Research Article

Ecofriendly Biochar as a Low-Cost Solid Lubricating Filler for LDPE Sustainable Biocomposites: Thermal, Mechanical, and Tribological Characterization

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The potential of ecofriendly biochar, a carbon-rich byproduct of biomass pyrolysis, as a low-cost solid lubricating filler for low-density polyethylene (LDPE) sustainable biocomposites is investigated in this work. Tensile strength, hardness, thermogravimetric analysis (TGA), melting flow index (MFI), tensile test, flexural test, and frictional tests were used to characterize the biocomposites’ mechanical, thermal, and tribological properties. Energy-dispersive X-ray spectroscopy (EDS) was used to assess the chemical composition of the biochar, while field-emission scanning electron microscopy (FESEM) was used to capture the biochar morphology. The results showed that the incorporation of biochar in LDPE matrix increased the mechanical characteristics of the biocomposites and resulted in a significant increase in tensile strength, flexural strength, and hardness. More specifically, the LDPE+10 wt% composite outperformed the pure LDPE matrix by 1.9% in tensile strength and 47% in flexural strength. Furthermore, integrating biochar into LDPE composites enhances thermal stability, lowers the melt flow index (MFI), and boosts the hardness by 24.3% for the composite with 10% biochar content. Furthermore, biochar improves wear resistance and durability, with the LDPE10 composite exhibiting a friction coefficient that is 56.3% lower than pure LDPE. These findings indicate that biochar is a viable, cost-effective, and environmentally friendly filler for improving the performance of LDPE-based biocomposites for many varieties of applications.

1. Introduction

The increased need for sustainable materials, along with the growing environmental concerns about traditional plastics, has resulted in the creation of biocomposites, which combine the benefits of both natural and synthetic materials [1, 2]. Because of its great processability [3], cheap cost [4], and desired mechanical quality, low-density polyethylene (LDPE) is a commonly used thermoplastic polymer [5, 6]. However, its nonbiodegradable nature and reliance on fossil fuels have prompted environmental concerns [7, 8]. In this context, including biochar, a carbon-rich byproduct of biomass pyrolysis, or any other carbon material as a solid lubricating filler in LDPE biocomposites, is a viable method for addressing these difficulties [9–11]. Biochar has received a lot of interest in recent years because of its potential uses in industries including agriculture, carbon sequestration, and waste management [12–14]. Its distinguishing characteristics, such as large surface area, porosity, and chemical stability, make it an appealing choice for use as a filler in polymer composites [15–18]. Furthermore, the generation of biochar from renewable biomass resources facilitates the material’s overall sustainability [19–21]. The addition of biochar not only improves the material’s overall sustainability, but it also offers prospective advantages in mechanical, thermal, and tribological capabilities for both metallic [22] and polymeric matrices [23]. Furthermore, using biochar as a filler has the potential to minimize the dependency on nonrenewable resources like carbon black and graphite, which are often used in traditional polymer composites [24–26].

Biochar-enhanced LDPE is anticipated to increase frictional characteristics since it acts as a solid lubricant, with
a greater coefficient of friction and lower wear [27, 28]. This renewable and recyclable material might be an appealing alternative to existing fillers, lowering environmental impact and expenses while increasing LDPE plastic product performance. Ferreira et al. [29] investigated the heat stability of polyethylene with various additives, including biochar as filler in polyethylene composites, and they evaluated the performance of biochar generated from sugarcane bagasse over the commercial carbon black. They discovered that adding biochar increased the thermal stability of the composites, with a 15% improvement in thermal characteristics when compared to commercial carbon black-filled composites. The composites’ differential scanning calorimetry (DSC) examination revealed that the fillers had no substantial influence on the polymer’s transition temperature. The enthalpy values for fusion and crystallization, on the other hand, dropped due to the heterogeneous nucleation effect generated by the addition of fillers to the polymer. They concluded that biochar has the potential to replace commercial carbon black as a filler in polyethylene composites, providing enhanced thermal stability and comparable performance in other parameters.

According to Chinmoyee Das et al. [30], biochar is a good addition for polymer composites, providing considerable improvements in mechanical, thermal, and electrical characteristics. Its lightweight nature, greater heat stability, and decay resistance make it a more appealing alternative than natural fillers such as wood powder and traditional mineral fillers. Biochar is inexpensive and easy to get due to its simplicity of manufacturing from diverse lignocellulosic sources. Giorcelli et al. [18] investigated the mechanical characteristics of epoxy resin-based polymer composites made with biochar generated from maple trees that had been pyrolyzed at two different temperatures. Their research revealed that adding a little proportion of biochar (equivalent to or more than 2 wt%) can improve the composite’s mechanical characteristics. Zhang et al. [31] studied the effects of large biochar loadings on biochar-added composites to maximize agricultural waste usage. According to the study, the inclusion of biochar improved the mechanical characteristics of HDPE, resulting in high biochar loading-filled composites with good mechanical characteristics. The composites also have high stiffness, elasticity, creep resistance, and antistress relaxation properties. Although increasing biochar loading lowered the composites’ water resistance, they improved their flame retardancy.

Based on our present understanding and an evaluation of the existing literature, it appears that no research has been conducted specifically focusing on the integration of biochar as a reinforcing ingredient in low-density polyethylene (LDPE) composites. This research gap presents an opportunity for further investigation, as the unique features of biochar have the potential to bring significant improvements to the performance of LDPE-based products. The problem statement is rooted in the need to improve the wear resistance of LDPE, particularly in applications where traditional lubrication methods may be less effective or environmentally undesirable. This concept is supported by several studies, including [32, 33], which highlight the challenges of wear in polymer matrices and advocate for the incorporation of solid lubricants to mitigate these issues. Our work builds upon this existing body of research by exploring the unique properties of biochar as a solid lubricating filler and its compatibility with LDPE.

Therefore, the objective of this research is to investigate the possibility of using environmentally friendly biochar as a low-cost solid lubricant filler for LDPE-sustainable biocomposites. The aim is to evaluate the impact of biochar inclusions on the mechanical, thermal, and tribological properties of the resulting biocomposites, as well as their processability and reshaping properties. By exploring these aspects, this study is aimed at providing valuable insights into the potential applications of biochar in the polymer sector and contributing to the development of sustainable materials. The novelty of this work lies in the specific focus on integrating biochar as a reinforcing ingredient in LDPE composites, which has not been extensively explored in previous research. By filling this research gap, this study seeks to advance the understanding of biochar’s potential as a sustainable filler material and its impact on the properties of LDPE-based biocomposites. The outcomes of this investigation will not only contribute to the scientific knowledge in this field but also have practical implications for the development of more environmentally friendly and high-performance polymer materials.

2. Experimental Procedure

2.1. Materials. The base polymeric matrix used in the study was low-density polyethylene (LDPE) from TASNEE LD, Saudi Arabia. The specific grade selected was 0725 N, which has a melt flow index of 14.75 g/10 min. Biochar was produced in our laboratory through another project based on the production of biofuels from agricultural waste.

2.2. Sample Preparation. Biochar is prepared through the burning of agricultural waste at 600°C in an atmosphere of inert nitrogen gas. This process takes around 4 hours to generate biooil before cooling down the furnace, and the resulting biochar is ground to a fine powder in order to use it as a bio filler into LDPE matrix.

The LDPE was mixed with biochar powder at various weight percentages of 2.5, 5, 7.5, and 10 wt% at room temperature using a 300 rpm mixer for 10 minutes. This was done to ensure that the biochar powders were evenly distributed around the LDPE pellets. The premixing process is aimed at achieving a homogeneous mixture of the LDPE and biochar powders. A twin-screw extruder manufactured by Lab Tech Engineering Company in Thailand (Model LHFD1-130718) was used to extrude the mixtures, as illustrated in Figure 1. The extruder had nine heating zones that started at 150°C and gradually increased up to 225°C at the extruder nozzle tip. In order to achieve a consistent composition, the screw speed for the extrusion process was optimized to run at 40 rpm for two consecutive shots. This adjustment resulted in a highly uniform composition with homogeneous dispersed biochar in the LDPE matrix. After the extrusion process, the composite wire is pulled by a set
of traction rollers and moves towards a water bath for immediate cooling. This ensures that the wire is solidified in its desired shape and can maintain its structural integrity. The process of cooling the composite wire is essential to ensure that it can be used for its intended purpose without deformation or damage. Once the wire has cooled down, it passes through a pelletizer equipped with the same extruder to cut it into small and uniform pellets.

The last step in the production process involves feeding the prepared pellets into an injection molding machine, manufactured by Chen Hsong company in Hong Kong (Model JM138-Ai-SVP/2). This process is used to create the final nanocomposite samples required for testing and characterization. The injection nozzle has four different barrel temperature zones, started by 180°C and ended by 220°C at the tip of the nozzle, each carefully controlled to ensure consistency in the final product shown in Figure 2. Once the injection molding process is complete, the samples can be further tested and analyzed for their properties and performance.

2.3. Characterization and Testing. The biochar morphology was investigated using FE-SEM, and the chemical composition of the composite samples was analyzed using EDS attached to the same SEM microscope. The FE-SEM model used was JEOL JSM-7600F from Tokyo, Japan, with Oxford EDS accessory on it. These methods allowed for a detailed analysis of the filler material, providing valuable information for understanding the characteristics and possible applications of this material.

The NKT-N9 laser particle size analyzer was used to characterize the particle size distribution of biofillers. ImageJ was used for analyzing the SEM micrographs. ImageJ is a free program that was used to analyze the pore size distribution. The sample’s MFI was determined using the ST-400A melt flow index tester from China using the ASTM standard D1238 [34], at a temperature of 250°C and a weight of 5 kg. The MFI is an essential indicator of the viscosity of a polymer and is used to assess its processability. The MFI measurement gives useful information on thermoplastic flow characteristics and may be used for verifying the material compatibility for particular applications.

Thermogravimetric analysis (TGA) was done on LDPE composites utilizing a TA Instrument TGA-Q600 equipment. Thermal analysis was performed in a nitrogen atmosphere on the samples in an alumina pan. The temperature range was 25 to 600 degrees Celsius, with a heating rate of 10 degrees Celsius per minute.

The Shore-D hardness of the composite was determined using the durometer and following ASTMD2240-15 standard [35]. The average reading was calculated from five measurements, which were recorded after two seconds of contact with the sample surface to ensure accuracy. Flexural tests were conducted on the composite samples in accordance with ASTM D790 standard [36] using a 3385H INSTRON testing machine of 150 kN load capacity. The crosshead was moved at a speed of 2 mm/min, and a three-point mechanism was set with a support span of 50 mm. Each composition was tested using five samples. Five test replicates of the tensile test were performed in accordance with ASTM D638-14 standard [37] using the same above-mentioned INSTRON tensile testing machine at a crosshead speed of 2 mm/min. Type I samples with dimensions shown in Figure 2 were utilized for the test.

Figure 1: Schematic of the biocomposites sample preparation steps.
The Bruker tribometer (UNMT-1 L) with a ball-on-desk setup was used to perform the tribology test. The rotating desk, which is our composite sample, had a speed of 100 rpm, while the ball was made of chrome steel (E52100, HRC 63) and had a diameter of 10 mm. The composite samples were tested at room temperature under dry sliding conditions according to the procedure of ASTM G99-95 standard [38] to evaluate the tribological properties of the samples. The wear performance and coefficient of friction of the LDPE/biochar composites were evaluated during the wear test with an applied load of 50 N for 30-minute time intervals. The results of the wear test will be crucial in establishing the fabricated composites’ reliability and durability.

3. Results and Discussion

3.1. Biochar Characterization. Figures 3(a) and 3(b) show scanning electron microscopy (SEM) micrographs of the produced biochar filler at different magnifications, (c) EDS analysis showing the chemical composition of the biochar, and (d) ImageJ analysis for the biochar porosity fraction.
biochar produced for strengthening the low-density polyethylene (LDPE) matrix. The images, which were taken at various magnifications, show that the granulated biochar has a significant degree of porosity. A conclusion that was confirmed by ImageJ analysis reveals that the median size of the biochar particles has been identified to be in the range of 20 and 80 μm, while the average pore size was determined to be between 2 and 12 micrometers. As shown in Figure 3(d), the overall porosity percentage is around 64%.

The observed porosity in the biochar structure helps to create channels throughout the filler, increasing the overall surface area. As a result, the contact surfaces between the matrix and the filler grow proportionally. Such an increase has a major influence on the material’s mechanical characteristics.

3.1.1. Particle Size Distribution. The biochar fine powder underwent particle size distribution analysis using an NKT-N9 laser particle size analyzer from China. This test, conducted at room temperature with water as a dispersant, yielded the results depicted in Figure 4. The graph indicates a particle size range between 10 and 100 micrometers. The software estimated the D10, D50, and D90 values to be 20.24 μm, 42.91 μm, and 79.08 μm, respectively.

3.2. Composite Characterization

3.2.1. Melting Flow Index (MFI). At 250°C and 5 kg, the MFI of LDPE was determined to be 14.81 g/10 min. Figure 5 clearly shows that adding carbon-structured types such as biochar to LDPE resulted in a drop in MFI, which is
consistent with prior research [39, 40]. The low MFI of LDPE with biochar is related to the fact that carbon additives have a high molecular weight and a widely scattered structure. This implies that they can interact with the LDPE chains, reducing mobility and causing a fall in flow rate and an increase in viscosity. Furthermore, the high thermal stability of carbon additions might contribute to a reduction in MFI since they need more energy to melt and hence are more resistant to flow [41, 42].

3.2.2. Thermogravimetric Analysis (TGA). Thermogravimetric analysis (TGA) experiments were conducted to evaluate the thermal stability of the biochar-reinforced LDPE composites and compare them to the unreinforced neat LDPE. Figure 6 presents the TGA curves for the neat LDPE and LDPE/biochar composites. Table 1 summarizes the key parameters, including the initial degradation temperature \( T_{5\%} \), maximum thermal degradation temperature \( T_{\text{max}} \), final degradation temperature \( T_f \), and weight of carbon residue at 600°C. All samples displayed a single degradation process.

As the biochar content increased, the \( T_{5\%} \), \( T_{\text{max}} \), \( T_f \), and carbon residue values for the LDPE composites also increased to varying extents. These thermal data indicate that the incorporation of biochar enhances the thermal stability of LDPE. This improvement can be attributed to the biochar’s ability to reduce chain motion and thermal vibration, acting as an effective thermal stabilizer and preventing the complete thermal deterioration of LDPE. Similar findings have been reported in other studies that investigated the reinforcement of polymer composites with carbon structure additions [43, 44].

3.3. Mechanical Testing

3.3.1. Shore-D Hardness Test. Figure 7 depicts the results for determining the hardness values of various produced composites using the Shore-D type. As the biochar content
When 10% biochar was used in the LDPE matrix, the highest enhancement of 24.3% was obtained. The improvement in hardness associated with higher biochar concentration is due to an increase in biochar surface area and pore volume [45]. This increases the number of contact sites between biochar and the LDPE matrix, which improves the interfacial interaction and the mechanical characteristics of the composite material [46].

3.3.2. Tensile and Flexural Test. Tensile test was conducted on the fabricated composite samples to examine the variations in key mechanical properties, including ultimate tensile strength (UTS), yield strength (YS), Young’s modulus (E), and failure strain (FS). The stress/strain curves of the biochar/LDPE composites, with different biochar contents, are visually represented in Figure 8. Additionally, Figures 9 and 10 and Table 2 provide a summary of the ultimate tensile strength, yield strength, Young’s modulus, and failure strain of the composites. It is worth noting that the failure strain (FS) refers to the point at which the tensile stress experiences a sharp decline.

The results indicate a notable enhancement in Young’s modulus (18%), yield strength (32.67%), and tensile strength (1.9%) when the biochar loading reaches 10 wt%, suggesting an effective reinforcement of the biochar. However, an increase in biochar loading leads to a rapid decrease in the failure strain (FS) reaching 49.5%, which is a common behavior observed in composites. This decrease is believed to be attributed to premature failure occurring at the biochar aggregates. Notably, Figure 2 demonstrates a moderate jump in Young’s modulus when the biochar content transitions from 7.5 to 10 wt%. This can be attributed to the structural changes within the composites as a continuous carbon network forms throughout the matrix with a biochar content of 10 wt% [47].
Upon examination, a distinct correlation is discernible between the proportion of biochar content in the composite and the ultimate tensile strength (UTS). The peak UTS value, recorded at 12.69 MPa, was achieved when the biochar loading was at 10 wt%. This enhancement in tensile strength could potentially be ascribed to the robust interfacial bonding that occurs between the biochar and the LDPE matrix. This strong bond at the interface facilitates efficient stress transfer, thereby augmenting the overall mechanical resilience of the composite material.

Figure 9 shows a graph of the determined flexural strength of the composites. The figure clearly shows that as the biochar content increases, the flexural strength also increases, reaching a peak at 10 wt% biochar loading.

Figure 10: Young’s modulus (E) and failure strain (FS) for neat LDPE and LDPE/biochar composites.

Table 2: Tensile parameters for the pure LDPE and its composites with biochar.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ultimate tensile strength (UTS) (MPa)</th>
<th>Yield strength (YS) (MPa)</th>
<th>Failure strain (FS) (mm/mm)</th>
<th>Young’s modulus (E) (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE 0</td>
<td>12.45 ± 0.03</td>
<td>6.95 ± 0.2</td>
<td>1.07 ± 0.02</td>
<td>117.22 ± 1.5</td>
</tr>
<tr>
<td>LDPE 2.5</td>
<td>12.49 ± 0.05</td>
<td>7.51 ± 0.3</td>
<td>0.98 ± 0.02</td>
<td>121.32 ± 2.7</td>
</tr>
<tr>
<td>LDPE 5</td>
<td>12.58 ± 0.03</td>
<td>8.11 ± 0.2</td>
<td>0.83 ± 0.02</td>
<td>126.67 ± 1.3</td>
</tr>
<tr>
<td>LDPE 7.5</td>
<td>12.6 ± 0.02</td>
<td>8.52 ± 0.4</td>
<td>0.64 ± 0.02</td>
<td>127.71 ± 2.0</td>
</tr>
<tr>
<td>LDPE 10</td>
<td>12.69 ± 0.04</td>
<td>9.22 ± 0.5</td>
<td>0.54 ± 0.02</td>
<td>138.36 ± 2.2</td>
</tr>
</tbody>
</table>
the biochar concentration in the LDPE matrix increases, correspondingly rises the flexural strength. This increase in strength might be due to the incorporation of a significant amount of hard and inflexible carbon-based components. These carbon additions improve the composite’s resistance to deformation, resulting in higher flexural strength values. When LDPE was mixed with 10% biochar, the most notable benefit was a 47% increase in flexural load at a strain of 0.07 mm/mm.

3.4. Tribological Performance (Wear Test). Biochar filler can improve the wear behavior of LDPE composite as a solid lubricant. The addition of biochar filler reduces the friction between the composite’s surface and the counter-body, resulting in decreased wear. The filler’s solid lubrication properties substantially enhance the composite’s wear resistance and durability.

To investigate the effects of incorporating different weight fractions of biochar on the tribological properties of
LDPE composites, a series of frictional tests were conducted. The composite samples were subjected to friction against a stainless-steel ball, with the tests consistently performed at a rotational speed of 100 rpm. The applied loads were adjusted to 50 N. During the tests, the average friction coefficient and wear mass loss were carefully measured. The results were graphically represented in Figure 12, which illustrates the fluctuations in the friction coefficient in response to changes in the biochar content. The steady-state coefficients of friction calculated based on the average values as well as the weight loss are given as a function of the biochar content in Figure 13. Notably, the inclusion of biochar in the LDPE composite samples led to a reduction in the friction coefficient and wear behavior compared to pure LDPE, which is fully consistence with other previous studies [32, 33, 48].

The findings revealed that the LDPE10 composite exhibited the lowest coefficient of friction, measured at 0.136. This value was 56.3% lower than the coefficient of friction observed in pure LDPE (0.311) under a normal load of 50 N. Table 3 presents the wear parameters, where the decrease in the coefficient of friction can be attributed to the formation of a carbon debris layer resulting from the presence of biochar. This layer acts as a protective barrier, reducing the abrasive wear between the two bodies in contact. The formation of the carbon debris layer occurs due to the cleavage of carbon within the biochar during loading. The weak van der Waals bonds between the layers of biochar contribute to this phenomenon. As the concentration of biochar in the composite increases, more cleavage occurs, leading to a decrease in the coefficient of friction. This suggests that the incorporation of biochar can effectively enhance

<table>
<thead>
<tr>
<th>Sample</th>
<th>COF (μ)</th>
<th>Wear amount (mg)</th>
<th>Mass loss (kg)</th>
<th>Wear resistance (kg⁻¹)</th>
<th>Wear rate (kg/S)</th>
<th>Specific wear rate (kg/N S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE 0</td>
<td>0.311</td>
<td>0.0042</td>
<td>4200</td>
<td>0.000238</td>
<td>2.33</td>
<td>0.0467</td>
</tr>
<tr>
<td>LDPE 2.5</td>
<td>0.292</td>
<td>0.0035</td>
<td>3500</td>
<td>0.000286</td>
<td>1.94</td>
<td>0.0389</td>
</tr>
<tr>
<td>LDPE 5</td>
<td>0.235</td>
<td>0.0032</td>
<td>3200</td>
<td>0.000313</td>
<td>1.78</td>
<td>0.0356</td>
</tr>
<tr>
<td>LDPE 7.5</td>
<td>0.171</td>
<td>0.0029</td>
<td>2900</td>
<td>0.000345</td>
<td>1.61</td>
<td>0.0322</td>
</tr>
<tr>
<td>LDPE 10</td>
<td>0.136</td>
<td>0.0027</td>
<td>2700</td>
<td>0.00037</td>
<td>1.50</td>
<td>0.0300</td>
</tr>
</tbody>
</table>

Figure 13: Changes in weight loss for neat LDPE and LDPE/biochar composites under 50 N applied load and 30-minute time intervals.

Figure 14: SEM images of the (a) pure LDPE and (b) biochar/LDPE 10 nanocomposite worn surfaces.
the tribological properties of LDPE composites by reducing friction and wear.

To delve deeper into the analysis of the worn surfaces, we conducted SEM imaging on both the pure LDPE and higher biochar percent concentration samples, as depicted in Figure 14. Upon examination, it is evident that the worn surface of the pure LDPE sample (LDPE 0) has suffered significant damage, displaying areas of plastic deformation and plowing. In stark contrast, the SEM images reveal that the surfaces of the nanocomposite sample (LDPE 10) exhibit considerably less damage compared to the pure LDPE sample.

This observation leads us to conclude that the incorporation of biochar filler has contributed to the enhancement of strength and resistance in the LDPE nanocomposites. The worn surface of the LDPE-10 sample showcases a remarkably smooth and intact appearance, suggesting that this particular composition of biochar filler represents the optimal choice when used in conjunction with LDPE. By shedding light on the contrasting states of the worn surfaces, these findings highlight the positive impact of the biochar filler in fortifying the structural integrity of the LDPE nanocomposites.

4. Conclusions

Biochar was utilized as a sustainable and cost-effective reinforcement in the LDPE matrix, achieving uniform blending through a twin-screw extruder and successful composite production via injection molding. Rather than reiterating procedural details, we highlight the novel findings suggested by our experimental results. The incorporation of biochar improved thermal stability by minimizing chain motion and thermal vibration, serving as a noteworthy thermal stabilizer. Biochar addition reduced MFI, attributed to the high molecular weight and dispersed structure of carbon additives, interacting with LDPE chains and increasing viscosity. Enhanced hardness, peaking at a 24.3% increase with 10 wt% biochar, was observed due to the higher modulus of the carbon filler. Tensile testing revealed significant improvements in Young’s modulus (18%), yield strength (32.67%), and tensile strength (1.9%) with 10 wt% biochar, but a subsequent increase led to a rapid decrease in failure strain (49.5%). Biochar emerged as a promising solid lubricant, showcasing improved wear resistance and durability in polymer composites, with the LDPE10 composite exhibiting the most notable reduction in friction coefficient—56.3% lower than pure LDPE. This study provides a comprehensive overview of the beneficial impacts of biochar reinforcement on LDPE composites, emphasizing thermal stability, melt flow modification, hardness improvement, tensile performance optimization, and the promising role of biochar as a solid lubricant for wear resistance.

Data Availability

The data that supports the findings of this study is available from the corresponding author upon reasonable request.

Additional Points

Highlights. (i) Fabrication of LDPE biocomposites reinforced by ecofriendly biochar. (ii) Ecofriendly biocomposites achieved high-performance thermal and mechanical properties. (iii) Biochar successfully utilized as a solid lubricating filler for enhancing tribological behavior.

Conflicts of Interest

The authors declare no conflict of interest.

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