Study on the Acetylation of Rice Straw-Biogas Residue and its Characteristic Effect on Rice Straw-Reinforced Composites

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To improve the compatibility between rice straw and reinforcing polymers, rice straw (RS) was pretreated by an anaerobic process, and its biogas residues (BR) were acetylated with acetic anhydride (AA) to prepare acetylated biogas residues (ABR). The optimum conditions of acetylation were determined by orthogonal experiments. When acetylation was performed at 140 °C with 10 mL AA/g BR and 0.08 g catalyst/g BR, the maximum weight gain rate (WGR) obtained was 23.7%. Fourier transform infrared (FTIR) analysis showed that many hydroxyl groups were displaced by acetoxy groups. Scanning electron microscopy (SEM) showed that many defects of BR were filled by the acetylation, and an ester layer was formed over the BR surface. However, the lower crystallinity of ABR than the BR and RS affected the mechanical properties of acetylated biogas residue/low density polyethylene (ABR/LDEP) composite. Interestingly, the BR and ABR showed higher onset decomposition temperature, but they exhibited faster decomposition rates because of the lower crystallinity of BR and ABR. Furthermore, the mechanical properties of the RS/LDEP, BR/LDEP, and ABR/LDEP composites were analyzed. Compared with RS/LDEP composites, the BR/LDEP and ABR/LDEP composites showed obviously better tensile and flexural properties. Consequently, rice straw fibers attained excellent compatibility with non-polar polymers.

Keywords: Biogas residues; Acetylation; Polarity; Compatibility; Mechanical properties

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INTRODUCTION

As abundant renewable resources, plant fibers have the advantages of low density, suitable properties, and low price. Hence, they have been researched intensively and applied to biogas production and composites (Pandey *et al.* 2010; Shah 2013). At the same time, plant fibers, especially agricultural residues, are utilized to produce bioenergy. For example, rice straw fermentation produces ethanol as the renewable fuel for industries and vehicles (Singh and Bishnoi 2012; Thomsen *et al.* 2014). In addition, biogas is produced by anaerobic digestion of agricultural straw materials such as wheat straw, rice straw, and corn straw *etc.*; as clean energy fuel, biogas decreases the utilization of fossil fuel (Yao *et al.* 2013). However, only a fraction of biogas residues are used as organic fertilizers, and most are discarded because of difficult treatment processes (Song *et al.* 2015). Furthermore, plant fibers have been widely researched as reinforcing polymer composites such as rice straw fiber-reinforced high-density

polyethylene (Yao *et al*. 2008), rice straw fiber/ poly lactic acid composite (Zhao *et al.* 2011), wheat straw and corn stem filled polypropylene composites (Panthapulakkal *et al.* 2006), and banana fiber-reinforced composites (Liu *et al.* 2009). Plant fibers effectively improve the properties of polymer composites. Rice straw is an especially rich resource, and it has been studied as a reinforcing material in composites (Shah 2013). Nevertheless, biogas residues containing lignocellulose have not been developed as reinforcing fillers. Although the plant fibers are used in composites, the lignocellulosic materials have strong polarity and hydrophilic character, which are attributed to the presence of hydroxyl groups. As a result, the rice straw fibers are generally incompatible with the hydrophobic polymer matrix as reinforcing materials (Khalil *et al.* 2001; Paul *et al.* 2010). In addition, some pectin and wax present on the surface of rice straw fibers impede the chemical modification in the interface between straw fibers and matrix. To solve these problems, pretreatment and other modifications have been explored. These methods are divided into three types including physical methods, chemical methods, and biological methods.

Physical methods involve heat treatment (Chen *et al.* 2015), mechanical-high pressure steam technique, and electron irradiation. The mechanical-high pressure steam technique is also a method of heat treatment. It uses high temperature and pressure to change the crystalline structure of rice straw fibers and thus partially remove hemicellulose and lignin. This method improves the fibers' crystallinity and thermal stability (Chen *et al.* 2011, 2013). Moreover, electron beam assisted coupling agents can be used to modify rice straw fibers, and increasing the electron beam irradiation dose in a certain range improves the flexural strength, modulus of elasticity, and impact strength of composites, and reduces the hydroscopicity of composites (Ismail *et al.* 2012).

Chemical methods are most frequently utilized to modify plant fibers because of the simple operations and better effects. Alkali treatment, especially sodium hydroxide solution, is the simplest method to pre-treat rice straw fibers in order to decrease the fibers' polarity and increase their compatibility with non-polar polymers (Jayamani *et al.* 2016; Tayfun *et al.* 2016). Alkali pre-treated wood powder increases biogas production by the disruption of lignocellulosic structures and by partial removal of hemicelluloses and lignin components (Lu *et al.* 2003; Yao *et al.* 2013).

Apart from alkaline reagents, coupling agents effectively strengthen the interaction between straw fibers and non-polar polymers, and they are able to promote thermal properties and mechanical properties such as tensile and flexural strengths of plant fiber composites (Khalil *et al.* 2001; Shih *et al.* 2012). In addition, many organic reagents have been introduced to improve the surface of plant fibers. For instance, the plant fiber-reinforced composites treated with maleic anhydride (MA) have lower water absorption and better mechanical properties than untreated composites (Mishra *et al.* 2000; Zhao *et al.* 2011).

Moreover, acetylation has been studied to modify plant fibers. When plant fibers react with acetic anhydride at a certain temperature, the acetyl group replaces the hydroxyl groups, which helps to link the plant fibers. This reaction process is showed in Fig. 1. These acetylated plant fibers acquire a smoother surface and better biological resistance than untreated plant fibers (Hill *et al.* 1998; Shah 2013), and acetylated plant fiber-reinforced polyester composites showed better mechanical properties (Khalil *et al.* 2007).

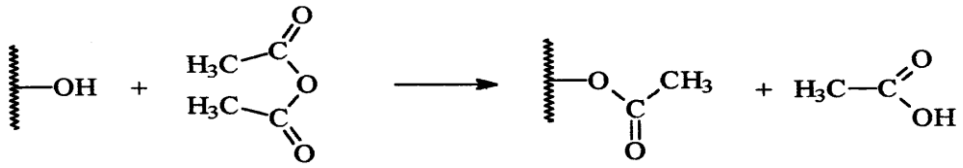

Fig. 1. Reaction of acetic anhydride and plant fibers

Biological methods include microbial treatments for modifying the straw fiber using bacterial culture, fungus, and enzymes. There are few biological methods available to modify straw fibers. Fungus has been used to degrade wheat straw; the mechanical strength and thermal property of wheat straw are effectively improved by fungal treatment (Sain and Panthapulakkal 2006; Panthapulakkal *et al.* 2006).

According to research into the biogas residues of rice straw, pectin and wax are mostly digested by anaerobic microorganisms, resulting in cellulose, hemicellulose, and lignin components exposed on the surface. Consequently, the digested rice straw can avoid chemical pretreatments such as benzene-ethanol extraction (Hill *et al.* 1998; Khalil *et al*. 2001). Biological methods play a significant role in decreasing the utilization of chemical reagents and thus protecting the environment. Moreover, the polarity and hydrophilic nature of rice straw fibers are slightly reduced as a result of partial digestion of cellulose and hemicellulose components in anaerobic processes. In the present study, rice straw was treated by a combination of biological and chemical methods. First, the rice straw was digested in anaerobic process, and then its biogas residues were acetylated with acetic anhydride. The optimum conditions for acetylation were determined by orthogonal experiments. The characteristic changes of rice straw fibers were then investigated by instrumental analysis to determine the feasibility of incorporating acetylated biogas residues into plant-fiber-reinforced composites.

EXPERIMENTAL

Preparation of Materials

Rice straw was obtained from a farm of Jiangsu Academy of Agricultural Sciences (China). It was ground to a 0.9-mm to 0.3-mm particle size. Rice straw powder (with moisture content about 3%) was oven-dried at 80 °C for 24 h. Waste activated sludge (total solids (TS), representing dry matter content in anaerobic digestion < 4%) was obtained from a pig farm in Jin Tan of Jiangsu province, China. Before the sludge was used in experiments, it was cultivated by adding 25 wt% sucrose solution for 2 days for the purpose of activating the microorganism in the sludge. Approximately 330 g of rice straw powder (8 wt%), 1670 mL water (42 wt%), and 2000 mL (50 wt%) waste activated sludge were added into a 5 L fermentation cylinder, which was stirred to mix the contents uniformly. The fermentation cylinders were tightly closed, and the anaerobic process was conducted at 37 °C for 30 days. When fermentation was completed, all residues were washed with clean water until the filter liquor became clean. Finally, the biogas residues (BR) were dried at 80 °C for 24 h. Acetic anhydride (AR) was supplied by Kelong chemical plant (Industrial development zone, Xindu, Chengdu, China), and *p*-toluenesulfonic (AR) was purchased from Shanghai Lingfeng Chemical reagent Co., Ltd. (Shanghai, China).

Preparation of Rice Straw Fiber-Reinforced Low-Density Polyethylene (LDEP) Composites

The samples of RS, BR, and ABR at 30 wt% loading were mixed with low-density polyethylene (LDEP 70 wt% loading) at 170 °C with a revolving speed of 60 r/min using a ZHL-LI-torque rheometer (manufactured by Changchun Intelligent Instrument Equipment Co., Ltd., Changchun, Jilin province, China). The mixed materials were fabricated by an injection molding machine (HAAKE MiniJet, Thermo Scientific, Shanghai, China), and the conditions were set as follows: cylinder temperature, 170 °C; mould temperature, 50 °C; injection pressure, 70 MPa. Dumbbell-shaped samples (10 × 3.18 × 3.18 mm) and rectangular samples (80 × 10 × 4 mm) were generated, and every specimen was tested in triplicate.

Optimization of Acetylation Reaction

The optimal conditions of acetylation were investigated according to an orthogonal experimental design; the experimental factors and levels are listed in Table 1. The orthogonal design of $L_9(3^4)$ was created and analyzed by SPSS Statistics19 software (IBM, Chicago, USA).

Table 1. Factors and Levels of the Orthogonal Experiment Designed for Acetylation

Level	Temperature (°C)	Time (h)	Acetic anhydride (mL/g BR)	Catalyst (g/g BR)
1	100	1	10	0
2	120	2	13	0.04
3	140	4	16	0.08

For every sample, 2 g of rice straw-biogas residues (noted as m_0) were added into a 50 mL round bottom flask, and other conditions were then arranged by the $L_9(3^4)$ orthogonal design with two repetitions in every experiment. The flasks were heated using an oil bath. After the reaction, the flasks were allowed to cool for about 30 min, and the mixtures were poured into glass-core crucibles (of weight m_1). Residues were washed with distilled water for 5 to 8 times and again with ethyl alcohol twice using suction filtration. Finally, the crucibles were again weighed (weight m_2) after being dried at 80 °C for 12 h. The experimental results were denoted by weight gain rate (WGR), which was calculated using Eq. 1 (Hill *et al.* 1998; Khalil *et al.* 2001).

$$WGR(\%) = \frac{m_2 - m_1 - m_0}{m_0} \times 100\% \quad (1)$$

Fourier Transform Infrared (FTIR) Spectroscopy

A NicoletS10 FTIR spectrometer (Thermo Scientific, Waltham, MA, USA) was used to analyze the molecular changes of the structures and chemical components of rice straw fibers. Samples for FTIR analysis were prepared with KBr, pressed into a disc, and placed on the sample stage. The spectral scan range was from 4000 to 400 cm^{-1}.

Characterization of Surface Morphology

A scanning electron microscope (SEM; EVO-LS10, Carl Zeiss, Jena, Germany) was used to characterize the morphology of the materials. These images reflected the

structure and interface conditions of rice straw fibers. The samples were observed under 1000× magnification.

X-ray Diffraction (XRD) Analysis

Rice straw fibers contain both crystal and amorphous structures, which adopt various X-ray diffraction patterns; the fibers were analyzed with an XRD-D2PHASERX instrument (Bruker AXS, Karlsruhe, Germany). The anode target was Cu, and the diffraction range was from 5° to 40° by 0.02 step-size and 0.15406 nm wavelength. The crystal characterizations of different rice straw fibers were determined by Eq. 2 (Thygesen *et al.* 2005; Chen *et al.* 2010; Zhao *et al.* 2011),

$$Cry(\%) = \frac{(I_{002} - I_{am})}{I_{002}} \times 100 \quad (2)$$

where I_{002} denotes the maximum intensity of the 002 crystal lattice reflection of the cellulose at 2θ angles of 22° and 23°, and I_{am} represents the intensity of diffraction of the amorphous structure, at a 2θ angle between 18°and 19°, where the intensity was at a minimum.

Thermal Characterization

Thermogravimetric analysis (TGA) is the main method of measuring the thermal stability of materials. A thermogravimetry/differential thermal analyzer (EXSTAR series TG/DTA7200, SII NanoTechnology Inc., Tokyo, Japan) was used to analyze the fibers. The temperature was raised from 35 °C to 650 °C at a rate of 10 °C/min.

Determination of the Mechanical Properties of Rice Straw Fiber-Reinforced Composites

The testing methods were based on GB/T 1447 (2005) and GB/T 1449 (2005). The dumbbell-shaped samples were used to measure the tensile properties, while the rectangular samples were used for flexural properties. All samples were tested with 10 mm/min loading speed using an electronic universal mechanical testing machine (HY-0580, Shanghai Hengyi Precision Instruments Co., Ltd., Shanghai, China).

RESULTS AND DISCUSSION

Orthogonal Experimental Design for Acetylation Reaction

The range and variance of the experimental data were analyzed by IBM SPASS Statistics 19 software (Chicago, USA). The orthogonal design and analytical results are listed in Table 2.

The values of K_{1j}, K_{2j}, and K_{3j} show that WGR increased with increasing temperature, time, and catalyst, respectively, while WGR declined with the increasing acetic anhydride content. On account of the highest value of R = 30.83 and the lowest p = 0.008 < 0.05, the catalyst had the biggest influence on WGR, which can be attributed to its strong acidity, non-oxidative and better compatibility with acetic anhydride than with inorganic catalysts such as sulfuric acid. Secondly, the temperature also showed a significant difference (p = 0.02 < 0.05), and the reaction time indicated a minor role in WGR than the temperature. However, the various volumes of acetic anhydride had no

difference with the minimal range and quadratic sum, so its significance was not analyzed. As a result, the four factors are ordered as follows: catalyst > temperature > time > acetic anhydride, and the optimal conditions of acetylation were determined to be 140 °C, 4 h,10 mL acetic anhydride/g BR, and 0.08 g catalyst/g BR. When the optimal conditions were verified experimentally, the WGR reached 23.66%.

Table 2. Analysis of the Orthogonal Series and Weight Gain Rate

Experimental Numbers	Temperature (°C)	Time (h)	Acetic Anhydride (mL/g BR)	Catalyst (g/g BR)	WGR (%)
1	100	1	10	0	4.63
2	100	2	13	0.04	10.96
3	100	4	16	0.08	17.76
4	120	1	16	0.04	13.57
5	120	2	10	0.08	19.20
6	120	4	13	0	10.42
7	140	1	13	0.08	20.41
8	140	2	16	0	11.48
9	140	4	10	0.04	20.69
K_{1j}[a]	33.35	38.61	44.51	26.53	
K_{2j}[a]	43.18	41.63	41.79	45.21	
K_{3j}[a]	52.58	48.86	42.80	57.36	
R[b]	19.23	10.25	2.27	30.83	
S_j[c]	61.71	18.53	1.26	160.83	
Sig[d]	0.020	0.064	--	0.008	

[a] The sum of factor-index values corresponding to j columns under i(1,2,3) levels
[b] The range of K_{1j},K_{2j},K_{3j}
[c] The quadratic sum of j columns
[d] The index of significance testing when significance level was set as 0.05

Molecular Structure Characterization

To determine the effect of anaerobic treatment and acetylation of rice straw fibers, the rice straw (RS), rice straw biogas residues (BR), and acetylated biogas residues (ABR, WGR = 23.7%) were characterized by FTIR, and the spectra are shown in Fig. 2. The peaks at 3343 cm^{-1} represented the stretching vibration of OH-groups in polysaccharide and lignin components. The sample BR had weaker absorption than RS, while the OH-absorption peak was not observed for ABR. This result implied that the hydroxyl content was extremely reduced so that the polarity and hydroscopicity of rice straw fibers were improved. However, the reasons of decreasing hydroxyl in rice straw were extremely different for BR and ABR, and the former resulted from the partial decomposition of cellulose and hemicellulose during anaerobic process, but the latter was due to the replacement of many –OH groups on the surface of rice straw fibers by acetyl groups through the acetylation reaction. The sample ABR displayed stronger absorption peaks at 2943 cm^{-1} due to C-H stretching vibration and at 1739 cm^{-1} for C=O stretching vibration than RS and BR. In particular, new peaks at 1739 cm^{-1}, 1367 cm^{-1}, and 1216 cm^{-1} appeared, suggesting that CH_3COO- groups replaced the –OH groups and were effectively grafted on the surface of rice straw fibers under the optimal conditions of acetylation. Among these peaks, the peak at 1367 cm^{-1} originates from the C-H flexural vibration of -CH_3 groups of acetyls, and the peak at 1216 cm^{-1} derives from the C-O-C stretching vibration of CH_3COO- groups. In addition, the peaks at 1607 cm^{-1} were

attributed to H-O-H flexural vibration of the crystal water in rice straw fibers. BR had lower peak intensity than RS, while it almost disappeared in the FTIR spectra of ABR. Therefore, the hydroscopicity of rice straw fibers was increased greatly.

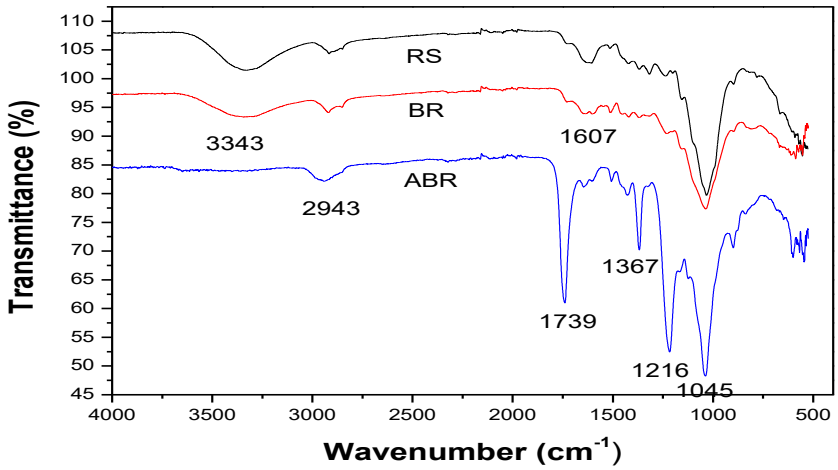

Fig. 2. FTIR spectra of RS, BR, and ABR

Surface Morphology Characterization

The surface condition of rice straw fibers critically impacts the compatibility of rice straw fibers and polymers, so the surface morphology of RS, BR, and ABR samples was observed by SEM (Fig. 3). RS had a smooth surface, and the microfibril and fiber bundles of rice straw fibers were covered under epidermis.

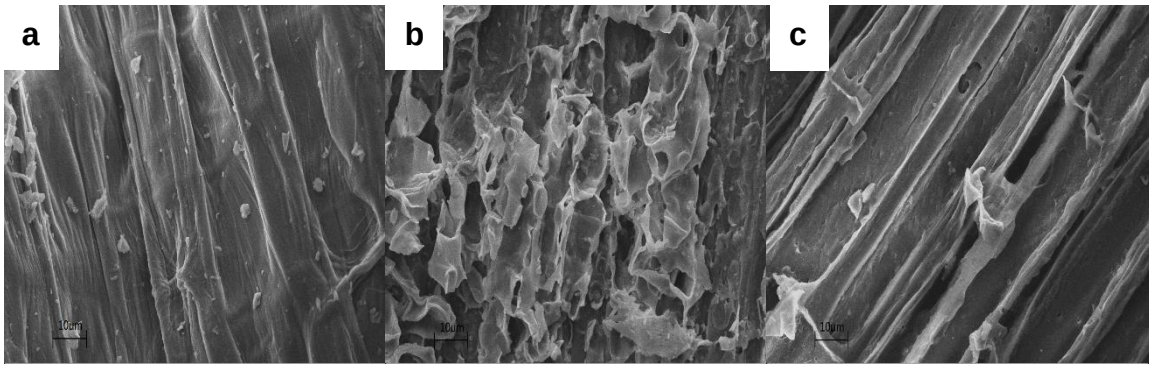

Fig. 3. Surface SEM images of (a) RS, (b) BR, and (c) ABR

When cellulose and hemicellulose were digested partly by the anaerobic microorganism, the rice straw structure was destroyed, and its surface became extremely coarse with many holes. However, the ester layer was formed after acetylation to cover the surface of BR because BR linked with many carbethoxyl functions, which repaired most of the surface defects, so that the surface became smooth and hydrophobic. Predictably, the compatibility of rice straw and polymers were greatly strengthened.

Crystalline Structure Analysis

The crystal structure of rice straw revealed both crystalline and amorphous cellulose, which were involved in determining its physical and mechanical properties (Thygesen *et al.* 2005; Dobreva *et al.* 2010). The XRD patterns reflected the changes in the crystal structure of rice straw fibers (Fig. 4). The peaks at 2θ values of 16° and 22° are ascribed to the 110 and 002 lattice planes, respectively, and the peak valley at 2θ = 18° represented the diffraction intensity of amorphous cellulose. BR had stronger peaks at 2θ values of 16° and 22° than RS, illustrating that BR had relatively higher crystal content (including ordered and amorphous crystal structures) than RS. The crystallinity of BR was approximately 40.1%, which was lower than the crystallinity (44.9%) of RS. This result indicated that the cellulose crystal structure was partially destroyed and was converted into amorphous structure during the anaerobic process. When BR was treated by acetylation, the peak intensity of the 002 lattice plane slightly decreased, but the intensity of the 110 lattice plane peak and the peak valley at 18° increased, which accounts for the reduction of crystalline cellulose and the increase in amorphous cellulose content. As a result, the crystallinity of ABR was only 23.6% because of the fracture of hydrogen bonds in the cellulose crystal. Thus, the ABR might have better rheological property but worse mechanical properties because of the presence of cellulose that is more amorphous and less crystalline.

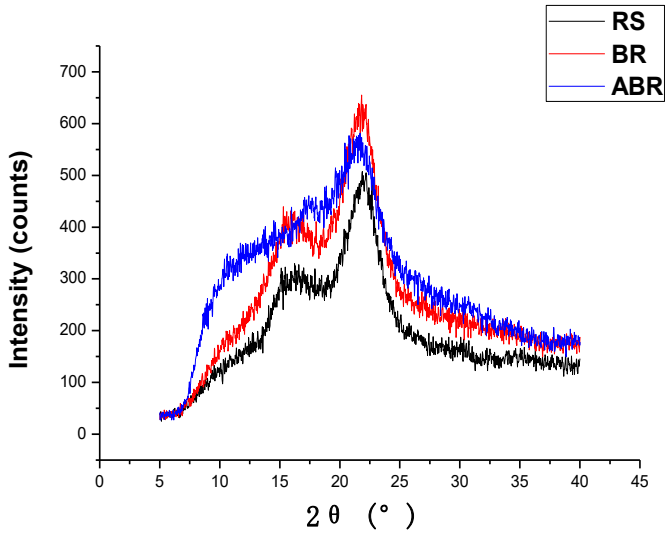

Fig. 4. X-ray diffraction patterns of RS, BR, and ABR

Thermal Properties

The onset decomposition temperature was obviously increased when rice straw fibers were treated by anaerobic digestion and acetylation, as shown in Fig. 5. The onset decomposition temperature of RS was only 170 °C, but it increased to 210 °C for BR, resulting from the removal of pectin, and fat from the surface of rice straw fibers and the accumulation of lignin. On the other hand the ABR sample indicated higher onset temperature (240 °C) due to the carboethoxy groups present which contributed to the thermal stability of material. In addition many defects were repaired on the surface, which enhanced the tightness of the structure of rice straw fibers. The ABR sample had the maximum rate of decomposition (610 μg/min) at 345 °C, which was much higher

than the rate of RS and BR, which were 340 µg/min and 383 µg/min, respectively. The phenomenon can be explained by the crystallinity of RS, BR, and ABR. The higher the crystallinity of rice straw fibers, the slower its decomposition rate became. Therefore, the lower crystallinity of ABR affected the physical and mechanical properties of the acetylated rice straw composites.

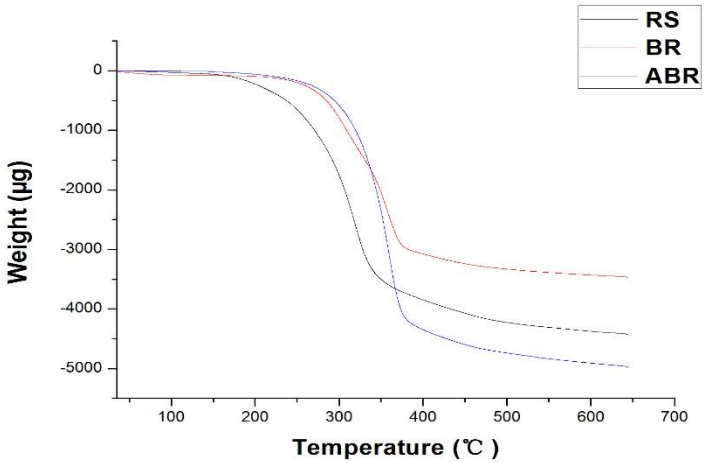

Fig. 5. TG curves of RS, BR and ABR

Mechanical Properties of Rice Straw/LDEP Composites

The mechanical properties of the composites RS/LDEP, BR/LDEP, and ABR/LDEP are compared in Table 3. All parameters demonstrated in Table 3 showed that BR/LDEP exhibited better tensile and flexural properties than RS/LDEP composites because of better compatibility between BR and LDEP components. The tensile strength increased by 13.9% with the 15.6% increase of flexural strength in comparison to RS composites. The elongation increased 16.6% due to improved composite malleability.

Table 3. Comparison of Mechanical Properties of RS/LDEP and BR/LDEP Composites

	Tensile Strength (MPa)	Flexural Strength (MPa)	Tensile Module (MPa)	Flexural Module (GPa)	Elongation (%)
RS/LDEP	13.7	33.8	141.4	1.5	24.1
BR/LDEP	15.6	39.1	161.8	2.1	28.1
ABR/LDEP	16.2	41.5	169.6	2.1	25.4

The essential reason for the improvement of mechanical properties was the increase of relative content of lignin in anaerobic digestion. In fact, lignin is one of the plants' defensive mechanisms against microbial attack and is practically undegradable under anaerobic conditions so that lignin was accumulated (Thomsen et al. 2014). Lignin structure contains aromatic groups, phenolic hydroxyl groups, alcoholic hydroxyl groups, and conjugated double bond, so lignin is easier to react with many chemical reagents, which declared that high lignin content is beneficial for modifying rice straw fibers. Furthermore, lignin is appropriate as a reinforce material on account of its better strength, stiffness, and rheological property than cellulose (Holladay *et al*. 2007). Therefore, although ABR had lower crystallinity than RS and BR, ABR/LDEP composites gained

better tensile properties and flexural strength than the BR/LDEP composite. However, their flexural module showed little variation, and the elongation of ABR/LDEP was lower than BR/LDEP. These results suggested that anaerobic digestion and acetylation enhanced the compatibility of rice straw fibers and polymers and improved their mechanical properties.

CONCLUSIONS

1. The optimal conditions of acetylation were studied using an orthogonal experiment. The optimum conditions were 140 °C, 4 h, 10 mL/g BR, and 0.08 g/g BR, in which the maximum WGR was 23.7%. The catalyst *p*-toluene sulfonic acid played an important role in the acetylation of BR.
2. Based on FTIR, SEM, and XRD analysis, there were obvious differences in the structures of RS, BR, and ABR. BR contained less hydroxy than RS, while the -OH absorption peak was not observed in ABR. This result implied that the hydroxyl content of RS was extremely reduced so that the polarity and hydroscopicity of rice straw fibers were decreased. SEM and XRD showed that the fiber structure of rice straw was destroyed by anaerobic bacteria, which resulted in a rougher surface and lower crystallinity of BR than RS, but the many defects of BR were repaired by the acetylation. However, ABR had the lowest crystallinity (22.6%), which can be attributed to the high temperature of acetylation while its amorphous cellulose evidently increased, which can have an impact on the mechanical properties of rice straw.
3. TG curves indicated that the RS had the lowest onset decomposition temperature (170 °C), and the temperature of BR and ABR successively increased to 210 °C and 240 °C, respectively. This result indicated that the thermal property of rice straw was improved. ABR exhibited the fastest decomposition rate (610 μg/min) at 345 °C resulting from its lowest crystallinity.
4. To determine the mechanical properties of their composites, RS/LDEP, BR/LDEP, and ABR/LDEP composites were prepared. Compared with RS/LDEP composites, the BR/LDEP composites showed obviously better tensile and flexural properties, while the properties of ABR/LDEP composites were also slightly improved based on BR/LDEP composites. Comprehensively, the anaerobic digestion and acetylation were effective to modify the rice straw fibers.

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