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Swelling, Thermal and Mechanical Characterizations of High-Density Polyethylene/ Recycled Biochar Composites

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Abstract: The application of recycled natural materials waste as biochar fillers in polymer composites can be observed as a sustainable approach. This article aims to study recycled biochar (R-BCH) improvements on the high-density polyethylene (HDPE) matrix properties. A series of composites was developed with a different loading varying from 0 to 10 wt.% of R-BCH, using a twin-screw extruder followed by compression molding. The results showed that the addition of 3-10% of R-BCH in pure HDPE led to an increase in the tensile strength, modulus of elasticity, and a decrease of elongation at break. Furthermore, the differential scanning calorimetry analysis (DSC) results showed that incorporating R-BCH into pure HDPE improved thermal properties because interfaces between R-BCH and pure HDPE caused decreased brittle behavior and enhanced the high crosslinking of pure HDPE.

Keywords: HDPE, Recycled Biochar, Tensile Strength, Thermal Properties.

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INTRODUCTION

A composite involves combining two or more materials and that are blended in each other without a solubilizing material. At least one type of natural filler is incorporated in the dispersed phase in the polymeric material to form a composite. The performance of natural filler in composite materials can be enhanced to achieve appropriate materials regarding durability, thus being more economical than synthetic fillers composites. In addition, these natural fillers provide composites' stiffness and strength and enhance superior chemical and mechanical properties (1-4). High-density polyethylene, medium density polyethylene, low-density polyethylene polymers are commonly utilized to produce flexible films and laminates for bags, rigid containers, pipe extrusion, and injection molding of various objects (5). The advantages of HDPE are characterized by high shrinkage, simple molding, and excellent melt strength (6-11). Biochar can be considered neutral carbon or a negative material that may play an essential role in industrial and construction applications. Biochar is the solid product found from biomass pyrolyses such as wood, agricultural wastes, and municipal wastes. It has consisted of stacked graphene sheets inside crystallites of turbostratic carbon with an amorphous compound (12). Through the thermal decomposition of biomass, biocarbon is a porous solid obtained. It is chemically stable under ambient conditions. The properties of biochar are based principally on the raw material and the pyrolysis temperature utilized in the production procedure. The thermal stability of the biochar obtained from the high pyrolysis temperature typically exceeds 350 °C. Besides, it can have functional groups on its surfaces, facilitating its connection with the polymer matrix (13). In recent decades, natural fillers reinforced polymer composites companies and research institutions made no effort to modify alternative bio natural fillers based on the raw material limitation. However, in recent years, there is a scope for the biochar's effective application in thermoplastic composites as a result of its porous structure, large surface area, high carbon loading, which could facilitate the physical bonding with the polymer matrix (14). For example, the impact strength of the polyester reinforced 2.5% w/w of biochar increased by 77.50%, while the constant dielectric rise by 7% compared with the virgin polyester (15). Another study showed that the electrical conductivity of polyvinyl alcohol (PVA) reinforced with 2 and 10% w/w of biochar exhibited values similar to carbon nanotube and graphene-filled PVA composites. On the other hand, the thermal stability, tensile, and storage moduli for PVA/biochar composites were enhanced with the addition of BC (16).

Previous studies exhibited that utilizing crop residues or natural wastes such as rice straw, sugar cane, flax, hemp, jute, wood chips, or tea residues to replace wood fibers enhanced notably mechanical and thermal properties of wood-plastic composites (WPCs) (17-19). For example, Wu et al. (20) prepared cotton stalk bark (CSB) reinforced polypropylene (PP), and their mechanical, thermal, and morphology properties were investigated. They observed that the flexural properties and tensile modulus of CSB reinforced PP composites were improved with the increasing loading of CSB. In contrast, the tensile strengths showed a negative correlation with the loading of CSB, which achieved 32.9 MPa when the CSB incorporated was 30%. Another study by Cholake et al. (21) investigated the waste macadamia sell impact on improving the mechanical characterizations of WPC panel. It was displayed that incorporating macadamia shell increased the comprehensive modulus 548 MPa for 75% compared to the PP matrix.

This paper applied the extrusion fabrication method to prepare bio composites HDPE with (RBCH) obtained by recycled wood chips pyrolysis. The thermal characterizations of RBCH/HDPE composites were studied to investigate the crystallization performance. In addition, the mechanical properties of RBCH/HDPE composites were presented and discussed to provide a theoretical basis for the application. In this regard, this study attempts to utilize local resources of wood chips converted to R-BCH to reinforce thermoplastic polymers. The R-BCH could have a promising future as a new reinforcement in polymer composites as a result of their low cost, low density, environmental friendliness, and great mechanical characterizations.

MATERIALS AND METHODS

Materials

R-BCH was collected from waste wood chips, cleaned, and dried. HDPE matrix with a density of 0.955 g/mL was used as a matrix and provided by Indian Chemical and Petrochemical Manufacture (CPMA).

Preparation of R-BCH

The wood waste was dried and then operated through a chipper that turns it into woodchips (20-40 mm). The woodchips were then converted through slow pyrolysis at a temperature range (450–550 °C), and the heating rate range was 0.1–1 °C/s into syngas to produce biochar. Figure 1 shows a schematic diagram for R-BCH preparation.

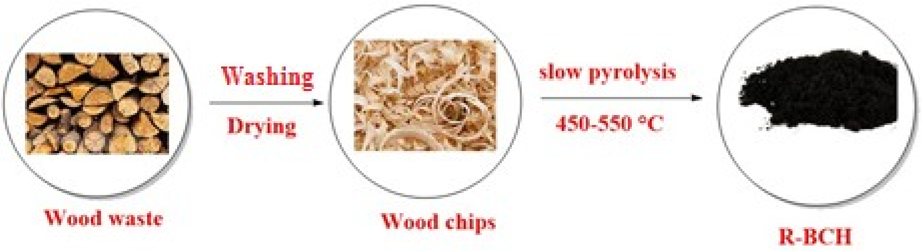

Figure 1: Schematic illustration of the Preparation of R-BCH.

Fabrication of HDPE Composite

Initially, the required amounts of HDPE and R-BCH were mixed thoroughly, utilizing a mixer to obtain a homogenous composite (the mixture speed was 50 rpm at mixing time six minutes). The mixture was then passed through a twin-screw extruder at a temperature of 180 °C and a screw speed of 10 rpm. Next, the extruded composites were taken out from the extruder and compressed in a Carver press at 140 °C for 30 min to obtain a sheet (15 x 15 cm^2) having a thickness of 1 mm. The amount of R-BCH powder added to the matrix varied from 0, 3, 7, and 10 wt%, respectively. Figure 2 exhibited the proposed scheme for R-BCH/HDPE composite.

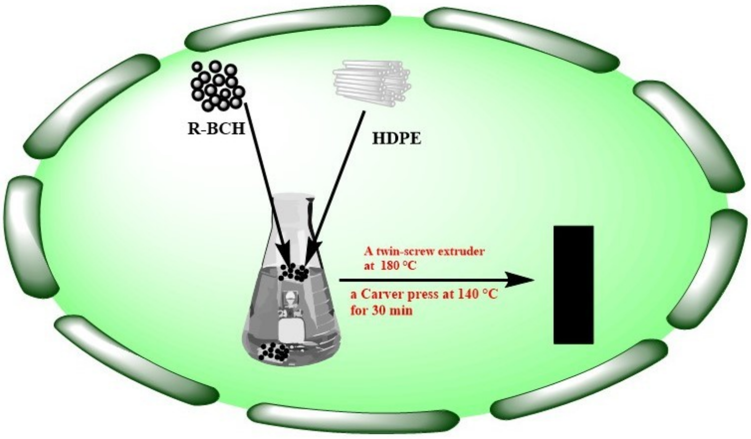

Figure 2: A scheme of HDPE/R-BCH composites preparation.

Swelling Ratio Test

To measure the swelling ratio (SR), dry HDPE composites (0.2±0.5 g) were immersed in 800 mL of distilled water solutions for 4 h at room temperature to achieve equilibrium. The swollen product was filtered through a 100-mesh screen to remove excess moisture and then weighed. Each specimen was significantly tested, and the average value was used. The capacity of water-absorbent was calculated utilizing the following Equation (1):

$$SR\% = \frac{(m_1 - m_0)}{m_0} \quad (1)$$

Where m_0 and m_1 are the mass of dried and swollen products, respectively.

Differential Scanning Calorimetry

The blends' characteristics of melting and crystallization were measured utilizing a machine type, a Mettler 820 DSC. The weight of samples was in a range of 5-10 mg. The first heating and second heating were done from 25 °C to 200 °C at 10 °C/min in a nitrogen atmosphere. The DSC thermograms provide details on the melting temperature (T_m), crystallization temperature (Tc), melting enthalpy heat (ΔH_m), and crystallization enthalpy heat (ΔHc). In addition, the crystallinity degrees (X_c) of the specimens were calculated using Equation 2.

$$\chi_c(\%) = \frac{\Delta H_m}{\Delta H_m^0} \quad (2)$$

Where ΔH°_m is the enthalpy heat of fusion of the fully crystalline HDPE, taken as 290 J/g (22-24). The ΔH_m, ΔH_c, and X_c values of HDPE and HDPE composites were normalized and accounted for based on the actual HDPE composites, as listed in Table 1.

Tensile Tests

Composite samples were tested utilizing an Instron tensile machine model type (Testometric, M500-50AT), UK, based on the standard of ASTM D 638. The crosshead speed was about 20 mm/min. Furthermore, three tests were replicated for each composite sample.

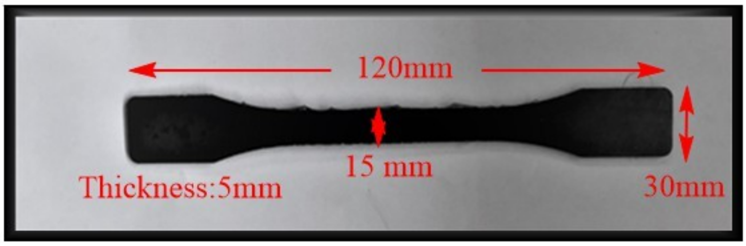

Figure 3: Tensile test simple with dimensions.

RESULTS and DISCUSSIONS

Swelling Analysis of HDPE Composites

The swelling ratio measurements against the loading of R-BCH composites are illustrated in Figure 4. The introduction of R-BCH into HDPE composites has shown a significant effect on the extrudate swelling ratio. It can be seen from Figure 1 that the swelling ratio of HDPE/R-BCH composites decreased with an increase in the R-BCH loading. The swelling ratio of 10% R-BCH/ HDPE composite was reduced by 64%, while the incorporation of 3% and 7% R-BCH in HDPE composites was decreased by 44% and 50%, respectively. The hypothesis produced concerns the ability of R-BCH in permitting further interactions of polymer molecules. An ease in the interaction of the molecules enhances the entanglement level and elastic property of HDPE melt, therefore affecting the deformation rate (in this case, referring to the extrudate swelling). Incorporating the highest loading (10% R-BCH) in the HDPE matrix showed a sharp decrease compared to other loadings of R-BCH (3% and 7%).

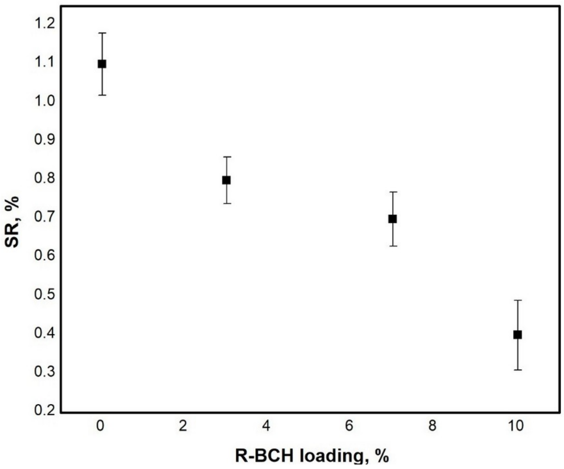

Figure 4*:* Effects of R-BCH loading on swelling ratio of HDPE composites.

Thermal Analysis (DSC) of HDPE Composites

The DSC curves (heating and cooling processes) at 10 °C/min of the HDPE and HDPE/R-BCH composites are illustrated in Figures 5 and 6. The relative factors, for example, crystallization temperature (T_c), melting temperature (T_m), crystallization enthalpy (ΔH_c), and melting enthalpy (ΔH_m) for HDPE/R-BCH composites, are summarized in Table 1. The DSC thermograms showed single peaks for the composites' heating and cooling scans (Figures 5 and 6). The T_m value of pure HDPE was 135 °C, while the T_m value of the R-BCH/HDPE composites increased with increasing the loading of R-BCH. The HDPE/10 wt. % R-BCH had the highest T_m, which was 141 °C (Table 1). Incorporating R-BCH in HDPE seemed to restrict the polymer chain's mobility, resulting in higher T_m. The addition of R-BCH to the HDPE matrix increased the melting peak temperature. Hence the crystallinity increases progressively with loadings of the R-BCH. As a result, they displayed a higher melting peak temperature and crystallinity. The reason may be that further lower cooling rates take place with the addition of R-BCH, which causes longer crystallization time, thus further ideal crystals. The ΔH_m is an important parameter since its magnitude is directly proportional to the polymer's overall level of crystallinity (X). The HDPE composite with higher R-BCH loading also showed a higher ΔH_m value when compared with those with lower R-BCH content. For the composite systems, it was observed that generally, the ΔH_m values of the composites increased with increasing R-BCH content. The ΔH_m of pure HDPE was 179.5 J/g and increased to 185 J/g at the highest loading of R-BCH. The results are listed in Table 1, which showed that the X values of these composites were slightly increased relative to that of pure HDPE (61%). Furthermore, the addition of 10% R-BCH in the HDPE matrix increased the X value up to 66%, as shown in Figure 7. Karagoz and Tuna (25) studied the impact of (various melt temperatures) on the thermal characterizations of the HDPE composite applied at different nozzle temperatures. They reported that the HDPE composite with the greatest nozzle temperature (200 °C) achieved a significant improvement in crystallinity compared to others (180 and 190 °C).

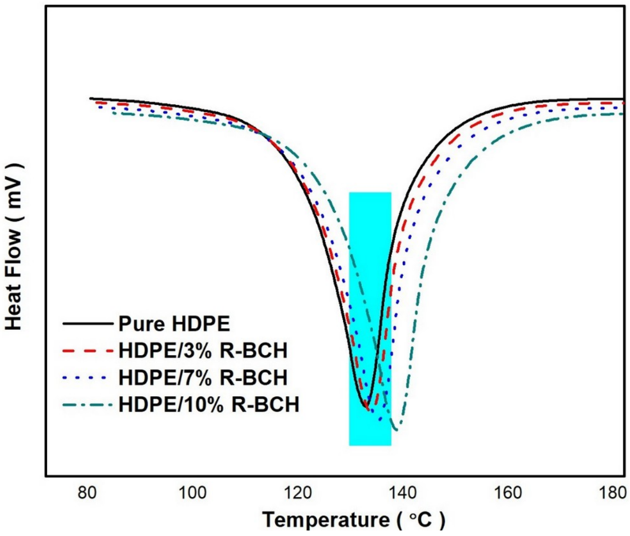

Figure 5: DSC thermograms (heating curves) of HDPE and HDPE/R-BCH composites.

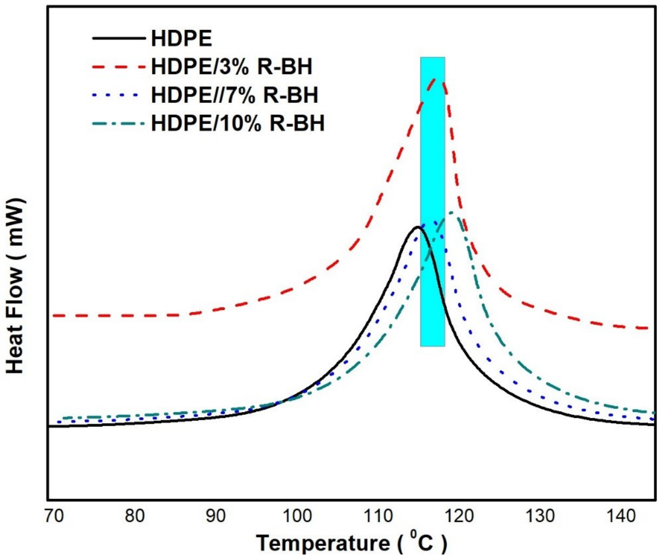

Figure 6: DSC thermograms (cooling curves) of HDPE and HDPE/R-BCH composites.

Table 1: DSC results of non-isothermal crystallization and melting of pure HDPE and HDPE composites.

Composites	T_c (°C)	T_m (°C)	ΔH_c (J/g)	ΔH_m (J/g)
Pure HDPE	115	135	184	179.5
HDPE/3% R-BCH	117	136	185	180.7
HDPE/7% R-BCH	118	138	188	182
HDPE/10% R-BCH	121	141	192	185

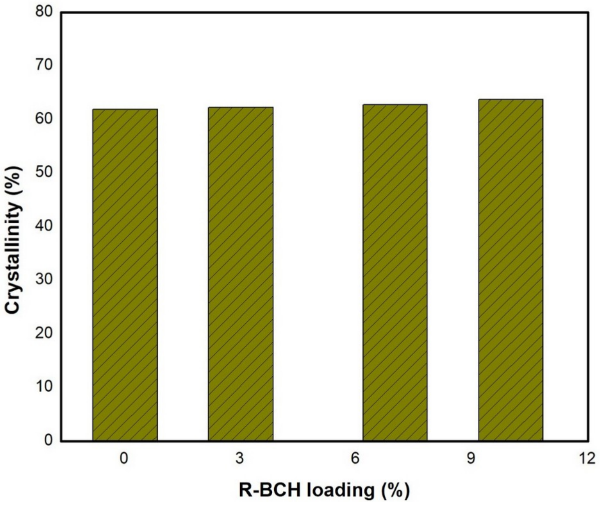

Figure 7: Crystallinity values of HDPE and HDPE/R-BCH composites.

Mechanical Properties

The results of the tensile tests are determined from tensile stress-strain curves, as shown in Figure 8. The HDPE/R-BCH composites displayed higher tensile strength and modulus when compared to the pure high-density polyethylene (HDPE). It is evident from Table 2 that tensile strength increased with increasing the loading of R-BCH from 3 to 10 wt.% in comparison to pure HDPE. The tensile strength of significant loading of 10% R-BCH was 42.5±4.8 MPa compared with pure HDPE, which was 26±2.5 MPa. The results of Young's modulus exhibited a significant increase with 10% R-BCH loading, which was 296±25 MPa by comparing to lower loadings (3 and 7% R-BCH), and HDPE which were (284±18 MPa and 289 ±22 MPa), and 280±15 MPa, respectively, as shown in Table 2. The addition of different loadings for R-BCH composites exhibited significant changes in the elongation at break, %. It decreased with increasing the loading of R-BCH in the HDPE matrix. Elongation at a break of 10% R-BCH in the HDPE matrix decreased to 7.4±0.6%, while pure HDPE matrix was 14.7±1.4%, as shown in Table 2. This may be attributed to the high loading of R-BCH in the HDPE matrix, which displayed better interfacial interaction and improved the blend's plasticity by incorporating the compatibilizer (26). Previous work was studied by Idress (27), who found that the highest tensile strength for HDPE composite with a mold surface temperature of 50 °C. By comparing with this work, Yu et al. (28) reported in their findings regarding the mechanical characterizations for particleboard dust (PB dust) and basalt fibers (BFs)/Recycled (R-HDPE), they found that the tensile strength was increased with the loading of (1BP dust:1BFs) in HDPE composite. They reported that the tensile strength of 1PB:1BFs/RHDPE composite was 28.3 MPa while the virgin RHDPE matrix was 19.4 MPa. Poulose et al. (14) studied the properties of date palm waste extracted as biochar (BC) and utilized as biofilters for polypropylene (PP) matrix. They observed that the mechanical characterizations of BC/PP composites improved tensile strength and modulus with increased loading of BC.

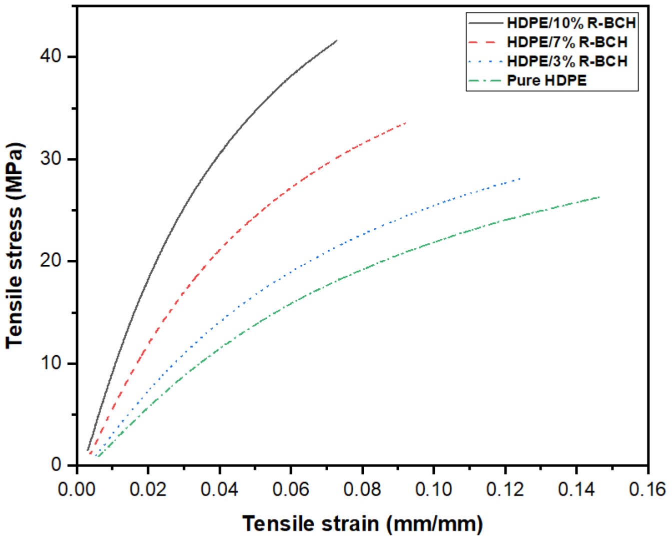

Figure 8: Tensile stress-strain curves of HDPE composites.

Table 2: Mechanical properties of pure HDPE and HDPE composites.

Composites	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break %
Pure HDPE	26.5±2.5	312.5±25	14.7±1.4
HDPE/3% R-BCH	28.2±3.5	400.7±60	12.5±1.1
HDPE/7% R-BCH	33.7±3.2	650.4±50	9.2±0.9
HDPE/10% R-BCH	42.5±4.8	1020.2±75	7.4±0.6

CONCLUSIONS

This study demonstrated that R-BCH could be used as an efficient filler for the HDPE matrix. R-BCH was reinforced into HDPE by increasing the weight fractions from 3 wt.% to 10 wt. The swelling ratio was reduced with increasing the loading of R-BCH in the HDPE matrix. The tensile strength and modulus of R-BCH/HDPE composites were found to be improved when compared to the virgin HDPE matrix, while the elongation at break was reduced with increasing the loading of R-BCH. The thermal studies revealed that the crystallinity of R-BCH/HDPE composites was increased compared to the virgin HDPE matrix. Further investigation could be addressed towards improving the BC/PP composites characterizations by improving the biochar properties such as porosity, surface functionalization, and purity. It can be concluded that this type of bio filler (R-BCH) enhances the interaction between the HDPE matrix and R-BCH filler and hence superior composite characterizations.

CONFLICTS OF INTEREST

The authors declared no conflict of interest.

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