Sustainable Biocomposites Produced From Cotton Stalk Wastes: Effect of Heat Treatment

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Abstract

The novelty of this study is to explore the effect of heat treatment of CS on the properties of biocomposites. 200°C, 300°C, 500°C, and burning of 500°C were selected to heat treat CS to obtain CS fillers, and the biocomposites were prepared using CS fillers and LLDPE. The heat treatment of CS can improve the interface bonding and compatibility of biocomposites by the results of FTIR, SEM, and CA. The crystal planes were not changed by the addition of CS fillers. The heat treatment of CS promoted crystallization, improved the heat resistance of LLDPE. In addition, the flexural properties, tensile properties, stiffness, elasticity, creep resistance and, stress relaxation resistance were all increased by the heat treatment of CS, although it exhibits an adverse effect on the impact strength of LLDPE. The best flexural properties (13.00 MPa and 0.75 GPa) were obtained in 200CSB-L due to the enhancement of CS rigidity by 200°C heat treatment, and the best tensile properties (10.89 MPa and 0.26 GPa) were obtained in 500CSB-L due to its mechanical interlocking structure. The results of this study indicate that heat treatment will play an important role in biocomposites in terms of the benefit in mechanical properties.

Introduction

Polymer materials have been very widely used in packaging, construction, and transportation due to their rich source of raw materials, low price, light quality, good insulation, low density, and corrosion resistance. Among all the polymer materials, polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC) have the largest share in the market. The application of polymer materials is closely related to human lives, most plastic bags, packaging bags, cling film and pipes are PE products. In order to meet the requirement under higher conditions, there is an urgent need to improve the properties of these polymer materials. As a typical semi-crystalline polymer, PE is an addition polymer formed from an ethylene monomer. PE can be processed by injection molding, blow molding, compression molding, and rotational molding, showing the diversification of molding methods and excellent processing performance [1]. According to the molecular chain structure, PE can be divided into ultrahigh molecular weight polyethylene (UHMWPE), high density polyethylene (HDPE), and low density polyethylene (LDPE). UHMWPE is a semi-crystalline polymer material with extremely high molecular chain entanglement density, moderate crystallinity, and extremely high relative molecular mass ($\sim 1.5 \times 10^6$), showing better impact strength, excellent wear resistance, low friction coefficient, better corrosion resistance, low water absorption, and good biocompatibility. UHMWPE is currently widely used in industrial and clinical medicine, especially as an artificial joint material [2]. The report showed that biochar particles can improve the tensile properties significantly, and the tensile strength of biochar/UHMWPE composites exceeds 100 MPa [3]. HDPE has higher crystallinity, better strength, but poor toughness and cold resistance. Therefore, it is mainly used in packaging materials, blow molded containers, hollow products and, low-end daily necessities, etc. Additionally, HDPE was used in biocomposites as the main matrix due to its lower shrinkage compared with PP and PVC [4]. Differently, LDPE exhibits better fluidity, lower density, and better toughness than UHMWPE and HDPE, and LDPE is mainly used as a thin film and electrical insulation layer [5]. As a type of LDPE, linear low-density polyethylene (LLDPE) shows better toughness, heat resistance, and acid and

alkali resistance compared with LDPE, and has attracted widespread attention in many areas. Nevertheless, poorer mechanical strength and rigidity of LLDPE greatly limit its application especially in composites, and there is an urgent need to overcome this issue [6]. In addition, the non-degradability of PE also caused serious environmental pollution and soil pollution, and the recycling of waste PE has gradually become the focus. Over the past decades, biocomposites produced from PE and plant fiber has been extensively employed in industry and construction applications. The waste PE composites can be reproduced with the same process, and this means that PE composites can be recycled. All in all, PE composites exhibit huge potential in terms of sustainability, energy saving, and environmental protection [7, 8]. The poor interface binding caused by polar differences between PE and plant fiber is the main reason for the poor mechanical properties of PE composites, which restricts the application to a wider range [9].

To overcome the shortcoming and enhance the interface bonding, there are lots of documented efforts have been done to date. Many literatures confirmed that coupling agents can connect plant fibers to a polymer matrix acting as a bridge, thus enhanced interface binding and improved mechanical properties of biocomposites [10]. Adding compatibilizer (maleic anhydride, styrene, glycidyl methacrylate, etc.) also was proved to be valid in improving the compatibility of biocomposites. The addition of compatibilizer can form a physical or chemical reaction between the two incompatible phases (plant fiber and polymers), and the existence of an effective interface layer can improve the overall performance of biocomposites [11]. The molecular chain of natural plant fiber contains a large number of active hydroxyl groups which can form intermolecular hydrogen bonds, which should be responsible for the strong hydrophilic properties and polarity of natural plant fiber. Most thermoplastic resins show strong non-polar and hydrophobicity, so natural plant fiber has poor compatibility with non-polar polymers [12]. Given, pretreating natural plant fiber to reduce polarity is a common means. Pretreatment including heat treatment, alkali treatment, and microwave treatment can effectively reduce the interfacial tension, increase the interfacial bonding strength, and improve the bonding force between the polymer matrix and natural plant fibers, which is beneficial to the mechanical properties of biocomposites [13–15]. Moreover, replacing natural plant fiber with biochar to prepare biocomposites has significantly increased recently. Compared with natural plant fiber, biochar has high carbon content, a large specific surface area, and stable physical and chemical properties. On the one hand, biochar shows lower polarity under high temperature carbonization, which is beneficial to the compatibility of biochar composites [16]. On the other hand, the melted polymer matrix can flow into pores of biochar, and a special structure was formed after cooling. The porous structure of biochar restricted the deformation of a polymer matrix, and the mechanical properties of biochar composites were therefore improved [17]. Additionally, biochar also exhibits good flame-retardant, waterproof, and electrical conductivity [18]. Most of the available reports are centralized around the biochar prepared at higher carbonization temperature ($> 500^{\circ}\text{C}$), there is no work to look at the effect of lower temperature on biochar and its impact on biochar composites. Based on this, the study aims to explore the effect of heat treatment on natural plant fiber and outline the influence of heat treatment on the properties of biocomposites.

Materials And Methods

2.1 Materials

The polymer matrix used in this work was LLDPE (PF0218) which was supplied by Xingyu Plastic Chemical Co., Ltd. (Suzhou, China). The density, melt flow index ($2.16 \text{ kg}/190^\circ\text{C}$), molecular weight, and particle size was $0.918 \text{ g}/\text{cm}^3$, $2.0 \text{ g}/10 \text{ min}$, $2 \times 10^4 \text{ g}/\text{mol}$, and $180 \text{ }\mu\text{m}$ respectively. The filler raw material used in this study was cotton stalk (CS) which was obtained from the countryside (Liaocheng, China)

2.2 Heat treatment of CS

CS was heat treated in a miniature box furnace (KSL-1100X-S). The heat treatment temperature was increased from ambient temperature to 200 , 300 , and 500°C respectively with a $5^\circ\text{C}/\text{min}$ heating rate, $20 \text{ mL}/\text{min}$ nitrogen atmosphere, and 2 h retention time. The resulted samples were named 200CSB, 300CSB, and 500CSB respectively. In addition, the last sample (ash) was heat treated under 500°C under an oxygen atmosphere, named CSA.

2.3 Composites preparation

LLDPE pellets and fillers particles were put into a dryer to remove moisture at 40°C and 105°C respectively. Subsequently, CS, 200CSB, 300CSB, 500CSB, and CSA were put into a mixer for 10 min with LLDPE pellets respectively. After melting and compounding in a micro twin-screw extruder (WLG10G) with a 30 rpm speed and 175°C compounding temperature, five composites were finally obtained using a micro-injection molding machine (WZS10D) with a 175°C injection temperature and 45°C cooling temperature. The five composites samples were named CS-L, 200CSB-L, 300CSB-L, 500CSB-L, and CSA-L respectively.

2.4 Composites characteristics

Fourier infrared spectrometer (Nicolet 5700, Thermo Fisher Nicolet, USA), X-ray diffractometer (Bruker AXS D8 Advance, Germany), scanning electron microscope (SEM) (FEI Sirion 200, USA), and contact angle measuring instrument (OCA20, GmbH) were used to analyze the five composites samples. The scanning range of the Fourier transform infrared spectroscopy (FTIR) was from 4000 cm^{-1} to 400 cm^{-1} , the X-Ray diffraction (XRD) curves were carried out using $\text{CuK}\alpha$ radiation with 2θ varying between 5° and 30° at $5^\circ/\text{min}$, the scanning voltage of SEM was 3.0 kV , and the left and right contact angles (CA) at 0 s were selected.

A differential scanning calorimetry (DSC) (DSC-Q100, TA Instrument, USA) and synchronous thermal analyzer (STA 449, NETZSCH) were used to characterize the thermal properties of the five composites. The composites samples were heated to 180°C to remove the thermal stress. After, they were cooled to 100°C and then heated to 180°C at $5^\circ\text{C}/\text{min}$ to obtain DSC curves. The mass loss curves (TG) and derivatives of the mass loss (DTG) curves were conducted to carry out thermogravimetric analysis (TGA)

with a 50°C ~ 500°C temperature range, 20 mL/min nitrogen atmosphere flow rate, and 10°C/min heating rate.

Flexural properties and tensile properties of the five composites were tested using an electronic universal testing machine (WDW1020, Changchun Kexin Co., Ltd., China) according to ASTM D 790M and ASTM D 638 standards. The impact strength of the five composites was tested using an electronic impact test machine (JB-300B, Jinan Hengsi Grand Instrument Co., Ltd) according to ASTM D 4508 standard. Dynamic mechanical analysis (DMA) of the five composites was characterized using a dynamic thermomechanical analyzer (Q 800, TA instrument). The viscoelastic behavior including storage modulus and loss factor was conducted in a single cantilever mode with a -50°C ~ 130°C temperature range and 5°C/min heating rate. The Creep TTS and Stress Relaxation TTS models were selected to carry out the 30min creep compliance and relaxation modulus of the five composites.

Results And Discussion

3.1 FTIR

FTIR spectra of neat LLDPE and the five composites are shown in Fig. 1. As can be observed that the typical peak at 3400 cm^{-1} was caused by the asymmetrical O-H stretching vibration which confirmed higher polarity of CS than LLDPE. This peak weakened with the increase of heat treatment temperature, which suggests that the polarity was reduced by heat treatment temperature. The peaks at 2920 cm^{-1} , 2850 cm^{-1} , and 1470 cm^{-1} are C-H stretching vibration which was contributed by CS fillers and LLDPE [19]. The peaks at around 1735 cm^{-1} and 1600 cm^{-1} were caused by C = O stretching vibration, C = C stretching vibration, and C-O stretching vibration contributed to the peaks at 1160 cm^{-1} , 1100 cm^{-1} and 1040 cm^{-1} [20]. These functional groups were contributed by the main components (cellulose, hemicellulose, lignin) of CS. Also, these peaks were reduced with increasing heat treatment temperature, which indicates that heat treatment caused the escape of the volatile fraction in CS. Besides, the peak at around 869 cm^{-1} can be attributed to CO_3^{2-} bending vibration, which indicates the enrichment of carbonate as the increase of heat treatment temperature. Moreover, the peak vibration of CO_3^{2-} of CSA-L is the strongest among all the samples, which was mainly since there was lots of salt in the ash [21]. The results show that the polarity of CS can be reduced by heat treatment, which is beneficial to the interface bonding of biocomposites.

3.2 XRD

Figure 2 shows the XRD spectra of neat LLDPE and the five composites. As shown in Fig. 2, two sharp peaks can be observed at 2θ of 21.6° and 24° in the XRD spectra of LLDPE, and the two peaks correspond to (110) and (200) crystal planes showing the typical XRD characteristic peaks of PE [22]. Also, the same two peaks can be seen in the XRD spectra of the five composites, which suggests that none of the additions of CS, 200CSB, 300CSB, 500CSB, and CSA changed the crystal pattern of LLDPE. It

should be noted that XRD peaks of all the five composites show lower intensity than neat LLDPE, the addition of amorphous fillers reduced the relative crystallinity of LLDPE.

3.3 SEM

Figure 3 demonstrates the SEM images to characterize the microstructure of neat LLDPE and the five composites. A smooth surface structure of neat LLDPE can be observed compared with others. The SEM image of CS-L shows a typical microstructure like other fiber reinforced polymer composites that CS fillers were wrapped in the LLDPE matrix. The gaps between CS and LLDPE can be observed significantly, which was due to the poor interface bonding caused by the difference in the polarity. Appearance of same gaps is not seen in the SEM image of 200CSB-L, which can attributed to the fact that some of the hemicellulose was degraded, and the polarity of CS was reduced under 200°C. As for the microstructure of 300CSB-L, CS fiber and pores can be observed together in the LLDPE matrix. Hemicellulose and part of cellulose were degraded to small molecules and escape and pores were formed under 300°C [23]. At the heat treatment temperature of 500°C, the higher temperature increased the volatile degradation of CS, and biochar was formed. It can be clearly observed that the LLDPE matrix was embedded into the pores of biochar and formed a mechanical interlock structure [24]. LLDPE bonded the biochar particles together acting as a binder. The SEM image of CSA-L shows that ash particles were wrapped in the LLDPE matrix with no gaps. Burning turns the CS into ash, and CSA showed no polarity. The heat treatment of CS reduced the polarity, which improved the interface bonding of biocomposites.

3.4 CA

Table 1 presents the left and right contact angles to characterize interface compatibility of neat LLDPE and the five composites. As presented in Table 1, the left and right contact angles of LLDPE are 91.68° and 90.53° showing a typical hydrophobicity. As the addition of CS to LLDPE, the left and right contact angles are 87.58° and 88.46° showing poor interface compatibility. It should be noted that the left and right contact angles of the composites increased with increasing the heat treatment temperature. As stated earlier, the polarity of CS decreased with the increase of heat treatment temperature, which reduced the polarity difference between CS and LLDPE and improved the interface compatibility of biocomposites. Also, the left and right contact angles of CSA-L are 90.35° and 89.33° showing better interface compatibility than CS-L. The results of CA are substantially consistent with the FTIR and SEM analysis.

Table 1
Left and right contact angles of composites samples

Samples	LLDPE	CS-L	200CSB-L	300CSB-L	500CSB-L	CSA-L
Left contact angle (°)	91.68	87.58	88.63	91.38	92.88	90.35
Right contact angle (°)	90.53	88.46	87.70	89.70	93.43	89.33

3.5 DSC

DSC curves of neat LLDPE and the five composites are shown in Fig. 4. Two typical peaks of DSC curves can be observed at around 109.30°C and 121.25°C, which are attributed to exothermic crystallization and endothermic melting [19]. As shown, the crystallization temperatures of CS-L, 200CSB-L, 300CSB-L, 500CSB-L, and CSA-L are 111.37°C, 109.92°C, 109.05°C, 112.06°C, and 111.19°C respectively, all higher than that of neat LLDPE. The increase of crystallization temperature indicates that the addition of CS fillers accelerated the crystallization and improved the crystallinity of neat LLDPE [25]. Among all the composites samples, 500CSB-L shows the highest crystallization temperature, which confirms an advantage of biochar composites crystallization. On the other hand, the melting temperatures of CS-L, 200CSB-L, 300CSB-L, 500CSB-L, and CSA-L are 122.25°C, 121.32°C, 120.65°C, 121.91°C, and 111.19°C respectively, all higher than that of neat LLDPE. The increase of melting temperature indicates that the five composites need to absorb more energy to melt compared with neat LLDPE showing better heat resistance [26]. The results indicate that the heat treatment of CS can accelerate the crystallization and improve the heat resistance of LLDPE.

3.6 DSC

TGA including TG and DTG curves of neat LLDPE and the five composites is shown in Fig. 5. As presented, LLDPE shows a typical thermal weightlessness behavior with no residues and reaching maximum thermal weight loss rate at around 484°C. A peak in CS-L, 200CSB-L, and 300CSB-L DTG curves can be observed at around 327°C, and this is the characteristic peak of hemicellulose and cellulose degradation. Also, the initial degradation temperature of CS-L, 200CSB-L, and 300CSB-L is at around 245°C lower than that of neat LLDPE, and the maximum thermal weight loss rate temperatures of CS-L, 200CSB-L, and 300CSB-L are also lower than LLDPE slightly. This suggests that the addition of CS, 200CSB, and 300CSB increased the decomposition and decreased the thermal stability of LLDPE. Compared with CS-L, 200CSB-L, and 300CSB-L, the initial degradation temperatures and the maximum thermal weight loss rate temperatures of 500CSB-L and CSA-L are higher showing better thermal properties, which is due to the high thermal stability of 500CSB and CSA obtained from higher heat treatment temperature [26]. The results of TGA shows that 500CSB and CSA improve the thermal stability of biocomposites by delaying initial degradation temperature and maximum thermal weight loss rate temperature.

3.7 Flexural properties

The flexural properties including strength and modulus of neat LLDPE and the five composites are illustrated in Fig. 6. The flexural strength of LLDPE is 6.36 MPa, and the flexural strengths of CS-L, 200CSB-L, 300CSB-L, 500CSB-L, and CSA-L increased to 12.85 MPa, 13.00 MPa, 11.62 MPa, 11.38 MPa, and 9.80 MPa respectively as the addition of CS, 200CSB, 300CSB, 500CSB, and CSA. CS, 200CSB, 300CSB, 500CSB, and CSA are all stronger than neat LLDPE, and they act as rigid fillers in biocomposites. 200CSB-L shows the best flexural strength compared to others, which is due to the fact that 200°C heat treatment temperature decomposed the hemicellulose and retained the rigid cellulose and lignin [27]. The increment of flexural strength from LLDPE to 500CSB-L can be attributed to the mechanical interlock

structure caused by embedding the LLDPE matrix to biochar pores. The mechanical interlock structure can transfer the stress effectively and improve the flexural strength of biocomposites [28]. Although CSA-L exhibits better flexural strength than LLDPE, the enhancing effect of CSA is lower than other CS fillers, suggesting that the strength of ash is poorer than fiber. Similarly, the flexural moduli of CS-L, 200CSB-L, 300CSB-L, 500CSB-L, and CSA-L increased to 0.74 GPa, 0.75 GPa, 0.63 GPa, 0.53 GPa, and 0.48 GPa from 0.28 GPa (LLDPE) as the addition of CS fillers. The flexural modulus of biocomposites is mainly dependent on rigidity. Figure 6 (B) shows that CS, 200CSB, 300CSB, 500CSB, and CSA reinforced LLDPE as rigid fillers. Among all the composites samples, 200CSB-L shows the best flexural modulus, which is attributed to the enhancement of CS rigidity by 200°C heat treatment.

3.8 Tensile properties

The tensile properties including strength and modulus of neat LLDPE and the five composites are illustrated in Fig. 7. The tensile strengths of neat LLDPE, CS-L, 200CSB-L, 300CSB-L, and CSA-L are 9.70 MPa, 10.08 MPa, 9.57 MPa, 9.62 MPa, and 9.64 MPa respectively. The tensile strength of LLDPE was not effectively improved with adding CS, 200CSB, 300CSB, and CSA. It should be noted that the tensile strength of 500CSB-L is 10.89 MPa over 12.27% of neat LLDPE, which indicates that the addition of 500CSB improved the tensile strength of LLDPE. On the one hand, 500CSB was obtained under 500°C, and the main polar functional groups were removed during the preparation process. The improvement of interface bonding is beneficial to the tensile strength of 500CSB-L. On the other hand, the mechanical interlock structure of 500CSB-L caused by porous structure and high specific surface area of 500CSB can effectively prevent the tensile deformation of the LLDPE, and thus the tensile strength was improved [29]. As for the tensile modulus, 200csb-l shows the best tensile modulus, which can be attributed to the decomposition of hemicellulose under 200°C heat treatment temperature and the retention of rigid cellulose and lignin. The adverse effect of 300CSB, 500CSB, and CSA on the tensile modulus of LLDPE may be due to the increase of brittleness caused by higher heat treatment temperature. The results show that 500CSB is beneficial to prepare biocomposites with excellent tensile properties.

3.9 Impact strength

Figure 8 presents the impact strength of neat LLDPE and the five composites. It can be observed that the impact strength of neat LLDPE is 24.45 kJ/m² showing excellent toughness, and the impact strengths of CS-L, 200CSB-L, 300CSB-L, 500CSB-L, and CSA-L decreased to 16.72 kJ/m², 17.34 kJ/m², 14.97 kJ/m², 8.50 kJ/m², and 19.02 kJ/m² respectively as the addition of CS, 200CSB, 300CSB, 500CSB, and CSA. The toughness of CS, 200CSB, 300CSB, 500CSB, and CSA is poor, and the addition of them has an adverse effect on the impact strength of LLDPE. Moreover, the fillers which have poor toughness can easily cause impact stress concentration in the polymer matrix, which also should be responsible for the decrease of impact strength [30]. But even so, CSA-L still keeps better impact strength (19.02 kJ/m²) indicating that the ash is less harmful to biocomposites toughness than fibers and biochar.

3.10 Dynamic viscoelasticity

The dynamic viscoelasticity including storage modulus and loss factor of neat LLDPE and the five composites are showed in Fig. 9. As can be observed from Fig. 9 (A), the storage modulus of all the composites samples decreased with increasing temperature, which is attributed to the fact that the increase of temperature aggravated the molecular thermal motion and decreased the stiffness of the composites samples [31]. Among all the composites samples, LLDPE shows the lowest storage modulus suggesting the best flexibility and the worst stiffness. Poorer flexibility and better rigidity are characteristic of CS fillers compared with LLDPE, and the addition of CS fillers improved the stiffness of LLDPE. As stated earlier, 200°C heat treatment temperature decomposed the hemicellulose and retained the rigid cellulose and lignin, and this resulted in the best stiffness of 200CSB-L. Figure 9 (B) presents the loss factor of neat LLDPE and the five composites to characterize their elasticity. The loss factor of all the composites samples increased with increasing temperature, which is attributed to the fact that the increase of temperature increased the viscosity and decreased the elasticity of the composites samples [32]. The loss factor of LLDPE is higher than all the five composites showing that the addition of CS fillers improved the elasticity of LLDPE. In the composites system, the cross-linking connection between CS fillers and LLDPE hindered the distribution of LLDPE molecular chains in the stress field, which obstructed the transformation of elastic potential energy into thermal energy, and thus the loss factor was decreased. Among all the composites samples, 500CSB-L exhibits the best elasticity compared with others, which can be due to the mechanical interlock structure of 500CSB-L. The porous structure of biochar effectively limited the deformation of LLDPE resulting in the best elasticity [33].

3.11 Dimensional stability

The creep and stress relaxation behavior of neat LLDPE and the five composites are presented in Fig. 10 to characterize the dimensional stability. As shown in Fig. 10(A), the creep compliance of LLDPE is higher than all the five composites showing the poorest creep resistance. The entanglement of CS fillers and LLDPE matrix hindered the slippage of the LLDPE molecules, and reduced creep compliance of LLDPE [34]. Additionally, the addition of CS fillers promoted crystallization (Fig. 4) and increased the defects in the LLDPE crystal as an impurity, which produced more pinning points for preventing the creep deformation of LLDPE. It can be observed from Fig. 10(B) that the stress relaxation modulus of LLDPE is lower than all the five composites showing the poorest stress relaxation resistance. The addition of CS fillers improved the stress relaxation resistance of LLDPE, which can be attributed to the obstacles of CS fillers to LLDPE deformation. On the other hand, the addition of CS fillers shared the stress and improved the modulus of LLDPE, which improved the stress relaxation resistance [35]. Among all the composites samples 200CSB-L shows the best stress relaxation resistance, which is related to the better stiffness of 200CSB. The results show that CS fillers improved the dimensional stability of LLDPE, and 200°C heat treatment temperature is more beneficial to obtain the biocomposites with better dimensional stability in view of good creep and stress relaxation resistance of 200CSB-L.

Conclusion

The aim of this study is to explore the effect of heat treatment on the properties of biocomposites. CS was heat treated under 200°C, 300°C, 500°C, and burning of 500°C to obtain different CS fillers for

preparing composites based on LLDPE. The results show that the heat treatment reduced the polarity of CS, which is beneficial to improve the interface bonding and compatibility of CS/LLDPE composites. The CS fillers did not change the crystal planes, but accelerated the crystallization and improved the heat resistance of LLDPE. TGA shows that 500CSB and CSA improved the thermal stability of biocomposites. The flexural strength and flexural modulus of 200CSB-L are 13.00 MPa and 0.75 GPa showing the best flexural properties, and the tensile strength and tensile modulus of 500CSB-L are 10.89 MPa and 0.26 GPa showing the best tensile properties. The dynamic thermomechanical analysis shows that the heat treatment of CS improved the stiffness, elasticity, and dimensional stability of biocomposites. The heat treatment of CS is beneficial to improve the mechanical properties of biocomposites, and the 200CSB-L and 500CSB-L present the best mechanical properties.

Declarations

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References

1. Mittermeier C, Lion A. Challenges in the experimental investigation of the caloric and thermomechanical behaviour of semi-crystalline polymers: a study on the example of polyethylene terephthalate (PET). *Polymer Testing*. 2020;81:106252.
2. Patel K, Chikkali SH, Sivaram S. Ultrahigh molecular weight polyethylene: Catalysis, structure, properties, processing and applications. *Progress in Polymer Science*. 2020:101290.
3. Li S, Li X, Chen C, Wang H, Deng Q, Gong M, et al. Development of electrically conductive nano bamboo charcoal/ultra-high molecular weight polyethylene composites with a segregated network. *Composites Science and Technology*. 2016;132:31-7.
4. Mazur K, Jakubowska P, Romańska P, Kuciel S. Green high density polyethylene (HDPE) reinforced with basalt fiber and agricultural fillers for technical applications. *Composites Part B: Engineering*. 2020;202:108399.
5. Penumakala PK, Santo J, Thomas A. A critical review on the fused deposition modeling of thermoplastic polymer composites. *Composites Part B: Engineering*. 2020:108336.
6. Na Y, Dai S, Chen C. Direct synthesis of polar-functionalized linear low-density polyethylene (LLDPE) and low-density polyethylene (LDPE). *Macromolecules*. 2018;51:4040-8.
7. Zhang Q, Khan MU, Lin X, Cai H, Lei H. Temperature varied biochar as a reinforcing filler for high-density polyethylene composites. *Composites Part B: Engineering*. 2019;175:107151.
8. AL-Oqla FM. Investigating the mechanical performance deterioration of Mediterranean cellulosic cypress and pine/polyethylene composites. *Cellulose*. 2017;24:2523-30.

9. Zhang Q, Lei H, Cai H, Han X, Lin X, Qian M, et al. Improvement on the properties of microcrystalline cellulose/polylactic acid composites by using activated biochar. *Journal of Cleaner Production*. 2020;252:119898.
10. Pan C, Kou K, Jia Q, Zhang Y, Wu G, Ji T. Improved thermal conductivity and dielectric properties of hBN/PTFE composites via surface treatment by silane coupling agent. *Composites Part B: Engineering*. 2017;111:83-90.
11. Yao H, Zhou G, Wang W, Peng M. Effect of polymer-grafted carbon nanofibers and nanotubes on the interlaminar shear strength and flexural strength of carbon fiber/epoxy multiscale composites. *Composite Structures*. 2018;195:288-96.
12. Zhang Q, Cai H, Yi W, Lei H, Liu H, Wang W, et al. Biocomposites from organic solid wastes derived biochars: a review. *Materials*. 2020;13:3923.
13. Li J, Zhang X, Geng L. Effect of heat treatment on interfacial bonding and strengthening efficiency of graphene in GNP/Al composites. *Composites Part A: Applied Science and Manufacturing*. 2019;121:487-98.
14. Chandrasekar M, Ishak M, Sapuan S, Leman Z, Jawaaid M. A review on the characterisation of natural fibres and their composites after alkali treatment and water absorption. *Plastics, Rubber and Composites*. 2017;46:119-36.
15. Akinyemi AB, Omoniyi ET, Onuzulike G. Effect of microwave assisted alkali pretreatment and other pretreatment methods on some properties of bamboo fibre reinforced cement composites. *Construction and Building Materials*. 2020;245:118405.
16. Zhang Q, Zhang D, Xu H, Lu W, Ren X, Cai H, et al. Biochar filled high-density polyethylene composites with excellent properties: Towards maximizing the utilization of agricultural wastes. *Industrial Crops and Products*. 2020;146:112185.
17. Das O, Kim NK, Kalamkarov AL, Sarmah AK, Bhattacharyya D. Biochar to the rescue: Balancing the fire performance and mechanical properties of polypropylene composites. *Polymer Degradation and Stability*. 2017;144:485-96.
18. Li S, Huang A, Chen Y-J, Li D, Turng L-S. Highly filled biochar/ultra-high molecular weight polyethylene/linear low density polyethylene composites for high-performance electromagnetic interference shielding. *Composites Part B: Engineering*. 2018;153:277-84.
19. Zhang Q, Khan MU, Lin X, Yi W, Lei H. Green-composites produced from waste residue in pulp and paper industry: A sustainable way to manage industrial wastes. *Journal of Cleaner Production*. 2020;262:121251.
20. Zhang X, Li Y, Wang M, Han L, Liu X. Effects of Hydrothermal Carbonization Conditions on the Combustion and Kinetics of Wheat Straw Hydrochar Pellets and Efficiency Improvement Analyses. *Energy & Fuels*. 2019;34:587-98.
21. Wei Y, Shen C, Xie J, Bu Q. Study on reaction mechanism of superior bamboo biochar catalyst production by molten alkali carbonates pyrolysis and its application for cellulose hydrolysis. *Science of the total environment*. 2020;712:136435.

22. Sugumaran V, Kapur GS, Narula AK. Sustainable potato peel powder–LLDPE biocomposite preparation and effect of maleic anhydride-grafted polyolefins on their properties. *Polymer Bulletin*. 2018;75:5513-33.
23. Zhang Q, Zhang D, Lu W, Khan MU, Xu H, Yi W, et al. Production of high-density polyethylene biocomposites from rice husk biochar: Effects of varying pyrolysis temperature. *Science of the total environment*. 2020;738:139910.
24. Das O, Bhattacharyya D, Hui D, Lau K-T. Mechanical and flammability characterisations of biochar/polypropylene biocomposites. *Composites Part B: Engineering*. 2016;106:120-8.
25. Ayilimis N, Kaymakci A, Güleç T. Potential use of decayed wood in production of wood plastic composite. *Industrial Crops and Products*. 2015;74:279-84.
26. Codou A, Misra M, Mohanty AK. Sustainable biocarbon reinforced nylon 6/polypropylene compatibilized blends: Effect of particle size and morphology on performance of the biocomposites. *Composites Part A: Applied Science and Manufacturing*. 2018;112:1-10.
27. Silveira EA, Lin B-J, Colin B, Chaouch M, Pétrissans A, Rousset P, et al. Heat treatment kinetics using three-stage approach for sustainable wood material production. *Industrial Crops and Products*. 2018;124:563-71.
28. Srinivasan P, Sarmah AK, Smernik R, Das O, Farid M, Gao W. A feasibility study of agricultural and sewage biomass as biochar, bioenergy and biocomposite feedstock: production, characterization and potential applications. *Science of the total environment*. 2015;512:495-505.
29. Zhang Q, Xu H, Lu W, Zhang D, Ren X, Yu W, et al. Properties evaluation of biochar/high-density polyethylene composites: Emphasizing the porous structure of biochar by activation. *Science of the total environment*. 2020;737:139770.
30. Shah KJ, Shukla AD, Shah DO, Imae T. Effect of organic modifiers on dispersion of organoclay in polymer nanocomposites to improve mechanical properties. *Polymer*. 2016;97:525-32.
31. Wang Y, Zhu W, Wan B, Meng Z, Han B. Hygrothermal ageing behavior and mechanism of carbon nanofibers modified flax fiber-reinforced epoxy laminates. *Composites Part A: Applied Science and Manufacturing*. 2021;140:106142.
32. Vieira PSC, de Souza FS, Cardoso DCT, Vieira JD, de Andrade Silva F. Influence of moderate/high temperatures on the residual flexural behavior of pultruded GFRP. *Composites Part B: Engineering*. 2020;200:108335.
33. Zhang Q, Cai H, Ren X, Kong L, Liu J, Jiang X. The dynamic mechanical analysis of highly filled rice husk biochar/high-density polyethylene composites. *Polymers*. 2017;9:628.
34. Ghosh SK, Prusty RK, Rathore DK, Ray BC. Creep behaviour of graphite oxide nanoplates embedded glass fiber/epoxy composites: Emphasizing the role of temperature and stress. *Composites Part A: Applied Science and Manufacturing*. 2017;102:166-77.
35. Garner A, Genedy M, Kandil U, Taha MR. Controlling off-axis stiffness and stress-relaxation of carbon fiber-reinforced polymer using alumina nanoparticles. *Journal of Composite Materials*. 2018;52:2483-91.

Figures

Figure 1

FTIR spectra of composites samples

Figure 2

XRD spectra of composites samples

Figure 3

SEM images of composites samples

Figure 4

DSC curves of composites samples

Figure 5

TG and DTG curves of composites samples

Figure 6

Flexural properties of composites samples

Figure 7

Tensile properties of composites samples

Figure 8

Impact strength of composites samples

Figure 9

Dynamic viscoelasticity of composite samples

Figure 10

Dynamic viscoelasticity of composite samples