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Converting Dead Leaf Biomass into Activated Carbon as a Potential Replacement for Carbon Black Filler in Rubber Composites

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Abstract

In this work, the feasibility of converting dead leaf biomass into green activated carbon for use as a reinforcement filler in natural rubber composites was assessed. The dead leaf activated carbon (DLAC) was prepared by pyrolysis at 550, 700, 900, and 1000 °C at a heating rate of 10 °C min\textsuperscript{−1} under nitrogen gas flow of 100 cm\textsuperscript{3} min\textsuperscript{−1} and was activated by CO\textsubscript{2} gas at the same flow rate when the pyrolysis temperature was reached. The properties of DLACs were characterized by particle size analysis, density, scanning electron microscopy, elemental energy-dispersive X-ray spectroscopy and Raman spectroscopy. The results revealed that the DLAC obtained by pyrolysis at 1000 °C had a small particle size of 28.86 µm; a highly porous structure; high carbon purity, at 82.58%; and a low density, at 1.588 g cm\textsuperscript{−3}. The effect of different DLAC contents (5, 10, and 15 phr) on the curing properties and the physical and mechanical performance of the rubber composites was
investigated and compared with rubber composites containing carbon black (CB). The results showed that the addition of DLAC increased the maximum torque and reduced the scorch and cure times. The tensile strength for rubber composites containing 15 phr of DLAC increased by 8%, the M100 and M300 improved 40%, and the elongation at break and crosslink density decreased by approximately 5% and 24%, respectively. The studied DLAC is a promising, cost-effective alternative to commercial carbon black for improving the performance of rubber composites.

**Keywords:** natural rubber; activated carbon; carbon black; crosslink density

1. Introduction

Rubber has been widely used in various engineering applications such as tires, bearings, gaskets, hoses and cables due to its outstanding dynamic mechanical properties as well as creep and wear resistance [1]. Rubber does not corrode and typically does not require lubrication during service; however, gum rubber is weak, exhibits widespread swelling in liquids and is effortlessly attacked by oxygen or ozone, which degrades the rubber [2]. Such drawbacks can be offset by the addition of reinforcing fillers, such as carbon black, to obtain the properties to suit specific applications [3,4]. The successful application of carbon black in rubber matrix considerably increases the material’s stiffness, tensile strength, tear strength, abrasion resistance and hysteresis loss [5,6]. This reinforcement effect is influenced by the physical interactions between carbon black surfaces and rubber chains as well as chemical interaction between functional quinonic groups on the carbon black surfaces with rubber chains which leads to formation carbon black filler network with different degrees of immobilized rubbers (bound rubber, occluded rubber and trapped rubber). The reinforcement
mechanism of carbon black in natural rubber is well elucidated in few previous studies which include the hydrodynamical effects, Mullin effects and Pyne effects and sufficient investigation and modelling on relationship between carbon black filler network with immobilized rubbers has been performed in many detailed studies [7,8].

Carbon black (CB) is derived from non-renewable resources through the chemical-thermal conversion of petroleum. This process requires approximately two and a half kilograms of oil to obtain one kilogram of carbon black. Therefore, the carbon black industry is a major contributor to carbon dioxide emissions, which have been implicated in global warming [9,10]. Increasing fears about global warming due to the use of fossil fuels, high dependence of carbon black on petroleum supplies, and the rising prices of petroleum and carbon black, have prompted work to explore viable carbon alternatives.

Another major challenge to the ecosystem is the large amount of withered leaves falling from the trees throughout the year in tropical climates and throughout the autumn in the northern and southern hemispheres. Dried leaves usually accumulate in piles and become habitats and breeding grounds for rodents, rats, snakes and other dangerous animals. The large piles in the forest are a fire hazard that could destroy hundreds of thousands of trees per year and emit carbon dioxide and smoke that contaminate the atmosphere [11].

In recent years, studies have focused on the use of plentiful renewable and green materials to replace carbon black [12–15]. Biochar is a renewable substitute for carbon black which is commonly produced from pyrolysis of biomass in the absence of oxygen [16]. Biochars derived from wood-based feedstocks have been utilized as fillers in natural rubber matrix, however the results showed that the tensile strength, modulus, and toughness were approximately 50% lower than carbon black reinforced rubber matrix [17,18]. Activated
carbon is another material that has great potential to replace carbon black. Activated carbon is derived from pyrolysis of biomass or other carbonaceous substances such as coal or tar and subsequently activated via physical or chemical process that greatly increase the micro porosity of the material, allowing absorption of larger quantity of molecules [19]. Previous studies found that plant biomass, such as wood, crop residues, sawdust, coconut shell, animal waste, aquatic plants and algae, is inexpensive and available in abundance with feasible compositions to produce activated carbon (AC) [20–23]. Although AC has been well established as an absorbent [24], a separation and recovery process material [25], and an electrode material [26,27], its potential use in rubber composites as a reinforcement filler has not been thoroughly explored.

The aim of this work is to assess the possibility of converting dead leaf biomass into low-cost activated carbon by pyrolysis. In this study, the feasibility of preparing dead leaves activated carbon by physical activation was investigated. Physical activation requires carbonization of the dead leaves biomass by pyrolysis at higher temperature (550 – 1000 °C) to remove moisture and bulk volatile matters followed by activation of the carbonized material in the presence of activating agents, such as carbon dioxide and steam at temperature range of 550 – 1000 °C. Carbon dioxide is preferred over steam because of its low reactivity enables slow oxidation process creating uniform porosity and enlarging the existing pores [19,28]. The carbon structures and particle sizes of the produced dead leaf activated carbon (DLAC) were characterized to determine the optimal condition of the DLAC to be used as a reinforcement filler in rubber composites. The influence of DLAC on rubber cure properties and on the physical and mechanical performance of rubber composites were investigated.
The reinforcement effect of rubber containing DLAC was compared with that of rubber containing carbon black.

2. Experimental

2.1 Materials

Standard Malaysian rubber (SMR L) was purchased from Malaysia Rubber Research Institute (RRIM), Selangor, Malaysia. Other additives, including zinc oxide, stearic acid, tetramethyl thiuram disulfide (TMTD), N-cyclohexyl-2-benzothiazyl sulfonamide (CBS), carbon black (N330), and sulfur, were supplied from Bayer (Malaysia) Sdn. Bhd. Dead leaves from Tecoma trees were collected from the campus gardens of Universiti Sains Malaysia (USM).

2.2 Preparation of dead leaf activated carbon (DLAC)

Dry Tecoma leaves from the Universiti Sains Malaysia gardens were washed several times with boiling water to remove impurities and undesirable materials and then dried for 24 h in the oven at 1000 °C until a constant weight was attained. After drying, the dead leaves were grinded using an RT-34 I HP grinder and subsequently sieved through 100 µm mesh to ensure a consistent powder size for the dead leaves. A horizontal tube furnace (Lenton 1200) was utilized for the pyrolysis and activation process. Approximately 15 g of dead leaf powder was placed in a ceramic porcelain boat, which was then placed in the middle of the furnace tube. Pyrolysis was performed at 550, 700, 900 and 1000 °C to turn the dead leaf powder into biochar under a steady nitrogen flow rate of 100 cm³ min⁻¹, and the heating rate was kept constant at 10 °C min⁻¹. When the final temperature of pyrolysis was reached, the flow of nitrogen gas was stopped, and then carbon dioxide was applied for 60 min at a flow rate of
100 cm$^3$ min$^{-1}$. Four different types of dead leaf activated carbon were prepared in this process, namely, DLAC 550, DLAC 700, DLAC 900, and DLAC 1000; the numbers refer to their activation temperature. The sample was cooled to room temperature under nitrogen flow once activation was complete. The samples were then kept in a desiccator until further use. Scheme 1 illustrates the process involved to prepare the dead leaf activated carbon.

2.3 Preparation of rubber composites

Table 1 presents the compound formulations used in this work. A laboratory-scale two-roll mill (XK-150) was utilized for the mixing and compounding process according to ASTM D3184-89. The compounding started with mastication of the raw rubber for 2–3 min. All ingredients were added following the sequence listed in Table 1. The compounding process was kept constant for approximately 30 min for all formulations. Subsequently, the rubber compound was placed in a mould ($124 \times 70 \times 3$ mm) and vulcanized using a compression moulder (GT 7014-A30C) at 150 °C under 12 MPa clamping pressure.

2.4 Cure characteristics

The cure properties of the rubber compounds were analysed using a Monsanto moving die rheometer (MDR 2000) as per ASTM D5289. Approximately 4 g of each compound was placed onto the rotor and tested at 150 °C for 15 min. The scorch time ($t_{s2}$), optimum cure time ($t_{90}$) and torque maximum ($M_H$) were measured and recorded.

2.5 Characterization

2.5.1 Particle size analysis

The DLAC and CB particle size distributions were analysed using a Malvern Mastersizer 3000 instrument (Malvern Instruments Ltd., Worcestershire, UK) equipped with
Hydro EV Flexible volume wet dispersion. The size distributions were calculated using Mastersizer 3000 software (version 5.54). The measurements were performed in triplicate.

2.5.2 Density

DLAC density was measured using a 10 cm³ sample cup with a pycnometer (Micromeritics Accupyc II 1340). The sample was prepared and loaded into the sample cup in the Micromeritics machine, and the density value was obtained from Accupyc II 1340 Foam Pyc software.

2.5.3 Morphology and elemental compositions

The morphology of DLAC and CB particles and of the fractured surfaces of rubber composites were investigated using a scanning electron microscope (SEM) (Zeiss Supra 35VP). The samples were coated with a thin layer of gold palladium, and observation was carried out under an acceleration voltage of 5–12 kV. The composition of elements, such as carbon, oxygen, and other elements, on the sample surfaces, which was expressed as a percentage, was obtained by using EDX Spectra [29].

2.5.4 Raman spectroscopy

Raman spectroscopy is an important technique for characterizing carbonaceous materials because the Raman spectra of these materials exhibit two characteristic bands (the G-band and D-band) in the region between 1000 and 1800 cm⁻¹. Raman spectra of DLAC and CB were obtained with a Raman station 400R spectrometer (PerkinElmer) fitted with an air-cooled charged coupling device detector. The calibration of the infrared laser was carried out using a regular polystyrene disc. The sample was placed on aluminium foil, and the surface area of each site to be analysed was marked in the Raman instrument. The laser power
was set at approximately 40 mW and kept consistent for accuracy across the sample range. The spectra measurement was carried out over 500-2200 cm\(^{-1}\), and an average of five experimental repeats of 60 s exposures was obtained for each spectrum.

2.5.5 Crosslink density

The efficiency of the cured vulcanizate of rubber composites was determined by crosslink density measurement. Five samples of each formulation were cut into rectangular shapes with 30×5×2 mm dimensions and were immersed in a glass vessel containing 25 mL of toluene. According to ASTM D471, the experiment was run at room temperature for 72 h in a dark environment to achieve equilibrium swelling. The swollen samples were taken out quickly, wiped with filter paper and weighed. The volume fraction of rubber (\(v_r\)) was calculated using Equation 1. The \(v_r\) value was then used to calculate the crosslink density \(M_c\) using the Flory–Rehner theory in Equation 2:

\[
v_r = \frac{(w_A/\rho_r)}{(w_A/\rho_r) + (w_B/\rho_s)}
\]

where \(w_A\) and \(w_B\) are the weights of swollen and unswollen rubber, respectively (g), and \(\rho_r\) and \(\rho_s\) are the densities of natural rubber (0.920 g cm\(^{-3}\)) and toluene (0.86 g cm\(^{-3}\)), respectively.

\[
\frac{1}{M_c} = -\frac{(\ln(1 - v_r) + v_r + \chi v_r^2)}{\rho_r \rho_v v_r^3}
\]

where \(M_c\) is crosslink density in mol cm\(^{-3}\), \(\rho_v\) is the molecular volume of toluene (106.4 cm\(^3\) mol\(^{-1}\)), and \(\chi\) is the Flory–Huggins interaction parameter for natural rubber and toluene (0.393) [30].
2.5.6  Tensile properties

A universal tensile testing machine Instron 3366 (Norwood, MA, USA) equipped with a 10 kN load cell was used to perform tensile tests according to ASTM D412-98. The mould sheet was cut using a Wallace die cutter to produce dumbbell-shaped samples. The thickness of the samples was measured using a thickness gauge. The test was carried out at 500 mm/min with a 50 mm gauge length. The average values for tensile strength, elongation at break (Eb), modulus at 100% elongation (M100), and modulus at 300% elongation (M300) were calculated from five specimens for each formulation.

2.5.7  Hardness

A digital Teclock Durometer JIS K 6310A, type shore A, was used to measure the sample hardness according to ASTM D2240. The moulded sheet was cut into a cylindrical shape with a 4 cm diameter and 0.5 cm thickness. A specific indenter was penetrated on the sample’s surface under defined conditions, and the measured values were recorded. At least five repeated measurements were performed to calculate the average values of the rubber composites.

3. Results and Discussion

3.1 Characterization of the DLAC and CB

3.1.1  Morphology and elemental compositions

The morphologies of the DLACs prepared at different activation temperatures and of the CB are shown in Figure 1. In general, the DLAC particles were fine with various shapes and sizes and porous structures. The external surface roughness and irregular grain shape of the DLACs became more pronounced as the temperature increased from 550 °C to 1000 °C. The small grains that migrated to the DLAC surface might have originated from inorganic
salts, as stated by Septien et al. (2012). Interestingly, soot particles composed of carbon were found in DLAC 1000, as circled in Figure 1(d). These structures appeared to be agglomerations of spherical particles with heterogeneous size distributions. This result indicates that DLAC 1000 had a highly porous structure compared with that of other activated carbon samples, which could be attributed to the vaporization of volatile substances on the surface of the activated carbon during pyrolysis [32]. The volatile substances include lignocellulose, cellulose, hemicellulose and non-carbon elements such as oxygen and hydrogen. These volatiles diffuse out through the particles at high temperatures to develop the porous volume of activated carbon [33]. In contrast, the surface of carbon black in Figure 1(e) had fewer pores, cracks, and voids, and the particle sizes were comparable with those of activated carbon.

The estimation of the elemental composition of DLACs at different activation temperatures and of carbon black was obtained from EDX spectral analysis (Table 2). The results showed that activated carbon had high carbon content at higher temperatures [28]. Dead leaves progressively lost their oxygen, hydrogen, and other elements, while carbon content increased as the temperature increased. DLAC 550 was composed of 68.35% carbon and 12.94% oxygen, with low mass loss (30%), while DLAC 1000 had 82.58% carbon and 3.73% oxygen, along with other elements, and mass loss of 47%. Pyrolysis at 550 °C led to incomplete conversion of dead leaves into biochar and tar. The pyrolysis process converted lignocellulose and lignin to biochar and tar, while moisture, some volatile substances, and most non-carbon elements, such as oxygen, hydrogen, nitrogen, and sulfur, were removed. The high mass loss of the 1000 °C sample can be explained; at temperatures between 600 °C and 900 °C, ash is converted to decarbonation, and potassium and sulfur are volatilized at
temperatures above 900 °C [31]. As expected, carbon black contained a high percentage of carbon, along with small percentages of oxygen and sulfur. The small amount of sulfur in carbon black was due to its presence in the hydrocarbon fuel feedstock.

3.1.2 Raman spectroscopy

Figure 2 shows Raman spectra for DLACs at different activation temperatures and CB. Spectra of activated carbons consist of two sharp peaks in frequency domains between 1300–1700 cm$^{-1}$, which correspond to the characteristic of a graphite structure [34]. The appearance of a Raman peak at 1500–1600 cm$^{-1}$, known as the G-band, is assigned to a single crystal of graphite, whereas the Raman band appearing between 1300–1400 cm$^{-1}$, known as the D-band (disorder band), indicates polycrystalline graphite. The peak position of the D-band mainly depends on the degree of carbonization and the properties of the disordered carbons, such as porosity, crystallite size distribution, and the concentration of amorphous components [35].

As the temperature of activation was increased, the D-band shifted to lower frequencies owing to turbostratic carbon, in which the carbon atoms became disordered and diffuse along the graphite sheets. The disorder-induced D-band was found to influence the intensity ratio of I$_D$/I$_G$ for all activated carbons [36]. As a result, I$_D$/I$_G$ values gradually increased from 1.07 to 1.13 with the increasing activation temperature from 550 °C to 900 °C. The increase in the peak intensity ratio indicates a larger disordered carbon structure. In contrast, the intensity ratio of activated carbon decreased to 0.92 at 1000 °C pyrolysis, which is smaller than that of carbon black. This decrease was mainly related to the loose carbons that were removed upon activation, which were highly disordered or amorphous microporous
structures comprised of aromatic sheets and strips [37]. On the other hand, the Raman spectrum and the ratio intensity of $I_D/I_G$ for the carbon black found in the present study are similar to those reported in the literature [38].

3.1.3 Particle size and density of the DLACs and CB

Figure 3 shows the particle size distributions of the DLACs and CB. For the DLACs, it was found that DLAC 700 had a narrow particle size distribution that was similar to that of CB. However, the mean particle size was 26.34 µm, whereas for CB, it was only 5.34 µm. Other samples, especially DLAC 550, showed slightly larger particle sizes and broader distribution due to incomplete conversion of dead leaves into biochar and tar. The large particle sizes and broad particle distribution of DLAC 900 and DLAC 1000 could be related to the agglomeration of soot particles during the carbonization and activation process.

However, the density of DLACs slightly decreased with the increasing activation temperature (Table 3), which is attributed to the increase in the porous structure of activated carbon materials. The formation of large cavities and pores occurred due to the release of volatiles, causing bubbling and fusion of the biochar, which in turn formed irregularities on the DLAC surface [31]. This result is in agreement with SEM micrographs in which the porous structure increased with increasing activation temperatures. Considering the morphology, EDX, Raman spectra, and particle size characterization results, the activated carbon produced at 1000 °C was chosen for subsequent stages to investigate the effect of the DLAC on the performance of rubber composites.

3.2 Curing characteristics of rubber composites
The curing characteristics of the rubber composites with the addition of different DLACs and CB contents are presented in Table 4. The control SMR L compound showed the lowest maximum torque value compared to DLAC- and CB-filled rubber compounds. It is known that the molecular chains of rubber are easily broken down by shear force during mixing on a two-roll mill [39]. The maximum torque increased with the increasing filler content. This could be attributed to the incorporation of fillers, which hindered rubber flow and increased the viscosity of the rubber melt [40]. Moreover, the formation of an interface region between filler and the matrix decreased the fluidity of the matrix, as rubber molecules were bonded to the filler surface, resulting in improved stiffness of the rubber compounds [41]. For rubber filled with CB, the small particle size and large specific surface area of the carbon black led to better interaction between the filler and matrix, which restricted the mobility of rubber molecules and therefore resulted in higher maximum torque than that of activated carbon-filled rubber.

The scorch time ($t_{s2}$) and cure time ($t_{90}$) of DLAC- and CB-filled rubber compounds slightly decreased with the increasing filler content. A shorter scorch time helps reduce energy consumption during the mould filling process, but the main drawback of a short scorch time is that it may lead to crosslinking of the rubber before the compound fills up the mould cavity. Extending the scorch time can avoid premature crosslinks during processing [42]. The faster cure time of DLAC- and CB-filled rubber compounds might be affected by the longer time on the two-roll mill during mixing. Additionally, a longer compounding time to disperse the filler within the rubber was needed, and thus, more heat was generated, as additional friction occurred when more filler content was added. On the other hand, DLAC-
filled rubber exhibited a shorter scorch time and cure time than CB-filled rubber with similar filler content. It may be that SMR L/DLAC started to vulcanize earlier than SMR L/CB based on scorch time data. The smaller particle size and larger surface area of CB formed difficult paths for the reaction of sulfur with the available cure sites between neighbouring rubber molecular chains and thus slowed the cure time of rubber compounds [12].

3.3 Properties of rubber composites

3.3.1 Crosslink density

The effect of different DLACs and CB content on the crosslink density of the rubber compounds is shown in Figure 4. The control SMR L has the highest crosslink density, as it is solely dependent on the extent of crosslinking in the rubber network. Crosslinking includes carbon-sulfur bonding involving sulfur atoms on polyisoprene chains and a TMTD accelerator as well as hydrogen bonding between proteins phospholipids at initiation and termination chain ends of the rubber chains [43]. The addition of filler to rubber compounds decreased the crosslink density. The filler-rubber interactions altered rubber molecular chains and reduced the sulfur vulcanization efficiency, and this interaction did not resist the penetration of solvents into the rubber compound [44]. Moreover, the large particle size of the DLAC might have disrupted the intermolecular interaction between rubber chains, leading to a higher degree of swelling. Additionally, the porous structure of DLAC at 1000 °C also caused a higher quantity of solvent to adsorb than when carbon black was used. As a result, SMR L/DLAC composites had a lower crosslink density than CB-filled SMR L vulcanizate.

3.3.2 Mechanical Performance
Figure 5 compares the tensile properties of SMRL/DLAC and SMRL/CB rubber composites with different filler contents. Figure 5(a) shows that the control SMRL had the lowest tensile strength, at 14.9 MPa, which was largely due to strain-induced crystallization of gum NR vulcanizates. Generally, the addition of both carbon-based fillers improved the tensile strength and Young modulus of the rubber composites. The strong filler-rubber interaction led to the formation of a rubber shell around the filler particles, which subsequently attached to each other, forming a filler network. In this filler network, the rubber tends to be trapped within the network, so it is commonly known as trapped or occluded rubber. These interactions constrain the mobility of rubber molecular chains and therefore lead to efficient stress transfer from the matrix to reinforcement filler particles [45]. However, rubber composite with 15 phr of DLAC had a decreased tensile strength. The soot particles of DLAC had a low density of 1.588 g cm$^{-3}$ which made them difficult to homogeneously disperse during the mixing process and tended to agglomerate. The stress transfer might have been concentrated at the shape edges and porous structures of activated carbon particles and thus promoted earlier failure compared to the spherical shape of carbon black [46]. Likewise, the reinforcement effect relies on the filler particle size and the carbon content of the fillers. As previously discussed, the particle size and the percent carbon content of the DLACs were larger than those of CB. These properties are the reason that the tensile strength for SMRL/DLAC is lower than that for the SMRL/CB composite. The tensile strength of the SMRL/CB composite increased with the increasing CB content. The strong filler-rubber and filler-filler interfaces contributed to efficient stress transfer from the rubber matrix to the reinforcement particles [47]. Results have shown that the average tensile strength of the
developed DLAC filled natural rubber composites was 50 – 80% higher compared to commercial activated carbon filled natural rubber composites [48–50].

In contrast, the incorporation of both DLAC and CB in the rubber matrix reduced the elongation at break (Figure 5(b)). This could be explained by the immobilization of rubber chains in which the molecules were attached to the filler surface by both physical and chemical interactions; this phenomenon is known as immobilized or glassy rubber shell [51]. The immobilized rubber chains constrained the elastic behaviour of the rubber molecular chains and acted as rigid bodies. Moreover, the strong interaction between CB particles and rubber molecules decreased the mobility of rubber vulcanizate and led to early breakdown of the samples. Therefore, CB-filled rubber vulcanizates had a lower elongation at break than DLAC-filled rubber vulcanizate. Similar findings have been observed in commercial activated carbon filled natural rubber composites [49,50].

The large increases in the M100, M300 and hardness shore A of the rubber composites in Figures 5(c–e) could be due to the filler-rubber and filler-filler interactions, as well as the formation of a filler network in the rubber composites. At equal filler content, the M100 and M300 of SMR L/CB composites were higher than those of DLAC-filled rubber composites. This behaviour was related to the small particle size, broad particle size distribution and high purity of carbon content in CB, leading to improved dispersion and distribution of its particles in the rubber composites [45]. This result is consistent with previous work carried out by Samsuri (2014). The results are comparable with commercial activated carbon filled natural rubber composites as reported elsewhere [48,49].
The SEM microstructures of the tensile fractured surfaces of rubber composites with different DLACs and CB content are shown in Figure 6. These images provide evidence that the tensile performance of the composites was improved due to good dispersion and physical interactions between the carbon-based fillers and the rubber matrix. Figure 6(a) shows that the fractured surface of the control SMR L vulcanizate was smooth and had a barely perceptible fracture line, which indicate that the sample had low resistance to surface tearing during tensile test. For rubber composites with the addition of DLACs, as shown in Figures 6(b–d), the fractured surfaces of SMR L/DLAC composites were rough, with uniform filler dispersion. At high filler content, the agglomeration of DLACs occurred, and therefore, some of the particles were loose and pulled out from the rubber matrix, creating voids on the fractured surface. It can also be seen that the DLAC particles trapped part of the rubber in the surface void, which potentially induced strain-independent contributions in the rubber composites and resulting in increased modulus and hardness [45].

The morphology of CB-filled SMR L vulcanizates in Figures 6(e–g) shows significant matrix tear lines and surface roughness in comparison with that of unfilled rubber and DLAC-filled rubber vulcanizates. The entanglement of rubber molecules plays a major role in rubber attachment on the surface of carbon black [53]. The strong chemical and physical interactions between rubber molecular chains with the CB particles dominated over interactions between the filler particles, thus preventing agglomeration. Therefore, SMR L/CB composites exhibited a good distribution of CB particles in rubber and filler–rubber interactions, which led to better filler-rubber interphase in the composites [54]. The strong interphase of the filler-rubber interactions latter altered the crack paths and increased
resistance for crack propagation, which resulted in higher tensile strength, modulus, and hardness of the rubber composites.

4. Conclusion

The present study attempts to produce a novel activated carbon from dead leaf biomass for use as a reinforcement filler in rubber composites. The dead leaf activated carbon (DLAC) produced at a 1000 °C activation temperature had high carbon content of 82.58%, an average particle size of 28.86 µm, and a density of 1.588 g cm\(^{-3}\). The effect of different DLACs and CB content (5, 10, and 15 phr) on the curing characteristics and the mechanical performance of the rubber composites was compared. The results revealed that both fillers increased the maximum torque and reduced the scorch time and cure time of the rubber composites. The cure characteristics of the SMR L/DLAC composite were better than those of the CB-filled rubber composite, especially at high filler content. The addition of DLAC increased the tensile strength at 5 phr but decreased with the increased filler content, while the tensile strength of the SMR L/CB composites increased with the increase in CB content. The smaller particle size and higher purity carbon in CB resulted in better filler-rubber interactions to form 3D networks, which contributed to greater stiffness and rigidity of the composites than those of the SMR L/DLAC formulation. The percentage differences in the tensile strength, M100, M300, and hardness of SMR L/CB over SMR L/DLAC composites at 15 phr were 33%, 14%, 48%, and 0.4%, respectively. The results suggest that activated carbon derived from biomass can be used as reinforced filler in rubber composites and will become a potential filler for the rubber industry.
Acknowledgements

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Scheme 1 Production of activated carbon from dead leaves via pyrolysis.

Figure 1 Micrographs of (a–d) DLACs at 550, 700, 900, and 1000 °C, respectively, and of (e) carbon black.
Figure 2 Raman spectra of DLACs at different temperatures and of carbon black.

Figure 3 Particle size distribution of DLACs and carbon black.

Figure 4 Crosslink density of rubber composites.
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Figure 6 SEM micrographs of tensile fractured surfaces of (a) control SMR L, (b–d) SMR L/DLAC, and (e–g) SMR L/CB with 5, 10, and 15 phr of filler content.
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Table 1 Rubber compound formulations.

<table>
<thead>
<tr>
<th>Raw materials</th>
<th>Part per hundred of rubber (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMR L</td>
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<tr>
<td>Zinc oxide</td>
<td>5</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>1</td>
</tr>
<tr>
<td>DLAC</td>
<td>0, 5, 10, 15</td>
</tr>
<tr>
<td>Carbon black (N330)</td>
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</tr>
<tr>
<td>CBS</td>
<td>2</td>
</tr>
<tr>
<td>TMTD</td>
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<tr>
<td>Sulfur</td>
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Table 2 Elemental composition of different DLACs and carbon black, expressed as a percentage.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Element composition</th>
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<tbody>
<tr>
<td></td>
<td>C (%)</td>
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<tr>
<td>DLAC 550</td>
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<tr>
<td>DLAC 700</td>
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<td>DLAC 900</td>
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<td>DLAC 1000</td>
<td>82.58</td>
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<td>Carbon black</td>
<td>97.07</td>
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</table>
Table 3 Average particle sizes and densities of different DLACs and carbon black.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Particle size (μm)</th>
<th>Density (g cm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>DLAC 550</td>
<td>32.98</td>
<td>1.774 ± 0.151</td>
</tr>
<tr>
<td>DLAC 700</td>
<td>26.34</td>
<td>1.673 ± 0.112</td>
</tr>
<tr>
<td>DLAC 900</td>
<td>32.85</td>
<td>1.691 ± 0.141</td>
</tr>
<tr>
<td>DLAC 1000</td>
<td>28.86</td>
<td>1.588 ± 0.123</td>
</tr>
<tr>
<td>Carbon black</td>
<td>5.34</td>
<td>2.529 ± 0.172</td>
</tr>
</tbody>
</table>

Table 4 Curing characteristics of rubber compounds.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Filler loading (phr)</th>
<th>M(_H) (dNm)</th>
<th>(t_{32}) (min)</th>
<th>(t_{90}) (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control SMR L</td>
<td>0</td>
<td>8.11</td>
<td>3.02</td>
<td>6.38</td>
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<tr>
<td></td>
<td>5</td>
<td>9.05</td>
<td>2.02</td>
<td>4.85</td>
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<td>9.44</td>
<td>1.51</td>
<td>3.11</td>
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<td>15</td>
<td>10.90</td>
<td>1.08</td>
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<td>5</td>
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<td>2.81</td>
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<tr>
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<td>10.47</td>
<td>1.75</td>
<td>3.75</td>
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