decreased with increasing PB filler, but the composite that replaced 50% of the CB with 1% silica-milled PB nearly matched the CB control in tensile strength (5.5% lower) and surpassed the control in terms of elongation and toughness, but had a lower Young's modulus. The stress–strain curves of the 1% silica-milled composites are also shown in Figure 3. The reduced stiffness of the biochar-substituted samples suggested that, although these composites had similar strength and enhanced toughness, they may be better suited toward applications that favor increased flexibility, such as tubing.

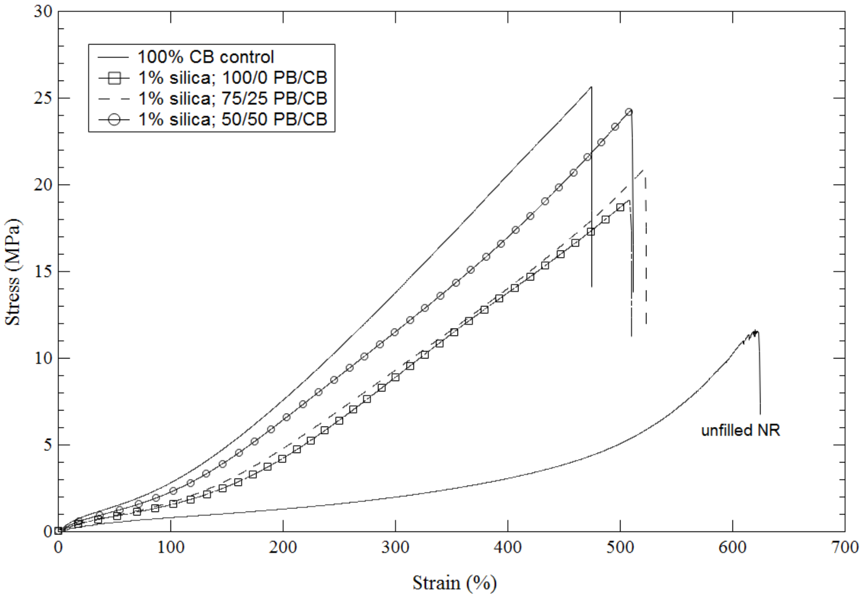


Figure 3. Stress–strain curves of the PB composites milled with 1% silica. It can be seen that, by increasing the amount of CB in the PB/CB ratio, the PB-substituted composites approach the performance of the CB control, with the 50/50 PB/CB composite (open circles) having slightly lower tensile strength and slightly higher elongation than the CB control (solid line).

Small-strain oscillation sweeps were carried out on the composite samples at 0.1% strain (well within the linear region) at a frequency of 1 Hz for 1000 cycles. All the composites showed constant storage modulus (G′) values, and these values are shown in Table 3. The CB control showed the highest G′ value, indicating the stiffest sample. The results did not show a clear trend in terms of silica concentration; rather, G′ of the composite seemed much more dependent on CB concentration.

Table 3. Small-strain cyclic behavior of NR composites with 30 wt.% total filler.

Sample	Average G′ (MPa)
Unfilled NR	0.256 ± 0.001
100% CB	1.18 ± 0.02
100% PB–0% Si	0.397 ± 0.001
100% PB–0.5% Si	0.362 ± 0.002
100% PB–1% Si	0.357 ± 0.001
100% PB–2% Si	0.410 ± 0.001
75/25 PB/CB	0.445 ± 0.003
50/50 PB/CB	0.609 ± 0.004

As biochar research continues, the challenge will be to cost-effectively improve sustainable biochar in terms of (increasing) carbon content, (reducing) ash content, and (reducing) particle size in order to make it a more worthy replacement for CB that does not sacrifice material properties.

4. Conclusions

P. elongata is a rapidly growing, sustainable source of hardwood that can be grown over a wide geographical footprint of the southern United States. This tree has a wide variety of potential uses including the production of honey [6], biocomposites [19–21], pencils [22], medicinal compounds [23], timber [24], and biomass [25]. Biochar made from *P. elongata* showed promise for athletic turf application [26] and other broader-based horticultural applications [11].

In this work, PB that was co-milled with silica to reduce its particle size was used as a direct substitute for carbon black in NR composites. Although there was some improvement in the elongational properties, the tensile strength and toughness properties of 100% PB filled NR composites were significantly lower than the CB control. By blending PB and CB in different ratios, it was found that a 50/50 blend of PB/CB yielded a composite that was only 6% lower in tensile strength while surpassing the 100% CB control in both elongation and toughness properties.

Funding: This research received no external funding.

Acknowledgments: The author would like to thank Steve Nichols of Biochar Options for providing biochar samples, Liz Krietemeyer for obtaining FTIR spectra, and Andrew James Thomas for composite preparation, tensile properties, and density and ash measurement. Mention of trade names or commercial products in this article is solely for the purpose of providing scientific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture. USDA is an equal opportunity provider and employer.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. An Unknown Object, the Tire: Materials. Available online: Thetiredigest.michelin.com/an-unknown-object-the-tire-materials (accessed on 6 September 2019).
2. Spahr, M.; Rothon, R. Carbon black as a polymer filler. In *Polymers and Polymeric Composites: A Reference Series*, 1st ed.; Palsule, S., Ed.; Springer: Berlin/Heidelberg, Germany, 2016; Volume 4, pp. 1–31. ISSN 2510-3458.
3. Lehmann, J.; Joseph, S. *Biochar for Environmental Management: Science and Technology*, 2nd ed.; Routledge: New York, NY, USA, 2015; p. 976. ISBN 0415704154.
4. Mukome, F.N.D.; Zhang, X.; Silva, L.C.R.; Six, J.; Parikh, S.J. Use of chemical and physical characteristics to investigate trends in biochar feedstocks. *J. Agric. Food Chem.* **2013**, *61*, 2196–2204. [CrossRef] [PubMed]
5. Demirbas, A. Effects of temperature and particle size on bio-char yield from pyrolysis of agricultural residues. *J. Anal. Appl. Pyrolysis* **2004**, *72*, 243–248. [CrossRef]
6. Yadav, N.K.; Vaidya, B.N.; Henderson, K.; Lee, J.F.; Stewart, W.W.; Dhekney, S.A.; Joshee, N. A review of Paulownia biotechnology: A short rotation, fast growing multipurpose bioenergy tree. *Am. J. Plant Sci.* **2014**, *4*, 2070–2082. [CrossRef]
7. Basu, C.; Joshee, N.; Gezalian, T.; Vaidya, B.N.; Satidkit, A.; Hemmati, H.; Perry, Z.D. Cross-species PCR and field studies on Paulownia elongata: A potential bioenergy crop. *Bioethanol* **2016**, *2*, 12–23. [CrossRef]

8. Jiménez, L.; Rodríguez, A.; Ferrer, J.L.; Pérez, A.; Angulo, V. Paulownia, a fast-growing plant, as a raw material for paper manufacturing. *Afinidad* **2005**, *62*, 100–105.
9. Paulownia Growing Zones. Available online: worldpaulownia.com/growing-zones (accessed on 6 September 2019).
10. Ayrilmis, N.; Kaymakci, A. Fast growing biomass as reinforcing filler in thermoplastic composites: Paulownia elongata wood. *Ind. Crop. Prod.* **2013**, *43*, 457–464. [CrossRef]
11. Vaughn, S.F.; Kenar, J.A.; Tisserat, B.; Jackson, M.A.; Joshee, N.; Vaidya, B.N.; Peterson, S.C. Chemical and physical properties of Paulownia elongata biochar modified with oxidants for horticultural applications. *Ind. Crop. Prod.* **2017**, *97*, 260–267. [CrossRef]
12. Peterson, S.C. Utilization of low-ash biochar to partially replace carbon black in styrene-butadiene rubber composites. *J. Elastomers Plast.* **2013**, *45*, 487–497. [CrossRef]
13. Peterson, S.C.; Chandrasekaran, S.R.; Sharma, B.K. Birchwood biochar as partial carbon black replacement in styrene–butadiene rubber composites. *J. Elastomers Plast.* **2015**, *48*, 305–316. [CrossRef]
14. Peterson, S.C.; Kim, S. Reducing biochar particle size with nanosilica and its effect on rubber composite reinforcement. *J. Polym. Environ.* **2019**. [CrossRef]
15. Gent, A.N.; Pulford, C.T.R. Micromechanics of fracture in elastomers. *J. Mater. Sci.* **1984**, *19*, 3612–3619. [CrossRef]
16. Peterson, S.C.; Joshee, N. Co-milled silica and coppiced wood biochars improve elongation and toughness in styrene-butadiene elastomeric composites while replacing carbon black. *J. Elastomers Plast.* **2018**, *50*, 667–676. [CrossRef]
17. Darmstadt, H.; Roy, C.; Kaliaguine, S.; Xu, G.; Auger, M.; Tuel, A.; Ramaswamy, V. Solid state 13C-NMR spectroscopy and XRD studies of commercial and pyrolytic carbon blacks. *Carbon* **2000**, *38*, 1279–1287. [CrossRef]
18. Difference between Conductive, Dissipative, Insulative, and Antistatic. Available online: Transforming-technologies.com/esd-fyi/difference-between-conductive-dissipative-and-insulative/ (accessed on 27 November 2019).
19. Tisserat, B.; Joshee, N.; Mahapatra, A.K.; Selling, G.W.; Finkenstadt, V.L. Physical and mechanical properties of extruded poly(lactic acid)-based Paulownia elongata biocomposites. *Ind. Crop. Prod.* **2013**, *44*, 88–96. [CrossRef]
20. Tisserat, B.; Reifschneider, L.; Joshee, N.; Finkenstadt, V.L. Properties of high density polyethylene—Paulownia wood flour composites via injection molding. *BioResources* **2013**, *8*, 4440–4458. [CrossRef]
21. Tisserat, B.; Reifschneider, L.; Joshee, N.; Finkenstadt, V.L. Evaluation of Paulownia elongata wood polyethylene composites. *J. Thermoplast. Compos. Mater.* **2013**, *28*, 1301–1320. [CrossRef]
22. Kaygin, B.; Kaplan, D.; Aydemir, D. Paulownia tree as an alternative raw material for pencil manufacturing. *BioResources* **2015**, *10*, 3426–3433. [CrossRef]
23. He, T.; Vaidya, B.N.; Perry, Z.D.; Parajuli, P.; Joshee, N. Paulownia as a medicinal tree: Traditional uses and current advances. *Eur. J. Med. Plants* **2016**, *14*, 1–15. [CrossRef]
24. Kalaycioglu, H.; Deniz, I.; Hiziroglu, S. Some of the properties of particleboard made from Paulownia. *J. Wood Sci.* **2005**, *51*, 410–414. [CrossRef]
25. Lopez, F.; Perez, A.; Zamudio, M.A.M.; de Alva, H.E.; García, J.C. Paulownia as raw material for solid biofuel and cellulose pulp. *Biomass Bioenergy* **2012**, *45*, 77–86. [CrossRef]
26. Vaughn, S.F.; Dinelli, F.D.; Tisserat, B.; Joshee, N.; Vaughan, M.M.; Peterson, S.C. Creeping bentgrass growth in sand-based root zones with or without biochar. *Sci. Hortic.* **2015**, *197*, 592–596. [CrossRef]