Mechanical property analysis of biochar derived from cashew nutshell waste reinforced polymer matrix

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Abstract
Disposal of organic wastes with no reduction in intensity produces greenhouse gas, which affects the environment and its climatic conditions. Because of the increasing urge to save the environment and to add value for the waste, these can be converted into a value-added product. The development of biochar-based polymer composites from such wastes could be an effective and efficient one for various applications. This work focuses on new development of composite reinforced with biochar, prepared from cashew nutshell waste (CNSL) by the pyrolysis process. The CNSL waste is closely packed in an airtight container and heated at the temperature of 500°C for 1 h in a stir casting furnace. This CNSL biochar is used as reinforcement in unsaturated polyester resin for composite fabrication. The composites are prepared by the solution dispersion method at different weight percentages of 5, 10, and 15. The prepared specimens are subjected to tensile flexural and impact strength studies. Compared to unfilled composite 10% biochar filled composite shows maximum tensile, flexural, impact and hardness strength and their improvement percentages are 21, 41 & 37 respectively. Interestingly, the maximum flexural strength is noticed at 15% filled composites with a 40% improvement in strength.

1. Introduction

The utilization of naturally available materials in various applications reduces the product cost and is resourceful to the farmers. Researchers are experimenting to find new material with specific properties that are harmless to humans and the environment. There are few reports on the development of composite by recycling agricultural waste [1, 2]. The disposal of a huge quantity of organic wastes produces greenhouse gases, and these gases affect climatic conditions [3]. This organic waste can be utilized as a reinforcement in polymer composites by converting it into a new product called biochar, and recently a few studies also have been reported [4–8]. Biochar is generally used for soil amendment in many countries. Incorporating biochar as a filler in polymers is recently been increasing, which can be viewed as one of the sustainable approaches in producing value-added products from Agro-waste. Improvement in mechanical and dielectric properties in rice husk biochar polyester composite was reported by Richard et al [9]. Strong interaction between high-density polyethylene and the rice husk biochar was observed by Zhang et al [10] in their study on rice husk high-density polyethylene composites. Sajjad Ahmad reported that the addition of micron-sized bamboo carbon particle improves the flexural strength and toughness of self-consolidating cement composite [11]. Mechanical, electrical, thermal and rheological behavior of polypropylene filled with biochar derived from date palm seed was investigated by Poulouse et al [12] and reported a significant improvement in the above properties. Good improvement in the mechanical properties such as ultimate tensile strength, strain at break was observed because of the addition of 2 to 4wt percentage 10 μm size heat-treated biochar particle prepared from maple wood. Homogeneous dispersion of biochar particle was cited as the main reason for this improvement, and uniform distribution of the particle was observed at the sub-micro static level which arrests the crack propagation. Particles pulled out the good matrix,
and filler interaction was also reported from the SEM [13]. Biochar made from oil palm empty fruit bunch at a pyrolysis temperature of 700 °C in the presence of nitrogen was the reinforcement in the PP matrix. Effect of addition of 10 to 40% wt EFB biochar on thermal and mechanical properties were studied, in which MAAP was the coupling agent and a constant 20 wt% of ethylene-vinyl acetate was a modifier. A little reduction in tensile modulus and heat transfer, improvement in impact properties was reported by Ketabchi, et al [14].

Incorporation of softwood biochar prepared by slow pyrolysis process in epoxy sisal (chemical treated) fiber composite improves the tensile (5 wt%), flexural (10 wt%) and impact (15 wt%) strength [13].

In today’s life, the cashew nut is used by food industries for making products [15]. The cashew nut consists of moisture, protein, fat, carbohydrates, fiber, minerals, phosphorous, calcium and iron. The cashew nutshell is mounted around the seed with 55%–65% wt [16]. Cashew nutshell has also been used to produce cashew oil as alternating fuel for engines [17, 18]. Some research has been undergone using this cashew nutshell oil which can be as biodiesel for alternating fossil fuels [19]. In Yang et al [20] used anaerobic all digestion method to produce biochar from cashew nutshell and it is used in various fields as paint coatings, bio-resin, chemical resistance, chemical derivatives, and adhesives.

Besides these, in the present work effort has been taken to convert CNSL into biochar also to manufacture composite using cashew nutshell biochar as reinforcement with varying volume fraction 5, 10 & 15% and to study the mechanical properties. Biochar reinforcement could improve the composite specific modulus strength, are biodegradable easy to process at a low cost. The main aim of this research is to develop a composite material suitable for commercial application building. The prepared samples were tested to know the tensile, impact, flexural and hardness performance of the composites.

2. Materials and methods

Polyester resin is used as a matrix that is purchased from Vasavibala resin PVT limited Chennai. Cashew nutshell is collected from the local market, figure 1(a) shows the CNSL used. The collected waste is heated in a stir casting furnace at two times treated, such as (1 h) and (3 h). The Cashew nutshell waste is filled in an airtight metal container and it is placed in the furnace at a temperature of 500°C. Then, the obtained biochar is crushed by using the ball milling machine up to five hours to get uniform sized biochar particles, as shown in figure 1(b).
Initially, two 5mm thick 30 × 30cm square glass plates were taken with wax coated for the easy removal of the cast plate. A 3mm thick 2 cm width inner ring (Rubber) is placed between the two glass plates and the plates are tightened on three sides to arrest the resin leakage which forms the mould. CNSL biochar is then added different weight percentages such as (5, 10 and 15) weight into one polyester resin. Then, the mixture is mixed manually to get a better dispersion of biochar with the matrix. Then the accelerator to the catalyst was added to initiate the curing process. The mixture is then poured gently into the glass mould which is kept at an angle 45° for easy flow of the mixture and to escape entrapped air in the mould. Much care is taken to avoid air bubble formation. It is left to cure for three hours to attain the final specimen formation of ASTM standard with a 3mm thickness. Once the curing is over, the cured composite is removed from the glass mould. The fabricated CNSL biochar filled polyester composite is shown in figure 1(c). The specimens are cut as per the ASTM standard to carry out mechanical testing.

2.1. Mechanical testing
The hardness test is performed using the shore-Durometer to determine the hardness properties of the CNSL biochar composite plate. For each plate, 10 different measurements were taken and the average value is reported. The impact test is carried out to study the toughness of materials. The absorbed energy is the measure of the given material toughness. It is used to determine whether the material is brittle or ductile. The prepared specimens are cut as per ASTM standard to perform the mechanical testing is as follows: Tensile strength ASTM D3039 of dimension 200 × 20 × 3 mm, Flexural strength ASTM D790 of dimension 127 × 13 × 3 mm and impact strength ASTM D256 of dimension 65 × 13 × 3mm. The samples are cut from the plate as per the size that is shown in Figure 2.

2.2. Physical characterization
The x-ray diffraction instrument is used to identify the crystal behaviour of the prepared cashew nutshell char material. This study is to measure the values between the diffraction angle and counts for 10 to 80, 100 to 800 ranges by using LYNXEYE software. The prepared CNSL biochar was placed on a sample holder at room temperature and the x-rays are generated from the Cu cathode, and the results are obtained. Fourier transform infrared method is used to identify the functional groups in CNSL biochar. By using the IRTRACKER-100 instrument, which generates the spectral wavelength between 500–4000 cm⁻¹. A scanning electron microscope instrument was used to determine the morphological studies on cashew char prepared composites. The SEM images are taken by secondary electron mode at accelerating voltage of 2.0 kV. X-Ray Fluorescence analyser assisted the presence of elements in both times treated CNSL biochar.

3. Result and discussion

3.1. XRD analysis of biochar
The different time variation of the produced CNSL biochar intensity is observed, and their presented intensity and angles are shown in figure 3. The maximum peak is observed for (3 h treated) biochar (2θ – 23°) when
compared to (1 h treated) biochar the peak observed ($2\theta - 21^\circ$). The shifted angle expressed in figure 3 mainly consists of the amorphous structure of CNSL biochar. Increasing time factors may be attributed to the reduction of the amorphous phase and to improve the crystallinity nature of biochar content. Similar results are observed in which the angle change effect lead to enhance the amorphous nature is reported [21]. The peak height increased at (3 h treated) biochar is identified compared to (1 h treated) biochar, which shows the enhancement of crystallinity nature. The crystallinity value calculated on (1 h treated biochar) was 26.4% and the (3 h treated) biochar increased up to 28.4%. It is concluded that the increase of time may attribute to the improvement of the crystallinity structure of CNSL biochar. Also, this behaviour may be the reason for the improvement of other properties of CNSL biochar.

3.2. FTIR spectra functional group studies
FTIR spectra were recorded using Shimadzu IR Tracer-100 with pressed KBr pellets, in the range of 4000–500 cm$^{-1}$. FTIR spectra of the title compounds are presented in figure 4. The OH stretching of the water molecule is observed at 3348 cm$^{-1}$ for the prepared biochar. The presence of O–H group due to the absorbance of moisture present in the atmosphere. The stretching frequencies of the aromatic C=C and aromatic C–H groups presented at 2816 cm$^{-1}$ and 2365 cm$^{-1}$, respectively [22]. With a broad absorption band occur at 3100 cm$^{-1}$, which indicates in the formation of amine group and the presence of nitrogen component is confirmed through the
peak 1574 cm$^{-1}$ and 1610 cm$^{-1}$ for (3 h treated) and 1 h treated respectively. In addition to the corresponding C–H bending vibration of the compound presented at 1440–1415 cm$^{-1}$ [23]. The N–H stretching vibrations of amine based compound is usually observed in the region 3700–3100 cm$^{-1}$. With a broad absorption band occur at 3615 cm$^{-1}$, which indicates in the formation of a N–H bond.

3.3. XRF analysis of prepared CNSL biochar
The x-ray fluorescence analysis is carried out for both (1 h treated) and (3 h treated) of CNSL biochar and the obtained results are shown in figures 5 and 6. From, XRF study it confirms the presence of Na, K and Ca elements for (1 h treated) biochar. Although the (3 h treated) biochar reveals that the presence of elements such as Na, K, Fe and Co.

3.4. Tensile test
Tensile tests are performed as per the ASTM standard on the universal testing machine with a crosshead speed of 2.5 mm min$^{-1}$. Five samples are tested in each case and its average value is presented. The tensile strength properties of preparing (1 h treated) and (3 h treated) CNSL biochar reveal that 3-h biochar composites have superior mechanical properties. Both times varied biochar composites are compared with the neat polyester matrix as shown in figure 7. The maximum value of tensile strength is observed for (3 h treated) 10% biochar composites and its value is 32MPa which is 41% enhancement on comparing with neat resin plate. The addition of 5% biochar also leads to the enhancement of tensile strength. Composite filled with 5% biochar showed a 16%
increase in strength compared with neat polyester. Non-uniform particle distribution and little voids are observed in the 5 wt% sample. Maximum tensile strength is observed for 10 wt% filled composites. Furthermore, the addition of biochar leads to a drop in their tensile strength because of the formation of clusters and agglomeration \cite{24}. The improvement of crystallinity behaviour may attribute to enhance the (3 h treated) biochar compared to (1 h treated) biochar. From the inclusion of biochar reinforced polymer composites, the minimum tensile strength was found at 15\% 1 h treated biochar. Generally, particles filled composites reinforced with particular optimum percentages show a drop in the mechanical properties because of the formation of agglomeration. In this present research also, some voids are present because of atmosphere air occupancy. Also, the more addition of biochar does not give better dispersion which forms some groups which in term creates weak tensile strength.

3.5. Flexural test
The flexural test has been carried out to observe the capability of the prepared polymer composites to withstand the bending load. ASTM standard size samples are cut from the plate and subjected to a three-point bending test in a universal testing machine with a crosshead speed of 2.5 mm min\(^{-1}\). Five samples are tested in each case and the average value is taken for discussion. The flexural strength of the various wt\% of the biochar filled composites is shown in figure 8. The addition of biochar into the polymer matrix, enhance the flexural properties. As the biochar particle content increases, the flexural strength also increases. Inclusion of 5wt\% (1 h treated) biochar leads to the enhancement of the flexural strength, which is about 15\% higher than the polyester. In the same manner, compared with (1 h treated) biochar, (3 h treated) biochar revealed on the enhancement of flexural strength at 4\% wt. Adding of biochar 10 wt\% enhanced the strength by 12\%. The flexural strength is found to be varying with particle content, particle size and distribution factors which also affect the properties \cite{9}.On analysing the flexural strength of the biochar composites it is identified that the maximum flexural strength is found to be for CNSL for (3 h treated) 15wt\% biochar plate which reveals 40\% of improvement compared with pure polyester. The inclusion of high percentage biochar particles may attribute to create the resistance against bending strength due to the uniform distribution with very fewer voids. The resin infiltrates into the biochar because of its porous nature, which provides very high bonding between the matrixes. Initial addition of biochar 5\% (1 h treated) biochar composites exhibited improvement of flexural strength compared with neat polyester. Initial weight percentage addition of biochar 5\% (1 h treated) biochar composites reached the minimum flexural strength. Particle distribution plays an important role in creating the failure of composites. However, incorporating biochar above 5\% both times treated composites simultaneously increased flexural strength. This high strength may be attributed because of the minimum addition of biochar content, which creates better adhesion between the polymer matrix.
3.6. Impact test

The impact test is performed on the unnotched sample of ASTM D256 size in the impact tester machine. Three samples were tested in each case, and the average value is presented. The impact strength of various percentage filled CNSL biochar composite is shown in figure 9. Incorporation of CNSL biochar leads to the improvement of the impact strength of the polyester composites. An increase in impact strength with the increase in the amount of reinforcement in polymer composites is observed. Richard et al [9] reported a similar trend of the increase in impact strength because of the addition of 0.5 wt% to 2.5 wt% of rice husk biochar in the polyester matrix and also it varies with particle size. Inclusion of 5 wt% of biochar leads to the enhancement of the impact strength compared to neat polyester by about 5 wt%, 10 wt% inclusion enhanced the impact strength by 20%. The maximum impact strength is observed for (3 h treated) 10 wt% of CNSL biochar composites, which shows a 37% improvement when compared to neat polyester. Incorporation of biochar in polymer composites increases the impact strength because of the absorption of more energy with high resistance to the crack propagations and also because of its porous nature. Biochar provides good adhesion and bonding in the polyester matrix, which is also one of the reasons for the improvement of impact strength. The time variation of prepared (1 h treated) and (3 h treated) biochar expressed that the increases of time may lead to the enhancement of mechanical properties.

![Figure 8. Flexural strength values of various wt% of CNSL biochar composites.](image8)

![Figure 9. Impact strength values of various wt% of CNSL biochar composites.](image9)
Lower impact strength is observed for (1 h treated) 15% wt reinforced composites. Here, a large amount of biochar addition creates weak adhesion between matrix and reinforcement. The addition of more wt% leads to a decrease in the adhesion between the matrix and forms the cracks on suddenly applied force.

3.7. Hardness test
The hardness test is performed on biochar reinforced composites using shore-Durometer and their values are shown in figure 10. Ten samples are subjected to hardness study and their average values are reported. The addition of CNSL biochar as a filler significantly improves the hardness properties. The inclusion of CNSL biochar along with pure polyester increases the hardness by 21% wt. This is noted for 10% wt (3 h treated) CNSL biochar among all-composite combinations. Also, 5% wt addition shows a slight increase in hardness. This may be because of the good inter bonding between the polyester matrix and CNSL biochar which produces a crystalline structure. The high porosity of the biochar, the polymer infiltrate into the biochar which improves the integrity and resulted in high hardness [6].

3.8. Failure analysis on CNSL reinforced polyester composites
3.8.1. Tensile strength of fractured surfaces
The fracture surface morphology of the tensile tested specimen is shown in figure 11 (a). At 15% wt biochar composites, the formation of the void was found to be high, which is clear from the SEM image in figure 11(a). The failed surface at 3 h of 10% wt biochar composites was found to be smooth. Figure 11(b) confirms the uniform dispersion of biochar and good bonding between the filler and matrix. This becomes the main reason for uniform tensile stress distribution through the matrix even at high load gives good yielding. The biochar particle acts as a barrier for the micro-crack development under tensile load, but when the stress has been increased the matrix and filler could not sustain and failed. This trend is opposite in the 5% wt and 15% wt biochar filler composite, the fracture surface of the 5% biochar composite is also smooth. Figure 11(c) shows good dispersion of the particle, yet these composites are likely brittle and show low tensile strength. The waviness in the surface as seen in figure 11(d) for one hour 15% and three hours 15% confirms higher stress development in the matrix because of biochar particle reinforcement. The main reason for this is the uneven distribution of biochar particles.

3.8.2. Flexural strength of fractured surfaces
The presence of voids in the matrix shows the poor interfacial bonding between the filler and matrix, as shown in figure 12(a). This leads to poor flexural stress transfer with the matrix. The uneven distribution of filler is also noted in figure 12(b). These reasons are the main factors for low flexural strength. Since the interaction is poor, the matrix deforms more quickly with no restrictions under the bending load. This is evident through the striation structure in the matrix creating crack development, as shown in figure 12(c). The dispersion of biochar...
Figure 11. (a)–(d) Fractured surfaces on tensile strength of CNSL biochar composites.

Figure 12. (a)–(d) Fractured surfaces on flexural strength of CNSL biochar composites.
is poor in such a way forming groups and agglomeration in the polymer matrix and this is identified from figure 12(d). This creates weak bonding behaviour, which reduces flexural strength.

3.8.3. Impact strength of fractured surfaces
The impact tested specimen fracture morphology is shown in figure 13. The rougher surface in the sample figure 13(a) shows the poor distribution of the biochar particle. This developed a weaker bond in the matrix and resulted in quick failure at the impact load. The brittleness of the composite at low biochar addition is the main reason for the failure at low impact load which is evident through the matrix separation as shown in figure 13(b). On 10% wt composite owing to the addition of biochar the brittleness of the composite decreases and developed a semi ductile property, which is more prominent for the increased impact strength and tensile strength. However, at a low biochar composite, the composite failed because of brittle fracture, which is evident through the breakage of the matrix, as shown in figure 13(c). The poor bonding between the matrix and the biochar developed a poor impact stress distribution through the matrix this results in the development of micro-cracks as shown in figure 13(d).

4. Conclusion
Biochar is successfully prepared from CNSL through the pyrolysis process at varying times and it is utilized for polymer composite fabrication. From the analysis of biochar characteristics and the mechanical performance of biochar composites, the following results are found,

- The XRD pattern of biochar confirms the presence of carbon peaks. The 3 h treated biochar crystallinity behaviour is increased while increasing the processing time of the pyrolysis process.
- Among all combinations of biochar, only 10%wt (3 h treated) composites showed higher tensile, impact and hardness properties and its enhancement percentage compare with pure polyester are 41%, 37%, and 21% respectively. However, the maximum flexural strength is identified at 15% wt (3 h treated) biochar composites, and its improved strength is 40% compared with the neat polyester.
- Fractured specimen analysis through SEM images evident the poor matrix biochar interface, the presence of voids and cracks in the matrix.
• This study concluded that 10% (3 h treated) biochar filled composites suitable for construction applications such as container boxes, storage tanks, etc.

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