

# Comparing Four Kinds of Lignocellulosic Biomass for the Performance of Fiber/PHB/PBS Bio-composites

Pei Pei,<sup>a,\*</sup> Yelin Sun,<sup>a</sup> Rui Zou,<sup>a</sup> Xinyao Wang,<sup>a</sup> Jinyan Liu,<sup>a</sup> Lulu Liu,<sup>a</sup> Xiaoyu Deng,<sup>a</sup> Xuehua Li,<sup>a</sup> Menghui Yu,<sup>b</sup> and Shizhong Li<sup>c</sup>

A new class of bio-composites was developed by utilizing four kinds of lignocellulosic biomass fiber (bagasse, bamboo, rice husk, and rice straw) as filling fibers. Poly- $\beta$ -hydroxybutyrate (PHB) and poly(butylene succinate) (PBS) in a mixture ratio of 7:3 were used as matrix materials with hot-press molding. The performance of the resulting composites was evaluated by compositional analyses, mechanical analysis, Fourier transform infrared (FTIR) spectroscopy, thermogravimetry, and morphological analysis. The interfacial adhesion, thermal stability, and comprehensive mechanical properties of the alkali treated bamboo/PHB/PBS composite were highest among the four bio-composites. The bending strength, tensile strength, and impact strength for alkali treated bamboo/PHB/PBS composite was 19.82 MPa, 12.97 MPa, and 4.30 kJ/m<sup>2</sup>, respectively. The thermal stability for NaOH modified bamboo/PHB/PBS composite was slightly superior to the other three composites, with the initial pyrolysis temperature of 248 °C, moderate pyrolysis speed, and the amount of pyrolysis residue (5.81%). The results showed the suitability of biomass fiber and biodegradable polymer for producing environmentally friendly composite materials.

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Contact information: a: Department of Information Science and Engineering, Changsha Normal University, Changsha 410000, PR China; b: School of Light Industry Science and Engineering, TUST, Tianjin University of Science and Technology, Tianjin 300000, PR China; c: Institute of Nuclear and New Energy Technology, Tsinghua University, Tsinghua Garden, Beijing 100084, PR China;

\* Corresponding author: crispei@163.com

## INTRODUCTION

Excessive development and massive use of traditional petroleum-based plastics in different fields has caused worldwide environmental problems (Mochane *et al.* 2021; Robledo-Ortíz *et al.* 2021; Song *et al.* 2022; Kumar *et al.* 2023; Masanabo *et al.* 2023). Since the 1950s, global plastic production has accumulated to approximately 10 billion tons, of which less than 10% has been recycled, and 76% of which eventually become plastic waste (Dixit *et al.* 2021; Aliotta *et al.* 2022). Balancing the relationship between environmental protection and industrial application has become an important issue for the survival and development of the current plastic packaging industry (Manikandan *et al.* 2020). Therefore, it is of great significance to develop novel biodegradable composite materials for partial replacement of petroleum-based materials (García-Depraect *et al.* 2022). Biodegradable composites made of completely or partially bio-resourced materials have garnered increasing interest (Marina *et al.* 2020; Xu *et al.* 2020; Nanni *et al.* 2021; Platnieks *et al.* 2021; Kong *et al.* 2022; Mohammad *et al.* 2023). Great efforts have been

made to synthesize novel green materials.

Among all sustainable polymers, poly(butylene succinate) (PBS) is one of the most promising. PBS is a commercially available aliphatic polyester with good comprehensive mechanical properties, high flexibility, ease of processability, excellent chemical resistance and thermal stability, good thermoplasticity, and superior biodegradability (Liu *et al.* 2021; Aliotta *et al.* 2022; Van der-Sluijs *et al.* 2023). PBS can be used under 100 °C without deformation, which could meet the needs of heat resistance for daily supplies (Qi *et al.* 2020). PBS can be used in the field of degradable packaging (such as food bags, bottles, lunch boxes, and tableware), agricultural fields (such as agricultural films and fertilizer slow-release materials), and medical fields (such as artificial cartilage, sutures, and scaffolds), *etc.* Additionally, good degradation performance of PBS can meet the needs of environmental protection. However, some limitations of PBS material have hindered its practical application. The softness, high cost, low gas barrier properties, and high crystallinity of PBS limit its applications and production (Chaiphut *et al.* 2021; Aliotta *et al.* 2022). To enhance its properties and decrease the high cost of PBS, biodegradable polymers and natural fibers have been blended with PBS for reinforcing the composite materials (Zhang *et al.* 2019; Singh and Kaneko 2023; Song *et al.* 2023).

At present, poly- $\beta$ -hydroxybutyrate (PHB) is one of the options for recombination with PBS for making the polymer matrix harder relative to PBS alone as well as to broaden the application range of composites (Zhang *et al.* 2017; Saratale *et al.* 2020; Samadhiya *et al.* 2023). The brittleness and impact resistance of PHB could also be improved and modified after compounding it together with biodegradable ductile PBS polymer (Liu *et al.* 2021). PHB could be produced in the bacterial fermentation process and eventually degraded into carbon dioxide and water in nature (Qiao *et al.* 2022). Raw materials for PHB can be completely derived from renewable resources. The crystallinity and melting point for PHB are relatively high (Iffa *et al.* 2021). The biocompatibility, thermoplasticity, and processability of PHB was found to be excellent, which benefits for its application in the field of food packaging and biomedical fields (including surgical sutures, bone tissue scaffolds, and drug delivery carriers, *etc.*). PBS/PHB blend alloy is a kind of biodegradable composite material obtained by mixing PHB and PBS in a certain proportion and blended in the molten state after cooling. Liu *et al.* (2021) have blended PHB with PBS (0:100, 20:80, 40:60, 60:40, 80:20, 100:0) to synthesize composite materials with good compatibility. Results showed that the tensile properties, impact resistance, degree of crystallinity, and the performance of the impact strength after UV aging were improved correspondingly after blended PBS with PHB in their published work. Iffa *et al.* (2021) have explored the suitability of blending poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) containing 5 and 17 mol% 3-hydroxyhexanoate with PHB, polycaprolactone (PCL), and PBS at different ratios by a solvent-casting method. According to their results, the thermal properties of the PHBH-5%/PBS blend composites suggested preferable miscibility. However, in general, the main research directions for the production of composites based on PBS or PHB in recent years were blending them with environmentally friendly materials respectively (Mochane *et al.* 2021; Nanni *et al.* 2021). The filler for PBS or PHB to prepare composite materials mainly used lignocellulosic fibers such as wood, bamboo, wheat straw, rice straw, lemongrass powder, nano fibrillated cellulose, grape stalks, coir, and starch in related research reports (Manikandan *et al.* 2020; Anjana *et al.* 2021; Mochane *et al.* 2021).

Lignocellulosic biomass fibers have been used as reinforcing fillers and substitutes in polymers for preparing green composites due to their advantages of environmentally friendly (renewable, completely or partially recyclable), low in price, available in large quantities, low density and biodegradability (Bartos *et al.* 2020; Marina *et al.* 2020; Dixit *et al.* 2021; Jiang *et al.* 2021). Mohammad *et al.* (2023) prepared fully biodegradable polymer composites by melt mixing of polylactic acid (PLA), PBS, and natural polymers including corn starch and wheat straw. According to their results obtained from optimizing the effects of independent variables on the mechanical properties of the bio composite sheet, the optimal formulation for the PLA, PBS, and natural fiber biopolymers blend were 48.2 wt%, 45.4 wt%, and 6.4 wt%, respectively. The values of elastic modulus, elongation at break, impact strength, and equilibrium moisture content for optimized bio-composite were 80.8 MPa, 11.4%, 2 kJ/m<sup>2</sup>, and 4.1%, respectively. Additionally, the biodegradability rate for the bio composite was 71.1% in the fifth month of their test. Robledo-Ortíz *et al.* (2021) prepared sustainable bio composites by using sugarcane straw as a reinforcement of commercial biopolymers through dry-blending and compression molding. Their results showed that the tensile and flexural strength of PLA, PHB, and polyhydroxy butyrate-co-hydroxy valerate (PHBV) based bio-composites were around 20 MPa. Zhu *et al.* (2018) studied the effects of lignocellulosic components (including cellulose, hemicellulose, and lignin) on the mechanical strength of sisal fiber as well as the interfacial strength between sisal fiber and polymer matrix. Their results indicated that the appropriate content of cellulose, hemicellulose, and lignin benefits the enhancement of the tensile strength for sisal fiber and the interfacial quality between different components.

Generally, the strong polarity and hydrophilicity of lignocellulose fibers results in poor interfacial and incompatibility with hydrophobic materials (Karakus 2016; Bartos *et al.* 2020; Marina *et al.* 2020; Qi *et al.* 2022). Pretreatments of lignocellulose fiber (such as chemical, physical, biological, and physicochemical methods) can enhance compatibility and improve the interfacial interactions between hydrophilic biomass fiber and hydrophobic polymer matrix (Dixit and Yadav 2019; Saratale *et al.* 2020; Dixit *et al.* 2021). NaOH treatment removes a portion of impurities, lignin, hemicellulose, and waxes in lignocellulosic fibers to improve the interaction between biomass and high molecular polymer as well as to improve the mechanical performances (including strength and stiffness) of composite materials (Feng *et al.* 2020; Dixit *et al.* 2021). Based on the published results (Bahrami *et al.* 2021; Bahrami and Bagheri 2022), silane coupling agent played an important role in promoting covalent bonding between the hydrophobic polymer matrix and the fibers. The compatibility between the hydrophobic polymer matrix and the hydrophilic fiber as well as the strength of the composite can be improved. Currently, no relevant studies have been reported on the preparation of novel biodegradable composites from PBS, PHB, and lignocellulosic fiber. In this study, a PHB/PBS blend was used as polymer matrix and four kinds of lignocellulosic biomass fiber (bamboo, rice husk, rice straw, and peanut husk) were used as filling materials. NaOH modification of fiber was carried out. Different analytical techniques were used to characterize and compare the performance of different biomass fiber-based composites. The purpose of this study was to produce promising biodegradable polymer and lay a foundation for further research on environmentally friendly composite materials.

## EXPERIMENTAL

### Materials

Four kinds of lignocellulosic biomass fibers (bagasse, bamboo, rice husk and rice straw) were purchased from Lianfeng Agricultural Products Deep Processing Co. LTD, Jiangsu Province, China. Bagasse, bamboo, rice husk and rice straw were oven-dried at 80 °C for 24 h and sieved through a 100 mesh (mean particle size between 0.154 and 0.125 mm).

Alkali treatment of four kinds of lignocellulosic biomass fibers: Biomass fibers (bagasse, bamboo, rice husk and rice straw) were placed into 9 w/v% NaOH aqueous solution for 24 h at room temperature. After alkali treatment, biomass fiber residues were filtered and washed to neutrality by deionized water. NaOH treated biomass fiber was oven-dried at 80 °C for 12 h for further experiments.

Poly- $\beta$ -hydroxybutyrate (PHB) and poly(butylene succinate) (PBS) (TH803S), both size 100-mesh, were procured from ShunJie Plastic Technology Co., Ltd., Guangdong Province, China.

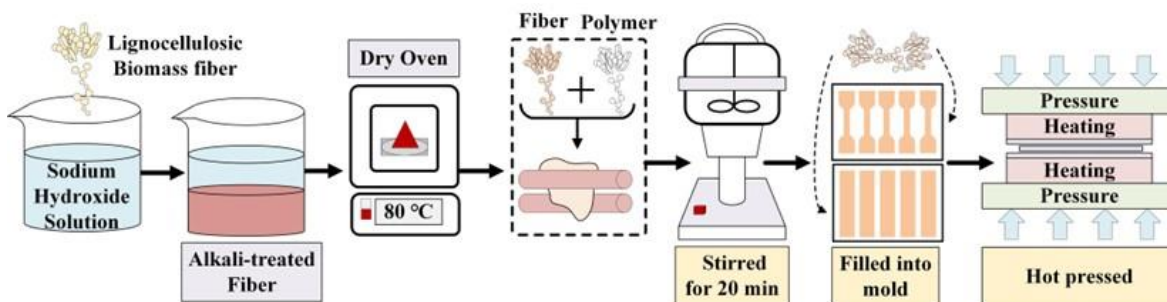
Silane coupling agent (KH-580) was purchased from Shanyi Plastic Chemical Co., Ltd., Guangdong Province, China. KH-580 (3-Mercaptopropyltriethoxysilane), CAS RN: 14814-09-6, EINECS number: 238-883-1, Molecular formula:  $C_9H_{22}O_3SSi$ , Molecular weight: 238.4197. KH-580 was used to treat inorganic fillers and plays the role of active agent, coupling agent, crosslinking agent, and reinforcing agent in polymers. Packaging and storage: Plastic drum packaging. This product (liquid) should be kept sealed in a cool, ventilated place.

### Preparation of Lignocellulosic biomass fiber/PHB/PBS Bio-composites

Alkali treated biomass fiber residues were modified with 5 wt% KH-580 solution (silane coupling agent) and dried in an oven at 80 °C. Matrix ratio: PHB and PBS were mixed in a ratio of 7:3. Our practical aim was to produce a plate composite that would be comparable to conventional materials and extend the range of applications for composites. The ratio (7:3) has been chosen in accordance with the practical purpose of producing plates of a certain strength and on the basis of the results of the pre-tests. The ratio of the polymer matrix and biomass fiber were 85% and 15%, respectively. Bio-composites were prepared by using hot-pressing method. The specific composition of the composites (by dry mass) was shown in Table 1.

**Table 1.** Ingredients for Bio-composites

Lignocellulosic Fiber	PHB (g)	PBS (g)	Fiber Weight (g)	Total Weight (g)
Bagasse	23.8	10.2	6	40
Bamboo	23.8	10.2	6	40
Rice husk	23.8	10.2	6	40
Rice straw	23.8	10.2	6	40



**Fig. 1.** Preparation process for lignocellulosic biomass fiber/PHB/PBS Bio-composite

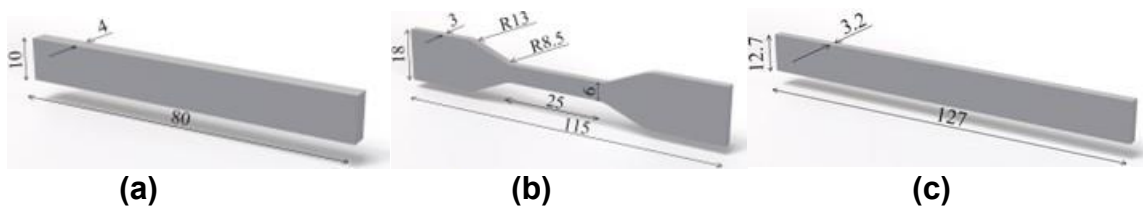
Polymer matrix and biomass fibers were mixed evenly for 20 to 25 min. The uniformly mixed materials were hot pressed after filled into the standard mold to prepare bio-composites. The conditions for hot pressing were 10 MPa under 160 °C for 20 min. The preparation process of lignocellulosic biomass fiber/PHB/PBS Bio-composite was depicted in Fig. 1.

### Composition Analyses of Lignocellulosic Biomass Fiber

The National Renewable Energy Laboratory (NREL) Method – Determination of Structural Carbohydrates and Lignin in Biomass – was used in this study to determine the component content of lignocellulosic biomass fiber (Sluiter *et al.* 2008). The content of cellulose, hemicellulose, and lignin for bagasse, bamboo, rice husk, and rice straw were investigated.

### Mechanical Properties

The dimensions for all bio-composite samples prepared for the bending strength test were 127 mm length  $\times$  12.7 mm width  $\times$  3.2 mm thickness referring to ASTM standard D790 (2017). A universal testing machine was used in this article (KRWDW-100E, Jinan Kerui Testing Machine Manufacturing Co. LTD, Shandong, China). Dumbbell-type samples (115 mm length  $\times$  6 mm width  $\times$  3 mm thickness, gage length 25 mm) were prepared for tensile strength test referring to ASTM D412 (2021). PC Auto Tensile Tester was used for testing (DLS-07, Jinan Sun spring Experimental Instrument Co. LTD, Shandong, China). The impact strength of composites (dimension 80 mm  $\times$  10 mm  $\times$  4 mm) was measured by using digital display impact testing machine (ST-5.5D, Xiamen Ester Instrument Co., LTD, Fujian, China) according to ISO 180 (2019).



**Fig. 2.** The dimension for all bio-composite samples prepared for the test of mechanical strength (a: bending strength; b: tensile strength; c: impact strength)

### FTIR Analysis

Fourier transform infrared spectroscopy analysis (IS50, Thermo Fisher Scientific, USA) was conducted to obtain the infrared spectra of bio-composites (Feng *et al.* 2020).

0.001 g of sample powder (oven-dried at 80 °C for 8 h) was used for FTIR analysis attenuated total reflection mode with resolution of 4 cm<sup>-1</sup> and 32 scans over a range of 500 to 4000 cm<sup>-1</sup>.

### Thermogravimetric Analysis

The thermogravimetric curves for composite materials were determined in this work. A thermogravimetric analyzer was used to test the thermostability for composite samples (TGA 8000, PerkinElmer, Inc, USA). The mass of composite samples was 10 to 20 mg with the heating rate under 10 °C/min. The protective gas (N<sub>2</sub> atmosphere) rate was 20 mL/min. The temperature range was room temperature to 600 °C according to ASTM E1131 (2020).

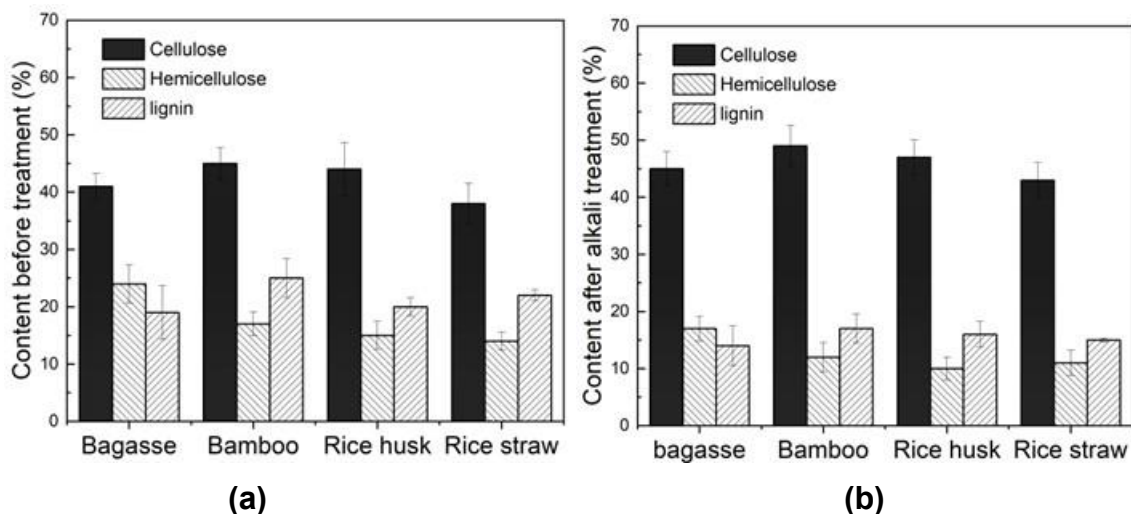
### Morphology Analysis

The surface morphological property for lignocellulosic biomass fiber/PHB/PBS composites (including bagasse/PHB/PBS composite, bamboo/PHB/PBS composite, rice husk/PHB/PBS composite, and rice straw/PHB/PBS composite) was measured. The surface of the samples was treated after being sprayed with gold for 1 minute using an ion sputtering device (Feng *et al.* 2020). Field emission scanning electron microscopy (SU5000, Hitachi High Technology Co, Japan) was used to analyze the microscopic morphology of composite samples.

## RESULTS AND DISCUSSION

### Compositional Analysis of Lignocellulosic Biomass Fiber

The compositional analyses for lignocellulosic biomass fiber (bagasse, bamboo, rice husk, and rice straw) are depicted in Fig. 3. The cellulose content for native bagasse, bamboo, rice husk, and rice straw were between 38% and 45%. The cellulose content for bamboo was 7% higher than rice straw. The content of hemicellulose for four native lignocellulosic biomass fibers was 24%, 17%, 15%, 14%, respectively.



**Fig. 3.** Compositional analysis result for lignocellulosic biomass fiber (a: before alkali treatment; b: after alkali treatment)

The lignin content for four native biomass samples were 19%, 25%, 20%, and 22%, respectively. The total fiber content in terms of cellulose, hemicellulose, and lignin for native bamboo was the highest among four lignocellulosic fiber samples, which was 13% higher than rice straw.

Figure 3b shows that after NaOH treatment, the content of hemicellulose and lignin for four samples (on dry basis) decreased to varying degrees. A possible explanation for this phenomenon was that alkali treatment could dissolve a portion of the biomass components (hemicellulose, lignin, and other macromolecules) as well as decrease the content of obstacles (Bartos *et al.* 2020). Here, the word obstacles mean any substance that occupies space in a contact zone without providing a suitable combination of interfacial bonding and cohesive strength. The complex structure for lignocellulose biomass could be partially destroyed, which is helpful for increasing the contact area between lignocellulose biomass materials and polymeric matrix as well as contributing to the subsequent preparation of bio-composites (Mochane *et al.* 2021). Figure 3b also exhibits the relative increase of desirable cellulose content in lignocellulosic biomass fibers after alkali treatment. Similar results were observed by Dixit *et al.* (2021). The mechanical properties of biomass fiber-polymeric composites are influenced by the strength of biomass fibers, the strength of polymeric matrix, and the compatibility between them (Marina *et al.* 2020). Generally, the strength of biomass fibers is affected by the cellulose content (Feng *et al.* 2020). The cellulose content and total fiber content for both native and alkali treated bamboo fiber were the highest among four biomass fiber samples. The cellulose content for rice straw (both before and after NaOH treatment) was the lowest. Therefore, biomass fibers with higher cellulose content (bamboo) tended to be chosen as reinforcement filler for wood-plastic biomass composite materials.

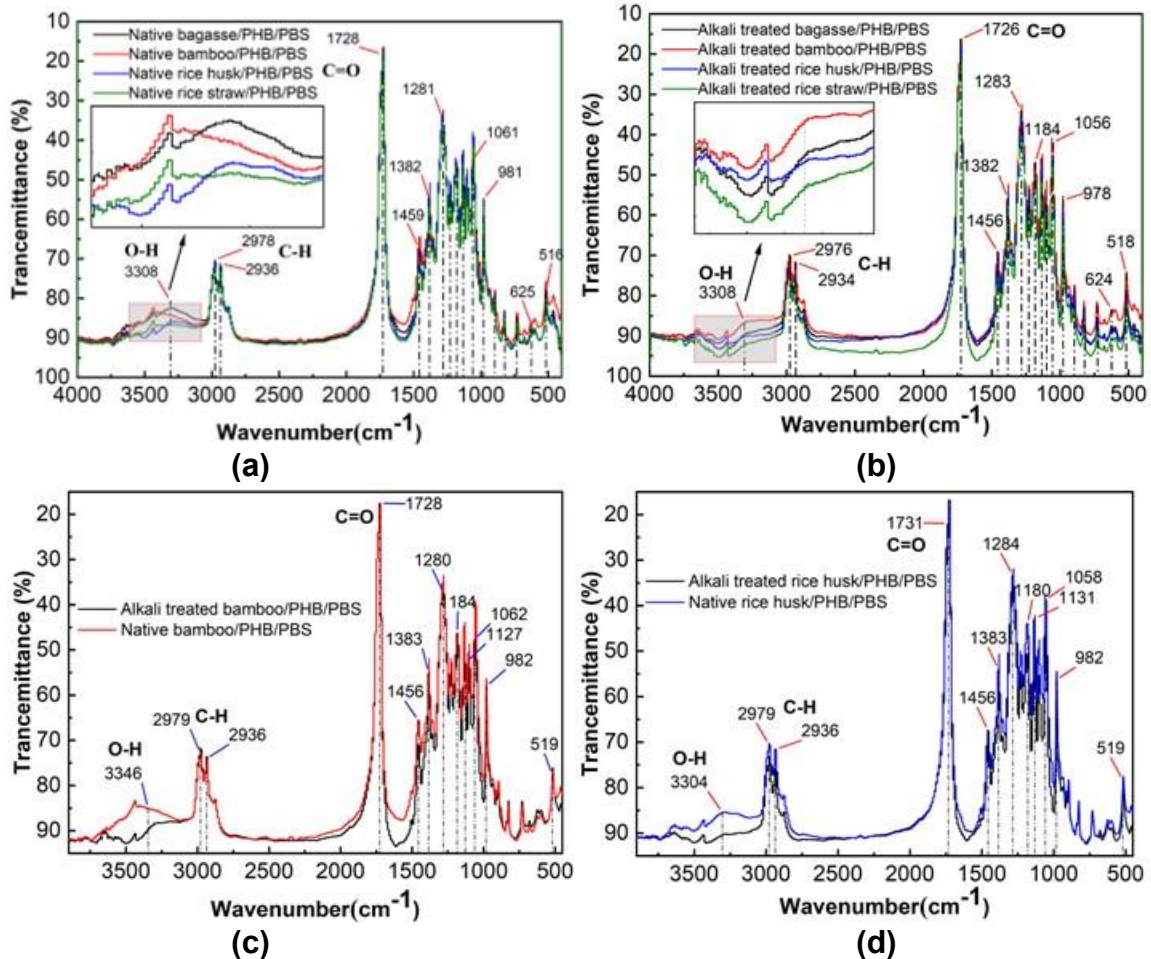
### FTIR Spectroscopy

The FTIR spectroscopy results are shown in Fig. 4. Characteristic absorbance peaks around  $3300\text{ cm}^{-1}$  corresponded to the telescopic vibration of -OH groups. All biomass fiber-based composite samples have characteristic absorbance peaks near this waveband, which represented the hydroxyl groups in lignocellulose components (including cellulose, hemicellulose, and lignin) of bagasse, bamboo, rice husk, and rice straw (Feng *et al.* 2020).

Double peaks in the range of  $3000$  to  $2850\text{ cm}^{-1}$  represented the stretching vibration of C-H. The peak around  $1465$  to  $1340\text{ cm}^{-1}$  represented the bending vibration of C-H in cellulose, hemicellulose, and lignin of bagasse, bamboo, rice husk, and rice straw as well as main chain of PHB and PBS. The absorbance peak in the range of  $1750$  to  $1700\text{ cm}^{-1}$  corresponded to carbonyl groups, which mainly come from PHB, PBS, hemicellulose, and grease on biomass fiber. The stretching vibration peak around  $1300$  to  $1000\text{ cm}^{-1}$  stands for the ether bond (C-O and aliphatic ether), which could be found in all bio-composite samples. C-O stretching vibration absorption in the range of  $1270$  to  $1230\text{ cm}^{-1}$  (Ar-O stretching) and  $1050$  to  $1000\text{ cm}^{-1}$  (R-O stretching) represented the presence of aromatic oxide which could be found in lignin of lignocellulose fiber.

As shown in Figs. 4a and 4b, there were significant differences between four kinds of fiber-based composites near the characteristic absorbance peaks of lignocellulosic components (near  $3300\text{ cm}^{-1}$ ). For native and alkali treated biomass fiber-based composites, the differences near this waveband corresponded to the compositional analysis result for native and alkali treated lignocellulosic biomass fiber (Fig. 3). Both the total fiber content and cellulose content for bamboo fiber before and after alkali treatment were the highest

among four fiber samples. The cellulose content for native bagasse and bamboo was higher than rice husk and rice straw. For NaOH treated biomass fiber that used in the following process of preparing composite materials for testing mechanical properties, the total fiber and cellulose content for rice straw was the lowest.



**Fig. 4.** FTIR analyze results for different samples (a: native biomass fiber-based composites; b:alkali treated biomass fiber-based composites; c: native and treated bamboo fiber-based composites; d: native and treated rice husk-based composites)

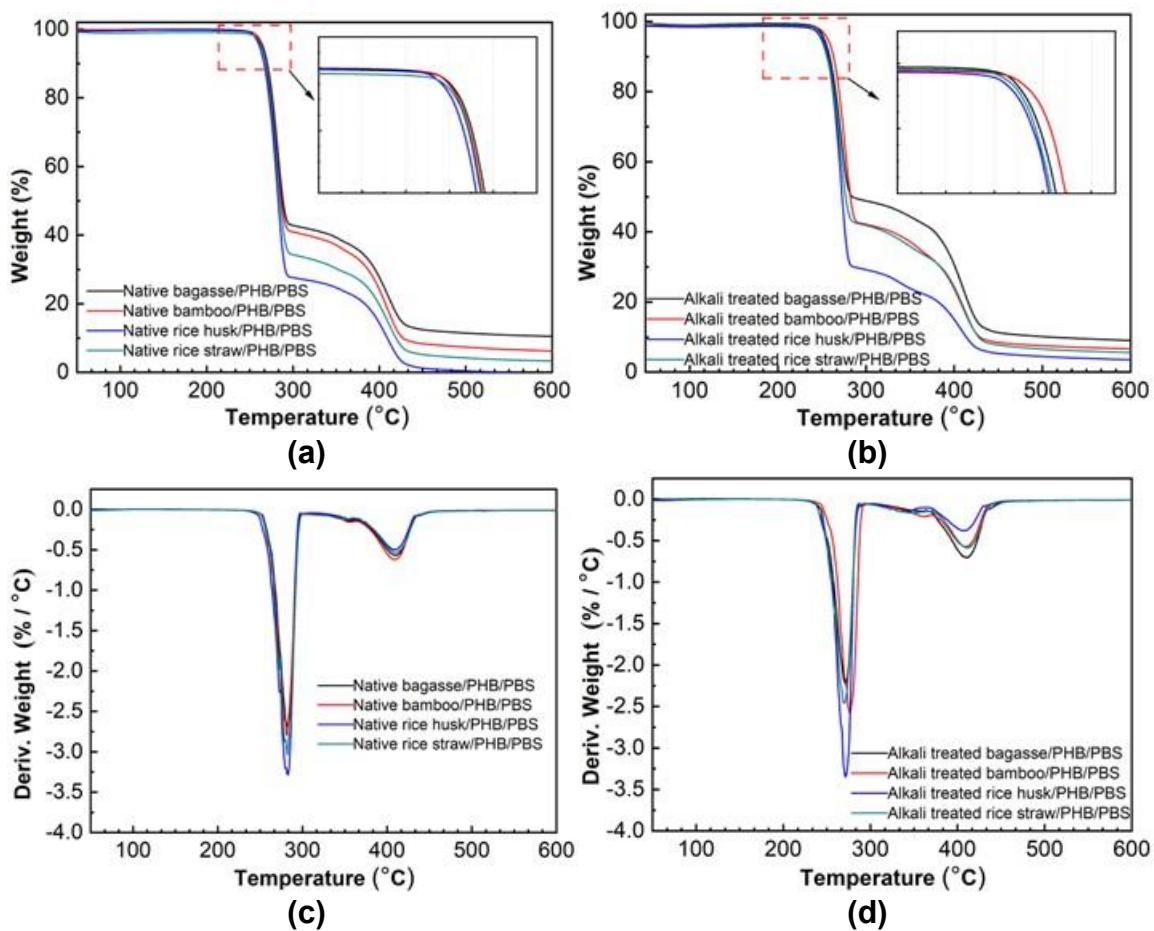
Taking bamboo fiber as an example (Fig. 4c), the transmittance of the alkali treated bamboo fiber-based composite around 3300 cm<sup>-1</sup> (the intensity of the -OH group) was significantly decreased compared with native bamboo fiber-based composite. The reason was probably that NaOH treatment dissolved a portion of lignin and hemicellulose as well as destroyed the hydroxyl groups in bamboo fiber. This result corresponded to the composition analysis result of biomass fiber above (Figs. 3a and 3b). The opening of a portion of hydrogen-bond interaction could swell up the fiber. Therefore, hydrolyzed silane coupling agent could be combined with the hydroxyl groups in biomass fiber more easily. The formation of new hydrogen bonds could improve the hydrophobicity of fibers and the binding ability of fibers with polymer matrix. The absorption intensity for the bimodal around 2900 cm<sup>-1</sup> was not changed obviously. The absorbance intensity of carbonyl group for native bamboo fiber-based composite in the range of 1750 to 1700 cm<sup>-1</sup> was higher than



NaOH treated bamboo fiber-based composite. A possible reason was that NaOH treatment could wash away a portion of the oily layer on the surface of fiber, reduce the compositional content (lignin component) of biomass fiber as well as increase the contact area between fiber and other high polymer materials. The suitability, accessibility, and adhesion for treated bamboo fiber in polymer matrix could be improved after removing a portion of the fibrillar components (Bartos *et al.* 2020; Dixit *et al.* 2021). Figure 4d showed similar trends for native and alkali treated rice husk-based composites. The absorbance peak for the characteristic group of KH-580 (-SH) was difficult to be observed in the infrared spectrogram.

### Thermogravimetric Analysis

The TG and DTG curves for the four kinds of composites are shown in Fig. 5. According to the result in Figs. 5a and 5c, the weight loss process for different kinds of composite samples could be roughly divided into 3 parts. During the first stage (from 100 to 251 °C), there was a slight decline in the mass of composite samples (about 0.63 to 2.39%). The volatilization for small molecular compounds and evaporation of water in composite sample occurred in this stage (Feng *et al.* 2020).



**Fig. 5.** TG and DTG analyses for composites (a: TG of native biomass fiber-based composites; b: TG of alkali treated biomass fiber-based composites; c: DTG of native biomass fiber-based composites; d: DTG of alkali treated biomass fiber-based composites)

During the second stage (between 251 and 431 °C), all the curves exhibited drastic declines in weight. Lignocellulosic biomass fiber, PHB and PBS matrix mainly decomposed during this process and caused mass loss. Generally, lignocellulosic fiber, PBS (pyrolyzed from 310 to 430 °C), and PHB are thermally decomposed in sequence (Mochane *et al.* 2021; Aliotta *et al.* 2022; Kumar *et al.* 2023). According to the published literature (Feng *et al.* 2020), the temperature range of the main mass loss of the fibers was between 200 °C and 380 °C. The lignocellulosic components are pyrolyzed sequentially. The pyrolysis temperature for cellulose, hemicellulose, and lignin was reported as 180 to 240 °C, 230 to 310 °C and 300 to 400 °C, respectively. The initial pyrolysis temperature of the pure fibers was slightly lower than that of the straw fiber-based composites. The pyrolysis temperature range of the pure fibers was also shorter than that of the straw fiber-based composites (matrix wrapped fiber).

According to published results (Cristina *et al.* 2015; Radu *et al.* 2021), the thermal analysis of pure PHB showed a major thermal degradation stage at around 230 to 280 °C, with a mass loss of around 90% for PHB degradation. There was further loss of mass due to residual organic matter and ash in pure PHB between 270 and 700 °C. Wu *et al.* (2017) showed that the TG curves of PBS and PBS-based copolymers were quite similar in shape. This result indicated that there was no significant difference in the mechanism of the thermal degradation of the materials. The initial weight loss was generally due to the loss of volatiles, the second stage started at around 300 °C, and the final stage (above 400 °C) was the main degradation zone of PBS (Li *et al.* 2013).

The second stage of degradation for native bagasse, bamboo, rice husk, and rice straw-based bio-composites started at around 250 °C with 0.75% weight loss, 251 °C with 0.81% weight loss, 247 °C with 0.63% weight loss, and 249 °C with 1.49% weight loss, respectively. The initial thermal-degradation temperature for bagasse, bamboo, rice husk, and rice straw-based bio-composites was similar. The second stage of degradation for alkali treated bagasse, bamboo, rice husk, and rice straw-based bio-composites started at around 240 °C with 1.28% weight loss, 248 °C with 2.39% weight loss, 240 °C with 2.18% weight loss and 239 °C, with 1.49% weight loss, respectively. The initial pyrolysis temperature for alkali modified bamboo-based composite was higher than the other three samples (Figure 5b). Comparing Fig. 5a with 5b, the main mass loss temperature range of native fiber-based composites started at around 247 to 251 °C, and the main mass loss temperature range of alkali modified fiber-based composites started at around 239 to 248 °C. The thermal degradation for all composite samples ended at around 432 to 437 °C for native fiber based composite samples and 437 to 440 °C for alkali treated fiber based composite samples. The pyrolysis temperature span for alkali modified fiber-based composites was slightly longer than that of native fiber based composite materials.

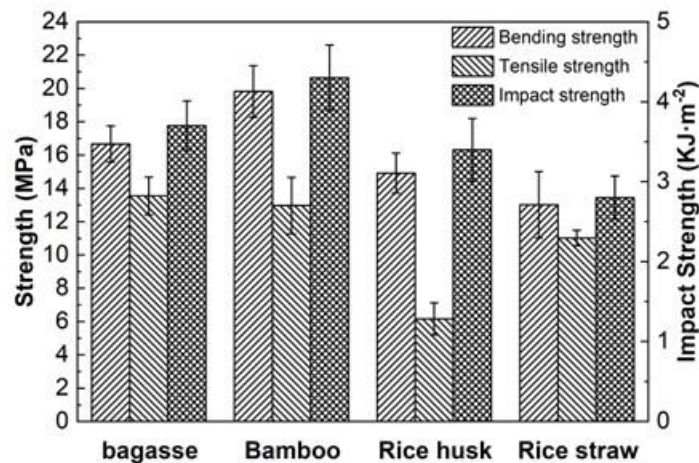
The third stage of degradation started when the temperature was raised up to 440 °C. Pyrolysis residues were carbonized and decomposed further in this stage. The mass of samples declined continuously and tended to be gradually stabilized. The residual amounts for native bagasse, bamboo, rice husk, and rice straw-based bio-composites were 9.85%, 4.21%, 0.01%, and 2.64%, respectively. The pyrolysis residuals for alkali modified bagasse, bamboo, rice husk, and rice straw-based bio-composites were 8.35%, 5.81%, 2.77%, and 4.79%, separately. The residual for bagasse-based composites was higher than the other three samples. The residual of rice husk-based composite was the lowest. Figure 5c and 5d show the pyrolysis speed for composites. The pyrolysis speed for four kinds of native biomass fiber-based composites was similar (Fig. 5c). The pyrolysis rate of alkali treated

rice husk-based composite was slightly higher than that of other samples (Fig. 5d). Moreover, it can be seen from DTG curves (Figs. 5c and 5d) that the mass loss rate of the treated bagasse, bamboo, and rice straw-based composites decreased slightly compared to native fiber-based composites. Longer pyrolysis temperature span and lower mass loss rate represents better thermogravimetric stability of alkali modified fiber-based composites than native fiber-based composites. Similar outcomes have been published by Dixit *et al.* (2021).

Additionally, it can be concluded from Fig. 5 that the thermal stability for NaOH-treated bamboo fiber/PHB/PBS composite was slightly superior to the other three composites according to the result of initial thermal-degradation temperature (248 °C), moderate pyrolysis speed, and moderate amount of pyrolysis residue (5.81%).

### Mechanical Properties of Fiber/PHB/PBS Bio-composites

The mechanical property for bio-composites based on alkali treated lignocellulosic biomass fiber/PHB/PBS were examined. The bending strength, tensile strength, and impact strength for four kinds of bio-composites are shown in Fig. 6. The bending strength for alkali treated bagasse, bamboo, rice husk, and rice straw-based bio-composites were 16.67, 19.82, 14.91, and 13.01 MPa, respectively. The tensile strength for four kinds of NaOH treated biomass fiber-based bio-composites were 13.55, 12.97, 6.16, and 11.02 MPa, respectively. Moreover, the impact strength for modified fiber-based bio-composites were in the range of 2.80 to 4.30 kJ/m<sup>2</sup>. Mechanical properties play an important role in the preparation of high-quality composite materials. Under the same condition of polymer matrix, the strength of composites could be influenced significantly by the strength of biomass fiber.



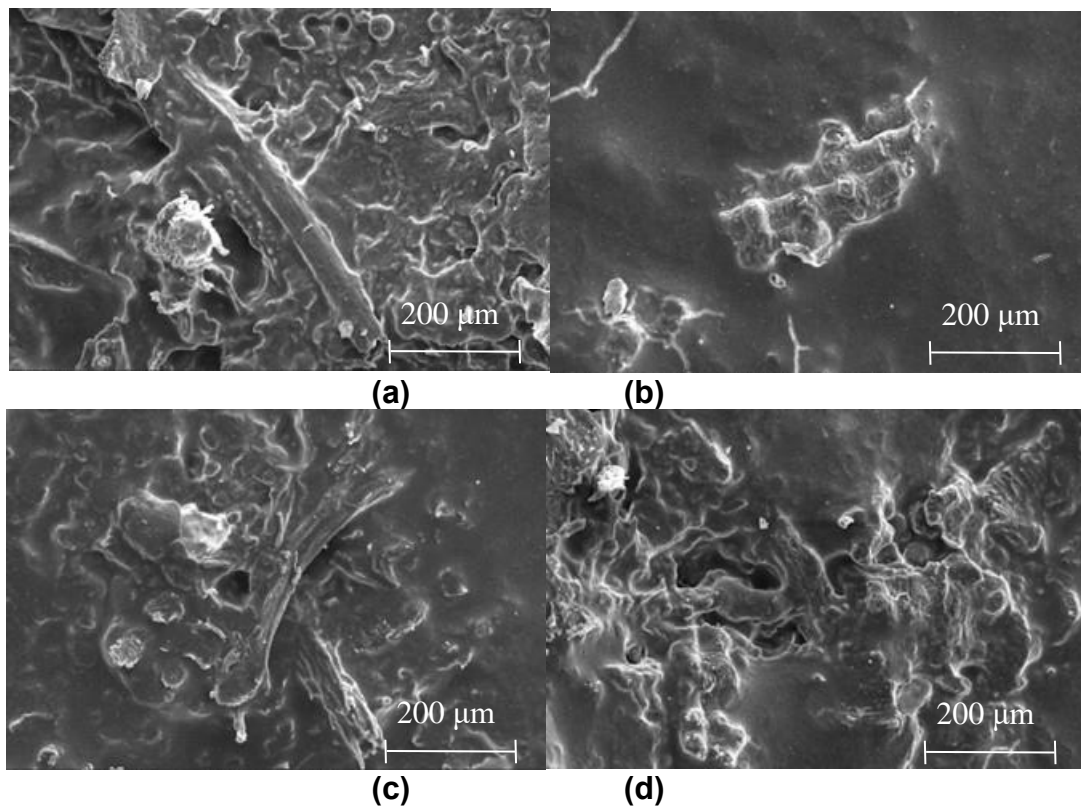
**Fig. 6.** Mechanical properties for four kinds of lignocellulosic biomass fiber/PHB/PBS bio-composites

The mechanical properties of lignocellulosic fibers are correlated with the content of cellulose and lignin. Cellulose mainly improves the bending strength of lignocellulosic fibers, whereas lignin negatively affects the tensile properties (Feng *et al.* 2020). As stated above, the cellulose content for bamboo fiber was the highest as compared to the other three lignocellulosic biomass fibers (both before and after alkali treatment). Alkali-treated bamboo reinforced bio-composite resulted in better strength values when compared with the other materials (Fig. 6). The performance of mechanical properties was consistent with the results of composition analysis in Fig. 3. The adhesion between polymer matrix and

alkali treated bamboo fiber could be better when the external force for biomass fiber and polymers was transmitted uniformly, while the stress concentration was avoided effectively, and the interfacial quality incremented notably. The bending strength and impact strength for NaOH treated rice straw/PHB/PBS bio-composite were the lowest. The tensile strength of pretreated rice husk-based composite was lower than that of the other samples. The reason was probably that the fiber structure of rice straw was soft, loose, and low in strength. The relatively high lignin content of rice husk affected its tensile property negatively. Alkali treated bagasse/PHB/PBS composite had moderate bending resistance, tensile strength, and impact strength. Better mechanical properties for modified bamboo fiber/PHB/PBS demonstrated its potential and suitability for preparing novel bio-composites (Zhu *et al.* 2018; Kumar *et al.* 2023).

### Morphology Analysis of Fiber/PHB/PBS Bio-composites

The microscopic morphology structure for alkali treated bagasse, bamboo, rice husk, and rice straw-based bio-composites are displayed in Fig. 7, which represents 500 x magnification for bio-composite samples. As shown, the best interfacial quality for biomass fiber and polymer material was the modified bamboo fiber/PHB/PBS composite, while the worst interfacial quality for biomass fiber and polymer material was the treated rice straw. A relatively plain surface for pretreated bamboo fiber-based bio-composite was observed in Fig. 7b.



**Fig. 7.** Microscopic morphology analysis of four kinds of lignocellulosic biomass fiber-based composites (a: bagasse/PHB/PBS composite, 500X magnification; b: bamboo/PHB/PBS composite, 500X magnification; c: rice husk/PHB/PBS composite, 500X magnification; d: rice straw/PHB/PBS composite, 500X magnification)

It can be seen from the figure that the treated bamboo fiber was intimately bound to the matrix materials (PHB and PBS) and that it was uniformly dispersed. There were no obvious void defects in the microscopic morphology and no significant delamination between components for the alkali treated bamboo fiber-based composite compared to the other three samples. Uniform distribution, strong adhesion, and good mixing ability of NaOH-treated bamboo fiber in the matrix were observed after hot pressing. The interfacial friction between fiber and matrix increased after the solidification of composite materials. Alkali modification could disrupt the complex structure of lignocellulosic components (including cellulose, hemicellulose, and lignin), increase the roughness of the fiber surface, and improve the compatibility and degree of bonding of the fiber with polymer materials in the molten state (Bartos *et al.* 2020; Dixit *et al.* 2021). Silane coupling agent was used to enhance the compatibilization of biomass fiber, PHB and PBS.

The roughness and voids of the surface for the other three fiber-based composites increased significantly compared with alkali treated bamboo fiber-based composite. This result was consistent with the higher mechanical performance results above (Fig. 6). Rice straw was low in strength with loose structure and absorbed water easily (Qiao *et al.* 2022). Thus, the morphological structure of the rice straw-based composites could be affected (Fig. 7d). Small cracks were formed probably in the process of hot pressing molding process due to water vapor, which makes it difficult for fiber and polymer matrix to integrate closely (Feng *et al.* 2020). This resulted in poor interfacial quality and mechanical properties of rice straw-based composite. The cross-sectional interfacial quality for bio-composite filled with bagasse and rice husk was similar, which ranked only second to the composite filled with bamboo fiber and higher than that of the rice straw-based composite. The structure of bagasse and rice husk was relatively dense (compared to bamboo fiber and rice straw), which was easily wrapped by the PHB and PBS polymer matrix during the hot pressing process (Feng *et al.* 2020; Dixit *et al.* 2021).

The silane coupling agent (KH-580) was used in the preparation process of NaOH-treated lignocellulosic biomass fiber/PHB/PBS composite. On the basis of the published results, the silane coupling agent was a critical treatment in promoting the compatibility between the fibers and the polymer matrix (Bahrami and Bagheri 2022). In the absence of the silane coupling agent, large gaps may appear between the matrix and the fiber. The dispersion between the matrix and the fiber could be particularly poor.

In general, the stiffness, surface roughness, and compactness of structure for biomass fibers was directly proportional to the interfacial quality for the four kinds of lignocellulosic biomass fiber reinforced PHB/PBS bio-composites.

## CONCLUSIONS

1. The incorporation of four kinds of lignocellulosic biomass fibers (bagasse, bamboo, rice husk, and rice straw) into poly- $\beta$ -hydroxybutyrate and poly(butylene succinate) (PHB/PBS) matrix was carried out for the preparation of novel bio-composites. Prepared composite materials were characterized by compositional analyses, Fourier transform infrared (FTIR) analysis, thermogravimetric (TG) and differential thermogravimetric (DTG) analysis, mechanical properties, and morphological property analysis. The interfacial quality, accessibility, thermal stability, and comprehensive mechanical properties for alkali treated bamboo/PHB/PBS composite was found to be

the best among four kinds of modified lignocellulosic fiber-based composites, which demonstrated its suitability for reinforcing degradable materials to produce environmentally friendly composites.

2. The cellulose content and total fiber content for both native and alkali treated bamboo fiber were the highest among four biomass fiber samples. The TG curves for four kinds of lignocellulosic fiber/PHB/PBS composites were similar. The thermal stability for NaOH-treated bamboo/PHB/PBS composite was slightly superior to the other three composites, with the initial decomposition temperature of 248 °C, moderate pyrolysis speed, and moderate amount of pyrolysis residue (5.81%). The bending strength, tensile strength, and impact strength for alkali treated bamboo/PHB/PBS composite was 19.82 MPa, 12.97 MPa and 4.30 kJ/m<sup>2</sup> respectively. The mechanical properties of modified rice straw/PHB/PBS composites were the worst. Experimental results indicated that novel composites based on alkali treated bamboo had relatively high interfacial adhesion between PHB and PBS components with no obvious voids.

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