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Coppiced Biochars as Partial Replacement of Carbon Black Filler in Polybutadiene/Natural Rubber Composites

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Abstract: Although carbon black has been the dominant filler material for rubber composites for over a century, it is a finite, fossil fuel-based product that is sensitive to geopolitical issues and economics. Renewable sources of carbon need to be developed to replace carbon black in order to reduce dependence on petroleum. Biochar is the solid material left over after the anaerobic treatment of biomass at high temperature. In this work, two biochars made from coppiced hardwoods, *Paulownia elongata* and *Populus tremuloides* were used to partially replace carbon black in rubber composites using a 50/50 blend of butadiene rubber and natural rubber. Rubber composite samples using these biochars were able to replace 30% of the carbon black with virtually no loss in tensile strength, and improved elongation and toughness compared to the reference sample containing 100% carbon black.

Keywords: biochar; carbon black; butadiene; mechanical properties; rubber composites; silica

1. Introduction

Polybutadiene rubber (BR) is a synthetic rubber that is a primary ingredient in automobile tires. One of its most prominent characteristics is its resistance to wear; it is a common ingredient in the sidewalls of truck tires due to its ability to reduce fatigue in the continuous flexing of those tires. Although rarely used on its own, it is commonly blended with natural rubber (NR) and styrene-butadiene rubber (SBR) in nearly all the components of automobile and truck tires [1–3].

Carbon black (CB), made from fossil fuels, has long been the standard filler used in the tire industry due to its superior purity as a form of carbon coupled with excellent reinforcement properties [4,5]. However, renewable substitutes for fossil fuels are being explored in order to provide alternatives should these finite resources disappear or become too expensive due to geopolitical conditions. Additionally, reducing the use of fossil fuels helps reduce global warming and is ecologically responsible. Biochar is a renewable material that can potentially replace CB, since it is a solid source of carbon produced from the thermochemical treatment of biomass in the absence of oxygen; this process is known as pyrolysis [6]. One significant drawback of biochar relative to CB is lack of purity; most industrial CB is greater than 98% pure carbon due to its sourcing from petroleum. Since biochar can be made from any carbon-containing biomass, it has a much more diverse array of chemical compounds present as a starting feedstock and will not be as pure. However, by carefully monitoring/controlling various feedstock parameters, it is possible to produce biochar with >90% carbon and <8% ash content. Past work has shown that biochars made from hardwood-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 [7,8]. Therefore, hardwoods have been our feedstocks of choice.

One fast-growing hardwood tree that has 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) is *Paulownia elongata* [9]. *Paulownia* plantations in the southern United States (density of ~1700 trees per hectare) are expected to generate 100 tons of biomass after only 3 years of growth [10], and a similar study with 2000 trees per hectare reported an annual yield of 300 tons of hardwood after only 6 years post-planting [11]. *Paulownia* is a robust tree that can grow well in hardiness zones 6–11 [12]. This means it could grow over virtually the entire southeastern United States from the Carolinas to Texas. *Paulownia* is currently being studied as potential feedstock for bioethanol production [13], filler for wood plastic composites [14], and biochar made from it has been studied as a horticultural amendment to soil [15].

Hybrid poplar is another excellent candidate as a coppiced hardwood feedstock. Poplar has been identified as one of the leading species of renewable, lignocellulosic feedstock in the United States along with switchgrass, miscanthus, southern pine, willow, and corn stover [16]. One of the main attractions of poplar as a biofuel is the fact that its genome has been sequenced and thus new clones have been tailored for specific traits that can maximize its potential for production [17]. Genetic modifications to poplar have also helped improve its drought tolerance, insect/pest resistance, and total yield, improving its value as a biomass feedstock yet further [18]. Poplar has an even larger footprint than *Paulownia* and grows well over nearly all of the United States and Canada; this makes it easy to grow near processing facilities and reduce transportation costs. In North America, the poplar yield of all species is estimated to range from 1.25–8.61 dry tons acre⁻¹ year⁻¹, depending on geographical region [19–21].

Particle size is a primary challenge in using biochar as a substitute for CB in rubber composites because biochar is made from pyrolyzing biomass and therefore the particle size is reduced by ‘top-down’ methods such as milling and grinding. Particle size is limited by these methods and it can be costly to match the particle size of CB, which is on the order of tens or hundreds of nm. With previous studies [22,23], milled biochar would have a small fraction of particles ranging from 10–100 µm, and these particles were problematic because they cause localized stresses in the rubber composite that weakened it and caused it to fracture [24]. To help with this issue, we have used small amounts of industrial silica during our milling processes to help reduce biochar particle size. Silica milling has several advantages; silica is a very hard substance (6–7 GPa), it has a very small particle size itself (5–50 nm), and since it is an effective reinforcing filler on its own it can be left in the biochar post-milling. Silica milling does an excellent job of breaking down biochar particles >10 µm, thus increasing the maximum packing fraction of the biochar and allowing a higher rate of CB substitution with biochar [25].

In this work, we demonstrate substituting CB with silica-milled biochar from two coppiced hardwood feedstocks, *Paulownia* and poplar, into a rubber matrix featuring BR to make rubber composites. 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 the coppiced wood biochars while still retaining the same desirable tensile properties as the control. Styrene-butadiene, natural rubber, and polybutadiene make up the three primary rubber matrices used in the tire industry. This work along with previous studies [26,27] demonstrates that renewable biochar can partially replace carbon black in all three of these rubber matrices with virtually no loss in tensile strength, plus improved elongation and toughness properties.

2. Materials and Methods

2.1. Materials Used

Biochars made from *Paulownia elongata* (PAUL) and *Populus tremuloides* (POP) using a proprietary method were supplied by Biochar Options (Whitewater, WI, USA) and used as delivered. The CB control used was Vulcan M brand N-339 produced by the Cabot Corporation (Alpharetta, GA, USA). Natural rubber and polybutadiene rubber samples (both TSR-grade) were supplied by Michelin

(Greenville, SC, USA) and used as provided. The densities of natural rubber and polybutadiene rubber were 0.93 and 0.90 g/cm³, respectively. 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) were carried out using a Perkin Elmer 2400 CHNS/O series II analyzer (Norwalk, CT, USA) using acetanilide as a standard. Each measurement used approximately 2 mg of biochar 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 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. Biochar absolute density was measured as detailed in a previous manuscript [23].

Fourier transform infrared spectra of the biochar samples 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.

X-ray diffractograms of biochar and CB were obtained by using a Bruker D2 Phaser (Billerica, MA, USA) using θ/θ geometry and Cu K α 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 LynxeyeTM detector was used in conjunction with a 2.5° Soller slit and a Ni-K α filter.

2.3. Formation of Rubber Composites and Tensile Testing

Coppiced biochars were milled with 1% (*w/w*) silica to reduce larger-sized particles as detailed in a previous manuscript [26]. All composite samples filled with either CB or some combination of CB and biochar were 50 phr (33%) total filler. Composites were also made with the coppiced biochars without silica milling for comparison. Rubber composites were formulated using a C.W. Brabender Intelli-Torque Plasti-Corder torque rheometer (South Hackensack, NJ, USA), using a 75 mL 3-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, a 50/50 mix of BR/NR was added, the loading ram chute was mounted, and then 2,2,4-trimethyl-1,2-dihydroquinone (antioxidant), N-1,3-dimethylbutyl-N-phenyl-p-phenylene diamine (antioxidant), CB and/or biochar filler, zinc oxide (activator), and stearic acid (lubricant) were added. 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 along with sulfur (vulcanizing agent) and N-cyclohexyl-2-benzothiazolesulfenamide (accelerator) were added and mixed for an additional 3 min. The phr 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 mm × 102 mm × 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.

Table 1. 33% Total Filler Control and Composite Formulations (phr).

Filler Composition	NR	BR	TMQ	6PPD	CB	Biochar	Stearic Acid	ZnO	Sulfur	CBTS
unfilled BR-NR	50	50	1	0.5	0	0	2	5	2.5	1
100% CB	50	50	1	0.5	50	0	2	5	2.5	1
100% PAUL	50	50	1	0.5	0	50	2	5	2.5	1
100% POP	50	50	1	0.5	0	50	2	5	2.5	1
100% PAUL Si milled	50	50	1	0.5	0	50	2	5	2.5	1
100% POP Si milled	50	50	1	0.5	0	50	2	5	2.5	1
50/50 CB/PAUL silica milled	50	50	1	0.5	25	25	2	5	2.5	1
50/50 CB/POP silica milled	50	50	1	0.5	25	25	2	5	2.5	1
60/40 CB/PAUL silica milled	50	50	1	0.5	30	20	2	5	2.5	1
60/40 CB/POP silica milled	50	50	1	0.5	30	20	2	5	2.5	1
70/30 CB/PAUL silica milled	50	50	1	0.5	35	15	2	5	2.5	1
70/30 CB/POP silica milled	50	50	1	0.5	35	15	2	5	2.5	1

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

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 testing directly measured the strain and stress of each composite sample, and toughness was calculated by the Instron software as the area under the resulting stress-strain curve [27]. Resistivity measurements and small-strain oscillation sweeps of the composite samples were collected as detailed in a previous manuscript [28].

3. Results

3.1. Biochar Characterization

Elemental composition, ash content, and densities of CB and each coppiced hardwood biochar can be seen in Table 2. Nitrogen content was low enough for the biochar samples that the detection limit of the instrumentation was challenged and this resulted in relatively large errors. Similar to a previous study [26], the FTIR spectra did not have any prominent functional peaks and are all very similar, since the biochars and CB are all nearly pure carbon material. The FTIR spectra of the biochars along with the CB used in this study can be seen in Figure 1. Figure 2 shows the X-ray diffraction spectra of CB and each biochar. In this figure the traces for *Paulownia* and poplar biochars are nearly indistinguishable, with *Paulownia* having slightly greater intensity from 15–30° 2θ. Both biochars show the characteristic carbon black graphitic d-spacing peaks at approximately 24 and 43° 2θ [29]. A lack of any strong and/or sharp peaks confirms that there are no significant crystalline impurities, which is to be expected of materials that are all >89% carbon.

Table 2. Material Properties of CB and Coppiced Hardwood Biochars.

Sample	C (%)	H (%)	N (%)	O (%) ^a	Ash (%)	Density (g/cm ³)
CB control ^b	>99	<1	<1	<1	<1	1.7–1.9
Paulownia biochar	95.15 ± 0.67	1.39 ± 0.27	0.03 ± 0.03	0.91	2.52	1.76 ± 0.01
Poplar biochar	89.07 ± 4.39	1.52 ± 0.18	0.02 ± 0.01	7.42	1.97	1.66 ± 0.01

^a oxygen content calculated by difference; ^b data supplied by the manufacturer.

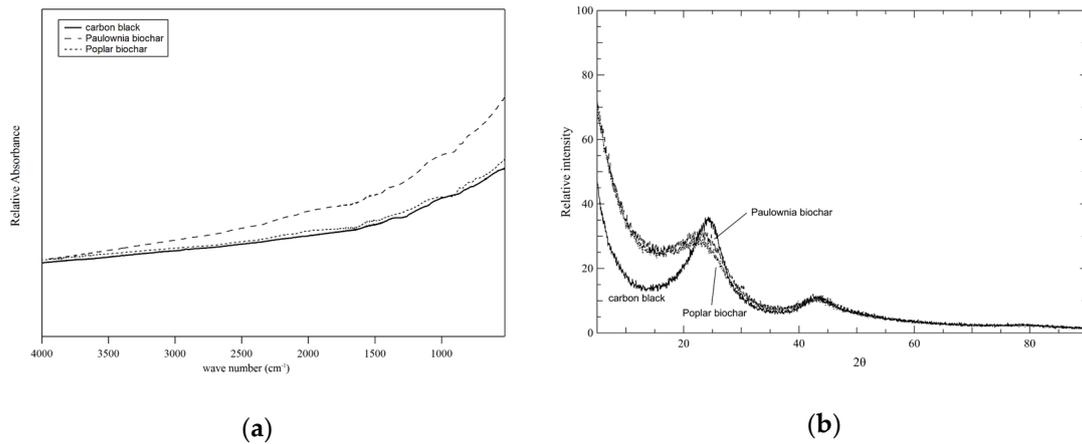


Figure 1. (a) Fourier-transform infrared (FTIR) spectra of carbon black, Paulownia biochar, and Poplar biochar. No significant functional group peaks are evident; (b) X-ray diffraction spectra of carbon black, Paulownia biochar, and Poplar biochar. Characteristic graphitic d-spacing peaks can be seen at 24° and 43° 2θ for all three samples.

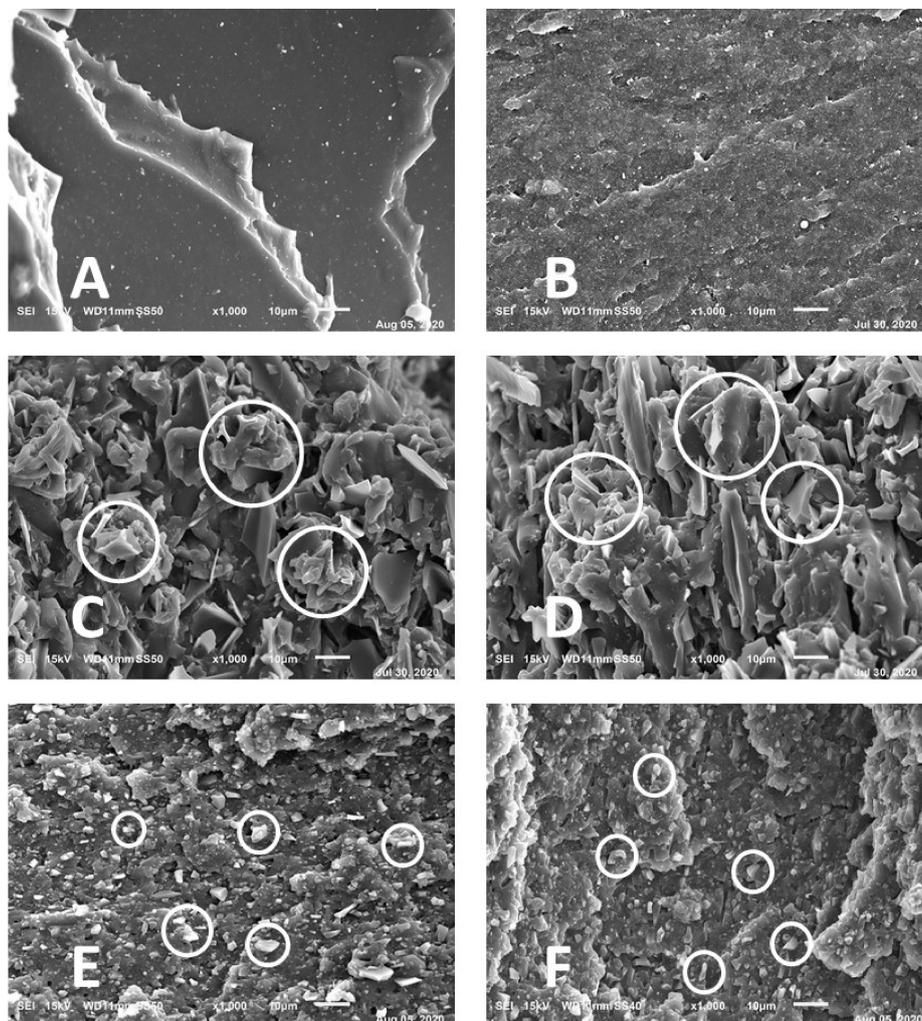


Figure 2. (A) Unfilled BR-NR rubber matrix. (B) 100% CB filled control. (C) 100% PAUL filled, no silica milling. (D) 100% POP filled, no silica milling. (E) 100% PAUL filled, after silica milling. (F) 100% POP filled, after silica milling. In each image the white scale bar at the lower right corner represents 10 microns. A few biochar particles have been circled to illustrate the size reduction that takes place during silica milling.

3.2. Composite Properties

All composite samples were measured for their electrical resistivity and the results can be seen in Table 3. Although the 100% CB control was the only sample classified as conductive, many of the composite samples are dissipative, with resistivities between 10^6 and $10^9 \Omega$. Only two biochar composite samples were insulative; both insulative samples were silica-milled samples of 100% POP and 100% PAUL, along with the unfilled BR-NR base rubber matrix sample. This data suggests that Paulownia biochar may have greater surface charge than poplar biochar, since there is a significant difference in resistivity between the two 100% filled samples of each biochar with no silica milling.

Table 3. Resistivity of Rubber Composite Samples.

Sample	Resistivity (Ohms)	Material Classification
100% CB control	10^4	conductive
100% PAUL	10^6	dissipative
70/30 CB/PAUL Si milled	10^6	dissipative
70/30 CB/POP Si milled	10^6	dissipative
50/50 CB/PAUL Si milled	10^8	dissipative
60/40 CB/PAUL Si milled	10^8	dissipative
60/40 CB/POP Si milled	10^8	dissipative
100% POP	10^9	dissipative
50/50 CB/POP Si milled	10^9	dissipative
100% PAUL Si milled	10^{12}	insulative
100% POP Si milled	10^{12}	insulative
unfilled BR-NR	10^{12}	insulative

SEM images of rubber composite samples at $1000\times$ magnification are shown in Figure 2. All the images in Figure 2 are taken from the fractured surfaces of the composites after they had been stretched and broken during tensile testing. Figure 2A shows the unfilled BR-NR matrix and 2B shows the 100% CB control. Figure 2C,D show 100% PAUL and POP biochar-filled samples, respectively; note the large biochar particles visible in these images. Figure 2E (PAUL) and Figure 2F (POP) are an excellent illustration of the benefit of silica milling; as these images show composites filled with 100% PAUL and POP biochars whose only difference from Figure 2C,D is being silica milled. While biochar particles are still visible and clearly larger than the CB particles in Figure 2B, the particle size has been reduced significantly and these results are reflected in the tensile properties of the samples (a few biochar particles have been circled to illustrate this).

Tensile properties of the rubber composite samples are shown in Table 4. The BR-NR matrix is very soft and pliable and requires reinforcement for most applications; this can be seen in the drastic increase in tensile strength and reduction in elongation going from the unfilled rubber matrix to the 100% CB control. The next two rows below the CB control show the effects of completely replacing CB with the biochars, with no silica milling. Because both samples introduce large biochar particles on the order of 10–100 μm (see Figure 2C,D), these large particles cause local stresses in the composites that weaken them and consequently reduce the tensile strength. Tensile strengths are significantly lower than the CB control. However, the positive effects of silica milling can be seen in the following two rows showing results for 100% silica milled PAUL and POP filled composites. The tensile strength and toughness values are roughly doubled compared to the unmilled biochar samples. Although silica milling shows an improvement, these samples are still much lower in tensile strength and toughness than the CB control. CB filled composites are stiffer than their PAUL or POP filled counterparts, and this can be seen in the higher Young's modulus values for the CB control relative to the other samples in Table 4.

Table 4. Tensile Properties of Rubber Composite Samples.

Filler	<i>n</i>	CB Replaced (%)	Tensile Strength (MPa)	Elongation (%)	Toughness (MPa)	Young's Modulus (MPa)
unfilled BR-NR	5	n/a	4.2 ± 0.4	457 ± 47	9.2 ± 1.4	1.4 ± 0.2
100% CB	5	0	21.0 ± 0.3	388 ± 8	34.6 ± 1.2	6.0 ± 0.3
100% PAUL	5	100	7.4 ± 0.4	275 ± 39	13.8 ± 2.9	7.6 ± 0.4
100% POP	6	100	7.0 ± 0.4	307 ± 33	14.0 ± 2.4	6.6 ± 0.7
100% PAUL Si	5	100	14.4 ± 0.2	397 ± 20	25.5 ± 1.4	3.2 ± 0.3
100% POP Si	5	100	14.6 ± 0.4	397 ± 9	26.4 ± 1.3	3.8 ± 0.5
50/50% CB/PAUL Si	5	50	18.3 ± 0.9	434 ± 22	35.7 ± 3.5	4.4 ± 0.5
50/50% CB/POP Si	8	50	17.6 ± 1.1	391 ± 14	31.1 ± 2.8	4.4 ± 0.5
60/40% CB PAUL Si	4	40	18.1 ± 1.5	393 ± 29	32.1 ± 4.4	4.5 ± 0.5
60/40% CB POP Si	6	40	19.2 ± 0.5	423 ± 10	35.9 ± 2.0	4.0 ± 0.5
70/30% CB PAUL Si	5	30	20.1 ± 1.1	443 ± 6	38.9 ± 3.0	4.3 ± 0.5
70/30% CB POP Si	6	30	20.9 ± 1.2	432 ± 21	39.8 ± 4.1	4.2 ± 0.2

n = number of replicates.

In order to create biochar filled composites that approach the same tensile strength as the CB control, the filler ratio of CB/biochar was increased to see how much PAUL and POP silica milled biochar could be substituted before the tensile strength dropped notably. The final six rows of Table 4 show these results. Predictably, as the ratio of CB/biochar increases, tensile strength and toughness increase as well. Young's modulus for CB/PAUL and CB/POP filled composites seems to level out at roughly 4.4 MPa, reduced from the control value of 6 MPa due to the addition of PAUL or POP biochar, which is not as rigid a filler as CB. For both 70/30 CB/biochar composites, the replacement of 30% of the CB with either PAUL or POP silica milled biochar results in a sample that is within experimental error of the tensile strength of CB, and superior in terms of elongation and toughness. Stress-strain curves of selected composites are shown in Figure 3. SEM images of the three highest tensile strength composite samples are shown below the stress-strain curve for visual comparison. To give an idea of the range of the stress-strain curves possible, the silica milled 100% PAUL and 100% POP filled composites are also shown. As the CB/biochar ratio is increased, the stress-strain curve of a given composite will trend upward and approach the 100% CB control.

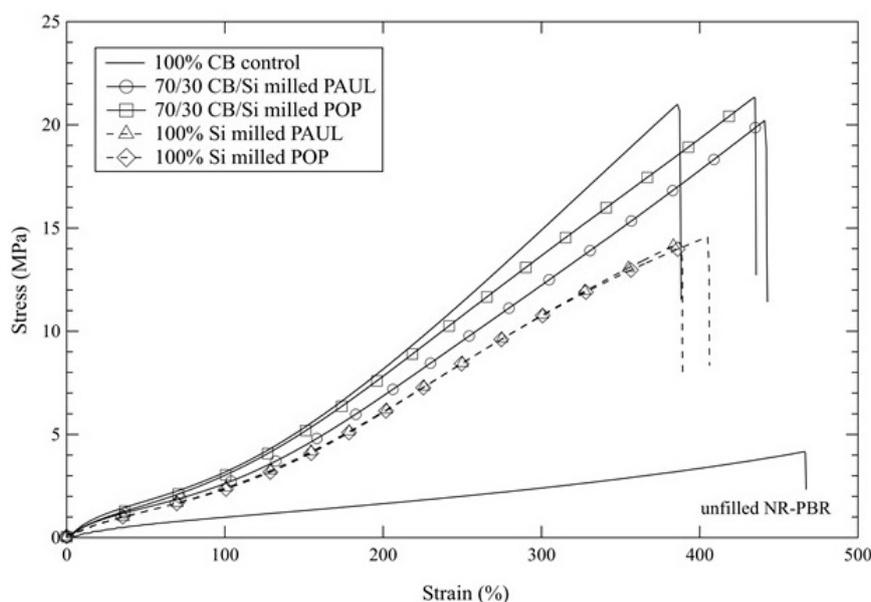


Figure 3. Cont.

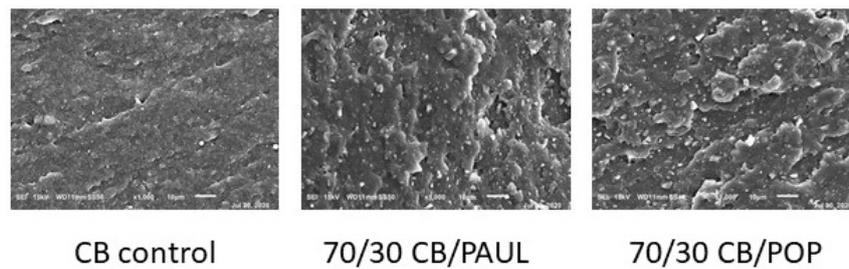


Figure 3. Stress-strain curves of the CB control (black line), 70/30 CB/silica milled PAUL (open circles), 70/30 CB/silica milled POP (open squares), 100% silica milled PAUL (open triangles), and 100% silica milled POP (open diamonds). Below the stress-strain curves SEM images at 1000 × of the 70/30 CB/biochar composites are shown next to the CB control for comparison. SEM images of the 100% silica milled PAUL and POP samples can be seen in Figure 2E,F, respectively.

Small-strain oscillation sweeps at 0.1% strain (within the linear region) and a frequency of 1 Hz were carried out for 1000 cycles on all composite samples. All samples showed constant storage modulus (G') values that are shown in Table 5. The results show G' as a function of CB concentration, since CB is a stiffer material than either PAUL or POP biochar. Comparing the results of the 100% PAUL and POP silica milled vs. no silica milling samples suggests that the larger biochar particles that are reduced in size and eliminated due to silica milling impart some stiffness to those samples; this is also corroborated by the Young's modulus results from Table 4. However, as shown in the corresponding tensile results, this stiffness is offset by significantly reduced tensile strength, presumably from local stresses of those large (>10 μm) biochar particles causing fractures in the composite at lower stress.

Table 5. Small-strain Cyclic Behavior of BR-NR Composites with 33 wt% Total Filler.

Sample	Average G' (MPa)
unfilled BR-NR	0.45 ± 0.01
100% CB	2.87 ± 0.03
100% PAUL	1.72 ± 0.01
100% POP	1.44 ± 0.01
100% PAUL Si	0.80 ± 0.01
100% POP Si	0.86 ± 0.01
50/50% CB/PAUL Si	1.27 ± 0.01
50/50% CB/POP Si	1.25 ± 0.01
60/40% CB/PAUL Si	1.60 ± 0.01
60/40% CB/POP Si	1.62 ± 0.01
70/30% CB/PAUL Si	1.90 ± 0.01
70/30% CB/POP Si	1.76 ± 0.01

4. Conclusions

For decades, carbon black, a fossil fuel-based feedstock, has been the dominant filler for rubber composites in the tire industry. It is prudent to explore renewable replacements for carbon black not only because petroleum supply is finite, but also because renewable alternatives are ecologically beneficial. Paulownia and poplar are both rapidly growing, coppiced hardwood feedstocks that can be grown over wide areas of North America and be pyrolyzed into high carbon content and low-ash biochar, in addition to many other uses [30–37].

In this work, silica-milled biochars made from Paulownia and poplar were tested as partial substitutes for carbon black in rubber composites using a 50/50 polybutadiene/natural rubber matrix. Biochars made from both hardwood feedstocks were able to replace 30% of the carbon black and match the tensile strength of the carbon black control, while having greater elongation and toughness properties.

Biochar made from coppiced feedstocks are viable sources for renewable carbon. Along with this work demonstrating successful partial replacement of carbon black in a polybutadiene/natural rubber matrix, these biochars have been shown to do the same in a styrene/butadiene matrix [26], and Paulownia biochar has done the same in natural rubber [28]. As these three rubber matrices make up the backbone of the tire industry, biochar from coppiced sources should be strongly considered to reduce carbon black usage in the future.

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Conflicts of Interest: The author declares no conflict of interest.

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