J Polym Environ (2013) 21: 648–657
DOI 10.10071/s10924-012-0562-y

ORIGINAL PAPER

Disk Refining and Ultrasonication Treated Sugarcane Bagasse Residues for Poly(Vinyl Alcohol) Bio-composites

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Published online: 18 December 2012

Abstract Disk refining and ultrasonication treated sugarcane bagasse residues reclaimed from the waste stream of a simplified bioethanol process after fermentation were used to fabricate biobased composites with poly(vinyl alcohol) (PVA) by film casting. The morphologies and the size distributions of residue particles were characterized by scanning electronic microscopy and various particle size analyzers. The results showed that the residue particle sizes were about hundreds nanometers to tens microns after disk refining treatment. After further treatment by ultrasonication, the particle sizes ranged from about tens of nanometers to several microns. The treated residues were expected to have a large surface area to reinforce PVA. The results indicated that the addition of treated fermentation residues significantly increased the tensile modulus of neat PVA with minimal impact on tensile strength. Furthermore, the PVA composites had higher thermal degradation temperature compared to neat PVA.

Keywords Fermentation residue · Bio-composites · Disk refining/grinding · Mechanical and thermal properties · Ultrasonication

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Introduction

Bio-based products (e.g. bioenergy, bio-based materials) from renewable resources are receiving ever-growing attention due to the concerns about the depletion of petroleum resources, the price escalation of crude oil, and the aggravation of climate change. As an abundant natural resource, lignocelluloses are potentially important feedstocks for the production of various forms of bio-based products. There are many other advantages for using lignocelluloses such as being renewable, environmentally-friendly (less greenhouse gas emissions), allowing independence of foreign oil, and helping rural economic development [1, 2].

Sugarcane bagasse residue derived after sugarcane juice extraction has primarily been used as animal feed or disposed as a solid waste. It has been studied for bio-ethanol production through simultaneous saccharification and co-fermentation (SScF) [3–5]. In our previous work, sugarcane bagasse residues from different steps of laboratory ethanol production, i.e. raw bagasse residues, pretreated bagasse residues, and bagasse residues after fermentation, were used to reinforce poly(lactic acid) (PLA) matrix through twin-screw extrusion [6]. The results of this work indicated that the application of fermentation residues lowered the physical properties of bio-composites compared with those reinforced by residues taken from up stream of fermentation steps, i.e.

raw bagasse and pretreated bagasse residues. This reduction in physical properties could be caused by significantly increased lignin content (about 60–70%) and the reduction in the aspect ratio of residue fibers (about 10–20%) in the fermentation residues [6]. In this study, we attempted to increase total surface area of fermentation bagasse residues and the aspect ratio of their residue fiber segments via multiple mechanical treatments including disk refining and/or ultrasonication. These treatments are expected to improve the interaction between biomass residues and the polymer matrix. The modified residues can then be used with poly (vinyl alcohol) (PVA) to produce a biodegradable composite with improved mechanical and thermal properties.

Disk refining (or super grinding) can generate very high shear force that is usually used to prepare micro- or nanofibrils from lignocellulosic fibers. Two disks with bars and grooves are parallelly placed with a small gap to crush and shear fibers by the repeated cyclic stresses. This mechanical treatment results in the irreversible change of fiber structures and reduces fibers to micro- or nano- scale [7–10].

The ultrasonication treatment, as another important mechanical treatment approach, has been used in many processes, such as emulsification, catalysis, homogenization, disaggregation, scission, and dispersion [11]. For example, several researchers used the ultrasonication treatment to break down cellulose fibers to small fibrils for the application of polymer reinforcements [12–15]. During an ultrasonication treatment, a very strong mechanical oscillating power produced by ultrasonic wave generates cavitation. Within the cavitation bubble and its immediate vicinity, violent shock waves are produced which can generate a high temperature and a high pressure field to coherently act on materials, which results in the rupture of the material structures [16].

Poly(vinyl alcohol) (PVA) has various advantages such as being biodegradable, resistance to solvents, being able to chemically bond with cellulose and lignin. PVA can also form films by casting because it is soluble in hot water. PVA has broad applications including protective colloids in the manufacture of polymer emulsions, the bindings of pigments and fibers, dip coated products, protective strippable coatings, the production of detergents and cleansing agents, adhesives, emulsion paints and solution cast films [17, 18]. However, a common feature of PVA is their low mechanical strength and integrity. Recently, many micro- or nano-scale fibers such as cellulosic nanofibers, nanocrystals, and fibrils were used to reinforce PVA to further improve the mechanical and thermal properties of PVA films [15, 19–22]. Although there is a depth of knowledge regarding the extraction of these materials from cellulosic fibers, little attention has been paid to the use of low value lignocellulosic biomass, such as residues (mainly lignin) reclaimed from the waste stream of bioethanol fermentation process, for PVA reinforcement.

Therefore, the focus of this study was to prepare PVA composite film reinforced with low-cost fermentation bagasse residues, after a size-reduction treatment by disk refining (DR) alone or followed by a high intensity ultrasonication (DR + US). We characterize the DR and the DR + US treated fermentation residues by Scanning Electronic Microscopy (SEM) and different particle size analyzers. Then, we investigate the influence of the addition of DR and DR + US treated bagasse residues on the mechanical and thermal properties, and surface morphologies of the reinforced PVA composites.

Experiment

Materials

The fermentation bagasse residues used as raw materials are solids separated from the fermentation broth of a bioethanol process, liquefaction plus simultaneously saccharification and fermentation process (L + SScF). At first, the raw bagasse underwent a multi-step hydrolysis process including steam explosion plus mild acid pretreatment and a liquefaction step, followed by a fermentation process at 37 °C for 144 h [4, 5]. The fermentation broth was collected and washed with standard test sieve #270 under warm water until effluent became clear, and then dried in an oven at 70 "C for at least 24 h. The components of the fermentation residues including lignin, cellulose, and a small amount of hemicellulose (Table 1) were analyzed according to a standard National Renewable Energy laboratory (NREL) procedure [23]. The higher percentage of cellulose (34 %) is due to the loss of significant amount of small-sized lignin particles and protein during the washing steps.

Poly(vinyl alcohol) (PVA) (Acros Organics, 99–100% hydrolyzed, average molecular weight of 86,000) was used as the matrix material in the composites.

Disk Refining Treatment (DR)

The fermentation bagasse residues were suspended in water (~3.1% consistency) and refined using a SuperMass-Colloider (model: MKZA6-2, Disk model: MKGA6-80#, Masuko Sangyo CO., Ltd, Japan) at 1,500 rpm. The SuperMassCollider is equipped with a power meter to record electrical energy input. Two stone disks were positioned on top of each other. The bottom disk rotates while the top one is stationary. Refining started with 210 g oven-dried fermentation residue. Pulp feeding was achieved by gravity. Pulp suspension was fed into the disk

Table 1 The main components of the fermentation bagasse residue

AIL (%)	ASL (%)	Total lignin (%)	Total ash (%)	Glucan (%)	Xylan (%)	Galactan (%)	Arabinan (%)	Mannan (%)	Acetic acid (%)	Total (%)
47.9±0.1	1.0±0.1	49.0±0.0	1.2±0.0	33.9±0.9	7.1±0.0	6.7±0.1	1.2±0.0	0.0±0.0	0.8±0.0	99.8 0.8

AIL acid-insoluble lignin, *ASL:* acid-soluble lignin

refiner continuously through a loop consisting of a peristaltic pump (Cole Parmer, Chicago, IL) and plastic tubing. The refiner disk-gap setting was gradually changed from 300 to ~–100 μm within 1 h. The zero position was determined right at the contact position between the two refining disks before loading pulp. Due to the presence of pulp, there is no direct contact between the two stone disks even at a negative setting of disk-gap position. The disk refiner was kept running for another 4 h 10 min. The total energy consumed for refining was approximately 6.61 kWh/kg.

Ultrasonication Treatment (US)

The water suspension of the disk refined bagasse residue was further treated for 30 min by high intensity ultrasonication at 80 % of the system maximal power scale and under a continuous mode to further reduce the size of the residue particles and fibrils. The ultrasonic (US) processor (Sonic Newtown, CT, 20 kHz, Model 1500 W, Newtown, CT) was directly applied to the water suspension of DR-treated residues in a 500-ml beaker. During the US treatment, the DR-treated suspension was diluted to 0.52 % consistency to improve stirring. The resultant sample after 30-min US treatment is referred to as DR + US in this study.

Characterization of Bagasse Residues

Scanning Electron Microscopy (SEM) (JEOL JSM-6400, operating voltage 5 or 15 kv, JEOL, USA) was used to examine the morphologies of the fermentation residue samples (DR and DR + US). All samples were coated with Au–Pd(~ 10 nm) before SEM imaging.

A Coulter Counter Multisizer 4 (MS4, Beckman, CA) was used to measure the particle size and its size distribution (under the maximum bin size of 400) of the DR and DR + US bagasse residues. Two tubes with 100 and 20 μm aperture diameter were used to detect the particles for DR and DR + US bagasse residues, respectively. MS4 with 100 μm aperture and 20 μm aperture tubes can be used to measure the particle sizes ranging from 2 to 60 μm and from 0.4 to 12 μm in diameter, respectively. Several drops of water suspension of bagasse residues were diluted to the desired concentration level (about 5–10% in a volume basis) with a balanced electrolytic solution (Isoton II, Beckman, CA) in a 100-ml measurement beaker. Then the samples were measured using the MS4 immediately with stirring. Five replicates were conducted for both DR and DR + US particles.

Dynamic light scattering (DLS) (Zetasizer ZS3600 with a non-invasive back scatter under 500 mw, 532 nm laser, Malven, UK) was used to estimate the size and the size distribution of the DR + US bagasse residues in a smaller size range. The DR + US samples were further diluted to about 0.1 wt%. A few drops of the diluted sample were suspended in 1 ml deionized water and measured immediately.

Film Casting of Composites

PVA in a water solution (10 wt%) and bagasse residues (DR and DR + US) in a water suspension (3.14 and 0.52 wt%, respectively) were mixed and stirred manually and then dispersed by ultrasonication treatment (Model 300 V/T, Biologics, Inc., Manassas, VA) for 3 min at a 50 % maximum power scale and under a continuous mode. The mixtures were degassed in a desiccator with vacuum and evaporated in petri dishes at room temperature (~ 22 °C) and the relative humidity (RH) of ~ 30 % until films were formed. After that, these films were thermally treated in an oven at 70 °C for more than 4 h. The samples were kept in a desiccator more than 3 days for conditioning before the mechanical and thermal properties were tested. A saturated solution of magnesium nitrate ($Mg(NO_3)_2$) was placed in the desiccator to regulate the desiccator RH to approximately 53 % at room temperature (~22 °C). According to American Society for Testing and Materials (ASTM) D1708 [24], the conditioning RH is 50 ± 5 % and the condition time is more than 40 h. The composites were prepared at four levels (0, 2, 5 and 10 %) of PVA substitution using fermentation residue of DR and DR + US. The nominal thickness of the composite films was 127 μm.

Characterization of Film Composites

Mechanical testing of the composites was performed on an Instron test machine (Model 5566, load cell capacity of 100 N, Grove City, PA) with the crosshead speed of 10 mm/min. The crosshead extension was used as specimen deformation. Samples were cut to dog-bone shapes

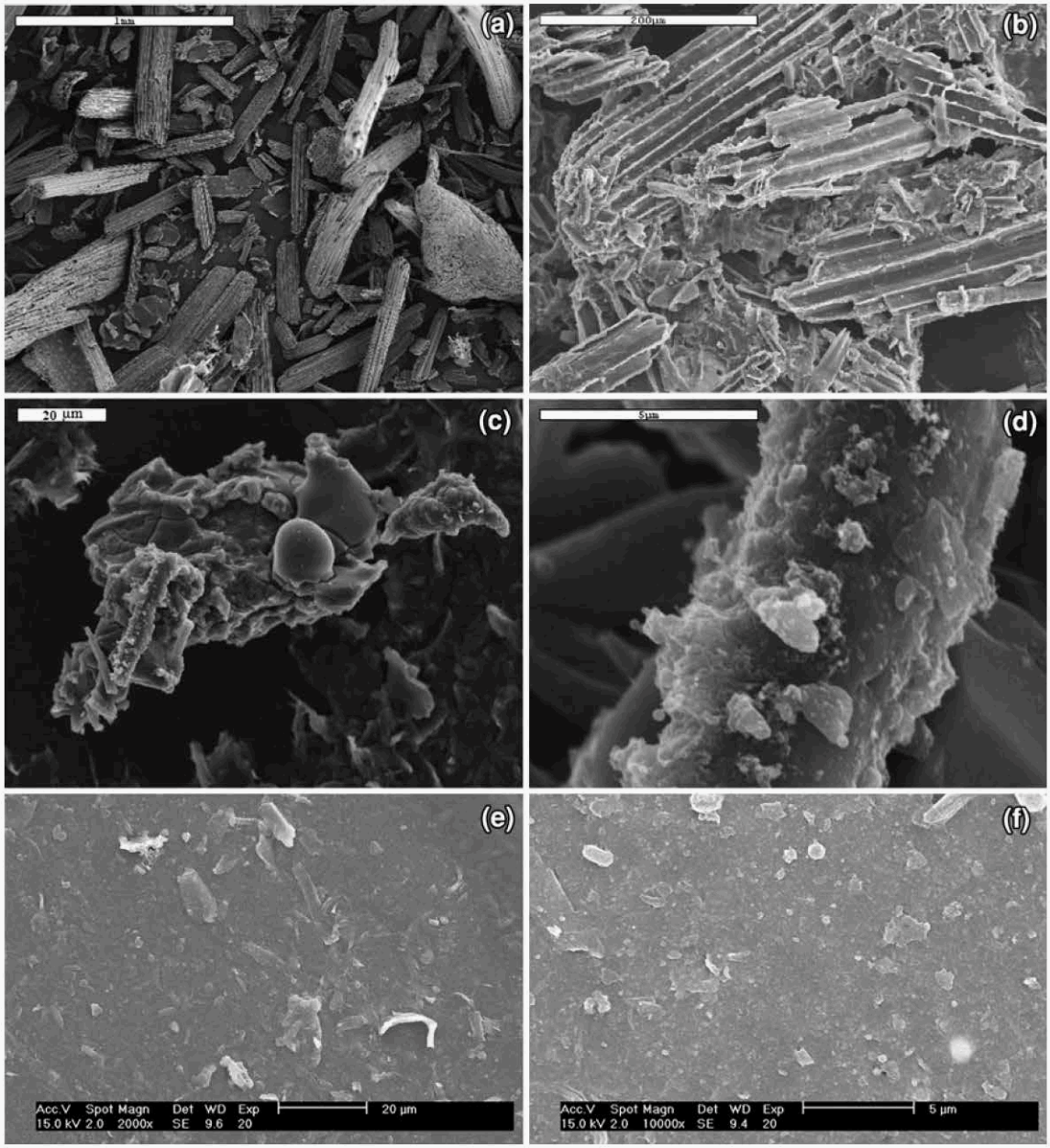

Fig. 1 SEM images of the bagasse residues, before disk refining (**a** Scale = 1 mm, **b** Scale = 200 µm), after disk refining (**c** Scale = 20 µm, **d** Scale = 5 µm), and after disk refining and ultrasonication treatment (**e** Scale = 20 µm, **f** Scale = 5 µm)

with the widths of 5 mm, the lengths of 20 mm for the narrow portions (gauge length 20 mm) and total lengths of 40 mm. In accordance with ASTM D1708-08, five specimens were tested for each composite [24]. Tensile elastic modulus of all composites was determined from the linear portion of the stress–strain curves (tangent modulus). Multiple comparisons by the Statistical Analysis System (SAS) (t tests (LSD)) were used to detect the overall significant differences of the tensile modulus, tensile strength, and maximal strain at the break point of the composites ($\alpha = 0.05$).

The thermal analysis process utilized a Thermogavimetric Analyzer (TGA/DSC1, Stare system, Mettler Toledo, Schwerzenbach, Switzerland) to determine the thermal behaviors of the composites, neat PVA, and neat bagasse residues. A 10 mg sample was placed in the TGA and heated from 50 to 500 °C at a 20 °C/min heating rate. The tests were conducted under nitrogen gas with flow at 20 ml/min to avoid oxidation.

Scanning electron microscopy (SEM) was also used to examine the topography of the fracture surface of the neat PVA and bagasse residues reinforced PVA composites

after tensile tests. All samples were coated and scanned using the same process as described above.

Results and Discussion

SEM Analysis of Untreated and Treated Fermentation Residues

SEM images of the fermentation residues before and after disk refining (DR) and after DR plus ultrasonication (DR + US) treatments are shown in Fig. 1. Particle size reduces upon DR treatment and further reduces upon ultrasonication. The dimensions of most untreated fermentation residues ranged from hundreds of microns to 1 mm. After DR treatment, the sizes of most particles were smaller than tens of microns. Particle size of bagasse residues were further reduced to sub-micron upon 30-min US treatment, due to the strong available hydrodynamic force generated by ultrasonication [16].

Size Analyzer Analysis of Treated Bagasse Residues

Figures 2 and 3 show the number and volume distributions of the DR and the DR + US treated fermentation residues measured by Beckman Coulter Multisizer 4 (MS4). MS4 has an overall detectable particle size ranging from 0.4 to 1,200 μm in diameter. The size range of measured particles is 2–60% of an aperture diameter range (20 to 2,000 μm). As shown in Fig. 2, residue particles treated with DR had an average diameter of approximately 5.82 μm and a broad particle size distribution ranging from 2 to 60 μm. Only a few particles with the diameter more than 45 μm were observed (Fig. 2), which was consistent with particle sizes shown in the SEM images (Fig. 1c, d). As shown in Fig. 1d, some small particles (<2 μm) were present in the residue but were not detected by MS4 with a 100 μm aperture. A smaller aperture was used but was found ineffective perhaps because the aperture was clogged by larger particles. It is speculated that the smaller particles of less than 2 μm are mainly lignin particles which can associate with the larger residue cellulosic fibril surface, which is agreed well with SEM results that small spherical particles (lignin particles) attached in fiber (large aspect ratio) surfaces. Figure 3 shows the average particle size and the size distribution of DR + US treated bagasse residues. It was observed that particles had an average diameter of 0.9 μm and a broad particle size distribution ranging from 0.4 to 11 μm. There were only a small number of residue particles with a diameter more than 7 μm, but with a relatively high volume due to their larger

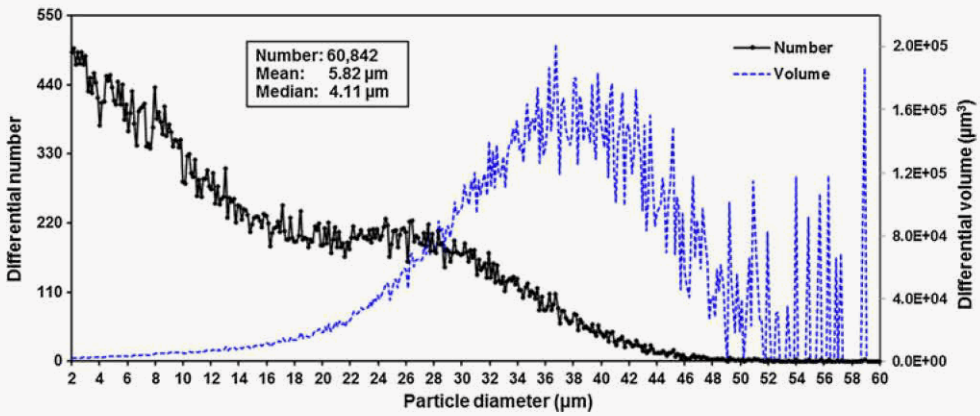

Fig. 2 Particle size distribution of disk refining (DR) bagasse residues measured by Beckman Coulter Multisizer 4 with 100 μm aperture

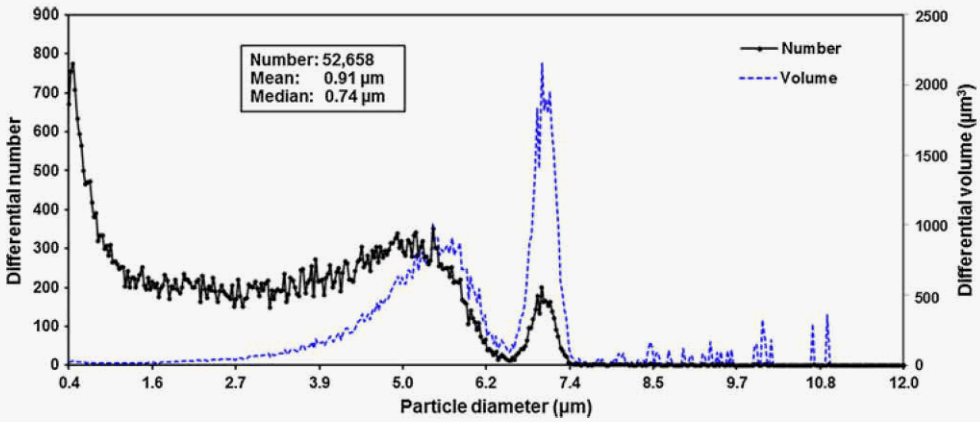

Fig. 3 Particle sire distribution of disk refining plus ultrasonication (DR + US) treated bagasse residues measured by Beckman Coulter Multisizer 4 with 20 μm aperture

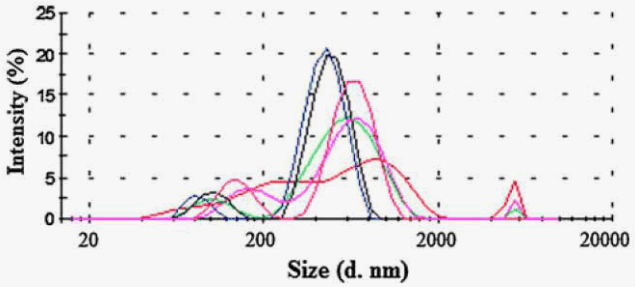

Fig. 4 Particle sire distribution of disk refining and ultrasonication treated bagasse residues (DR + US) measured by Zetasizer (six duplicates)

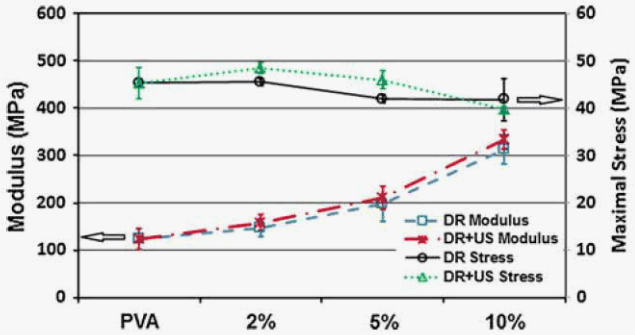

Fig. 5 Tensile moduli and maximal stress of PVA and its bagasse residue composites with 2, 5, and 10 % substitution (*DR* disk refining alone, *DR* + *US* ultrasonication after DR)

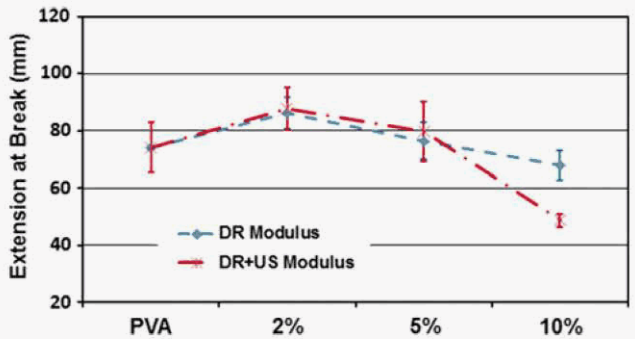

Fig. 6 The maximal tensile strain (elongation) of PVA and its bagasse residue composites (*DR* disk refining alone, *DR* + *US* ultrasonication after DR)

diameters. This agrees well With the SEM images (Fig. 1e, f). SEM images revealed a number of residue particles with diameters less than 0.4 μm (Fig. 1f). These particles were not detected by MS4 when using a minimum aperture of 20 μm. The DR + US sample was analyzed using a dynamic light scattering (DLS) based Zetasizer. The results showed the sample had a size ranging from 40 nm to 7 μm (Fig. 4). The results in Fig. 4 clearly show a bi-modal distribution in particle size. The large peak is most likely associated with the cellulosic fibrils.

Tensile Mechanical Properties of the Composites

Figure 5 summarizes the tensile moduli and tensile strengths (maximal stress) for neat PVA and PVA composites with the substitution of 2, 5, and 10 % DR and DR + US treated bagasse residues, respectively. The tensile modulus of PVA increased by 20, 61, and 154 %, respectively, by varying DR treated bagasse residues (2, 5, and 10 %). The introduction of both DR and DR + US treated particles significantly ($p < 0.001$, t test, $\alpha = 0.05$) improves PVA modulus (Fig. 5). Although DR + US produced smaller bagasse residue particles (Figs. 2, 3), the advantage of DR + US treatment over DR alone in improving tensile moduli was not statistically significant ($p = 0.21–0.52$). This is partly because of the aggregation of smaller particles and cellulose fibrils, as seen in the SEM images of cross sections of the composites, which will be discussed in the following section. The aggregation of smaller particles and/or fibrils might influence the reinforcement of their composites [12, 15].

Tensile strength of neat PVA was increased significantly by substituting 2 % PVA with DR + US treated bagasse residues ($p < 0.001$, t test, $\alpha = 0.05$) though the difference is within one standard deviation. Additions of 2, 5 and 10 % DR and 5 % DR + US treated bagasse residues did not affect PVA tensile strength. The substitution of 10 %

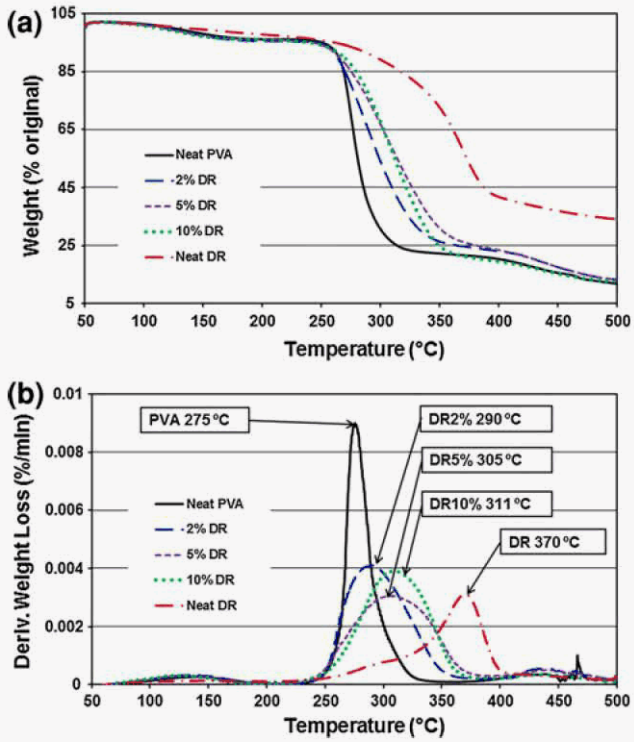

Fig. 7 TGA (a) and DTGA (b) diagrams of neat PVA, disk refining bagasse residue (neat DR), and PVA composites containing 2, 5, and 10 % DR treated bagasse residues

DR + US bagasse residues decreased PVA tensile strength ($p < 0.0001$). One of the possible explanations that most all the levels and treatments did not improve tensile strength was that the residue fibers have high lignin content (Table 1) and low aspect ratios (Fig. 1). The long fibers, the most important reinforcement component, were digested and shortened significantly by hydrolysis and fermentation. These fibers are different from microfibers and nanofibers directly produced from wood pulp [25] and soybean [26] that had high aspect ratios and could greatly improve the mechanical properties of their PVA composites. Another possible reason is that the aggregation of smaller particles at high concentrations (e.g. 10 %) can affect the mechanical properties of composites [12, 15]. The advantage of DR + US treatment over DR in improving tensile strengths was statistically significant ($p < 0.001$, t test, $\alpha = 0.05$) for 2 and 5 % loadings (Fig. 5) because DR + US produced smaller bagasse residue particles and fibrils (Figs. 2, 3). However, the addition of 10 % DR + US decreased PVAs strength as described above.

The maximal tensile strain (elongation) at the break point of neat PVA was increased significantly ($p < 0.0001$) by 17 and 19 % at 2 % substitution with DR and DR + US treated bagasse residues, respectively (Fig. 6). However, the change in maximal strain was minimal at increased substitution levels of 5 and 10 % DR and 5 % DR + US treated bagasse residues. The maximal tensile strain was reduced by more than 30 % at 10 % substitution with DR + US treated residues ($p < 0.0001$), suggesting the higher stiffness of the PVA composite with residue particles at a high concentration which resulted in the aggregation of smaller particles and therefore a brittle composite.

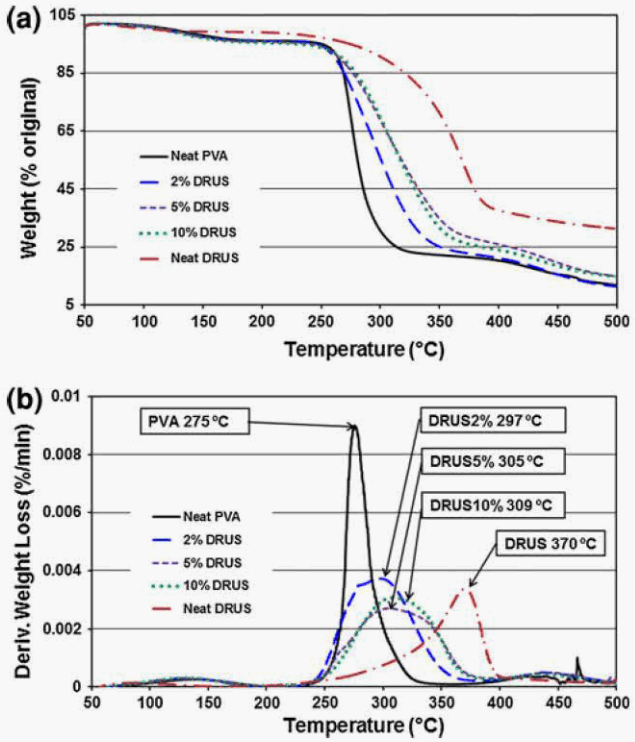

Fig. 8 TGA (a) and DTGA (b) diagrams of neat PVA, disk refining (DR) and ultrasonication treated bagasse residue (neat DR + US), and PVA composites containing 2, 5, and 10 % DR + US bagasse residues

Thermal Properties of the Composites

Thermogavimetric Analysis (TGA) was used to investigate the effect of treated fermentation residues on the thermal stability of the PVA composites. The TGA and derivative TGA (DTGA) thermograms are shown in Fig. 7 (the neat PVA, the DR-treated residue, the composites with DR-treated residue) and Fig. 8 (the neat PVA, the DR + US treated residue, and the composites with DR + US residue). There were three main weight loss regions for PVA and PVA composites with both DR and DR + US particles. Similar results were obtained by others [19, 27]. All samples exhibited an initial weight loss from 70 to 150 °C, which was attributed to the evaporation of water. The second degradation region (max weight loss region) was located between 250 and 400 °C with a weight loss from 50 to 70 % for different materials, which was attributed to the pyrolysis of bagasse residues and PVA degradation. The third weight loss region occurred above 400 °C, due to the decomposition of carbonaceous matter from PVA and lignin [19].

Table 2 shows the moisture contents, the max weight loss in the second region and their temperature ranges for

Table 2 TGA data for neat PVA and its composites containing 2, 5, and 10 % disk refining (DR) and DR plus ultrasonication (US) treated bagasse residues

Sample	PVA	DR2	DR5	DR10	US2	US5	US10	DR	DR + US
Water content (%)	1.98	2.64	2.62	2.93	2.73	2.70	2.91	0.48	0.63
Temperature range at max weight loss (°C)	250–310	250-335	250–355	250–350	250–342	250–360	250-356	250–390	250–390
Max weight loss (%)	69	64	65	69	67	63	65	52	57

all samples. The water content of the DR and DR + US bagasse particles were low because they were not conditioned after drying, while the PVA and all other composites had relative high water contents since they were conditioned at the RH about 53 % for more than 3 days. The neat PVA had about 2 % of water content and the composites had 2.6 to 2.9 % of water content as the biomass absorbed more water during the conditioning process. This water includes both physically bound and free water, which were reported to have strong plasticizing effect, and improve the movement of PVA chains [27].

Figures 7a and 8a indicate that PVA exhibits thermal degradation at a lower temperature than neat DR and DR + US fermentation residues. It was also observed that the composites of PVA with both DR and DR + US bagasse residues degraded at a lower temperature than the neat residues, but at a higher temperature than PVA. This agrees well with DTGA curves shown in Figs. 7b and 8b. Similar results have been reported in literature [28, 29]. The max degradation temperature of PVA increased after adding DR and DR + US treated residues because of the different degradation temperatures of the composite constituents. It was reported that PVA degradation occurred first, followed by cellulose and lignin thermal decomposition [28, 29]. Therefore, we can conclude that the inclusion of cellulosic materials improves the thermal stability of PVA and the degradation temperature of the composites [19].

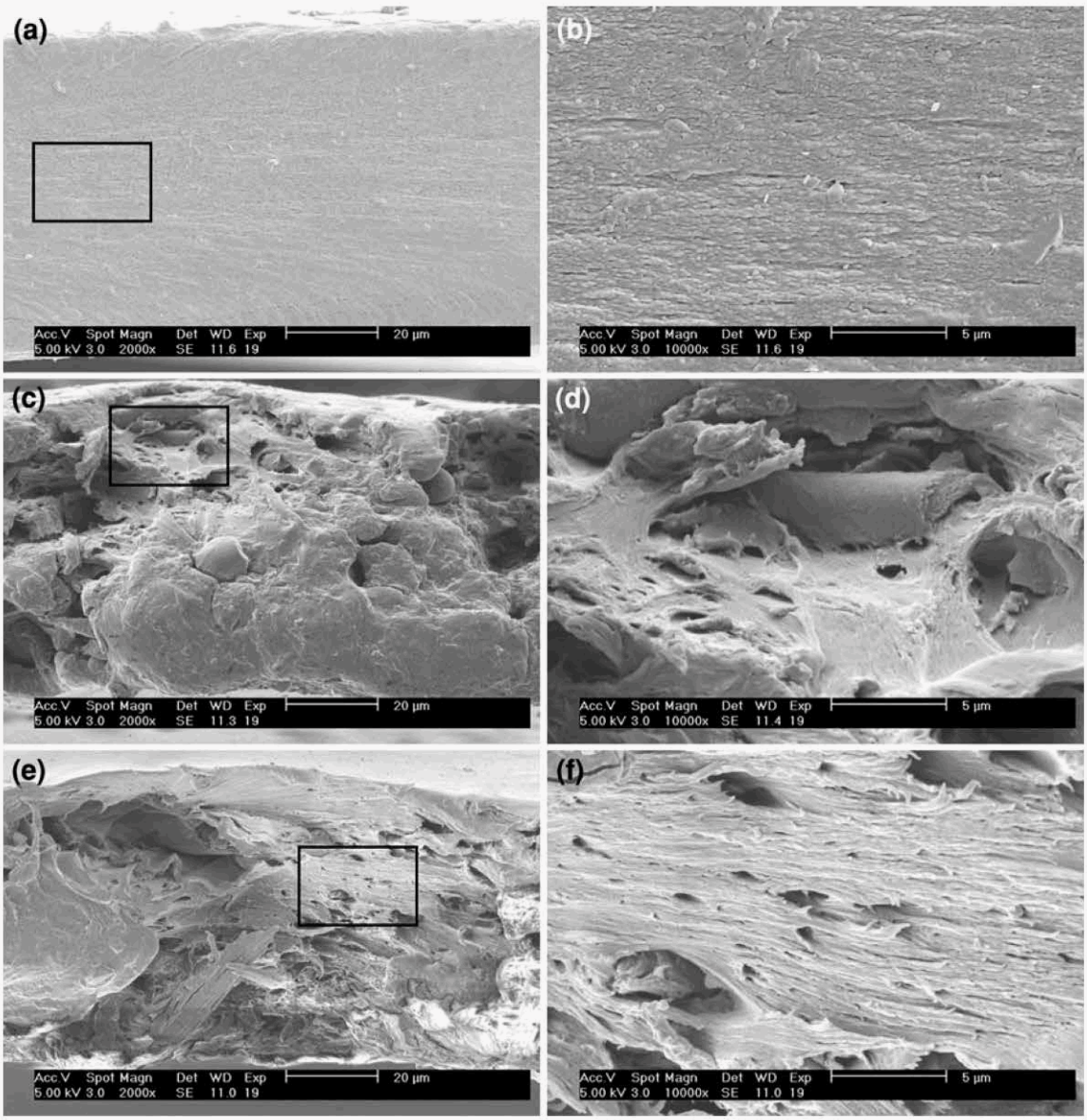

Fig. 9 SEM images of the fractured cross-sections of neat PVA (a Scale = 20 µm, b Scale = 5 µm), PVA composites reinforced with 5 % DR (c Scale = 20 µm, d Scale = 5 µm), and 5 % DR + US (e Scale = 20 µm, f Scale = 5 µm) bagasse residues

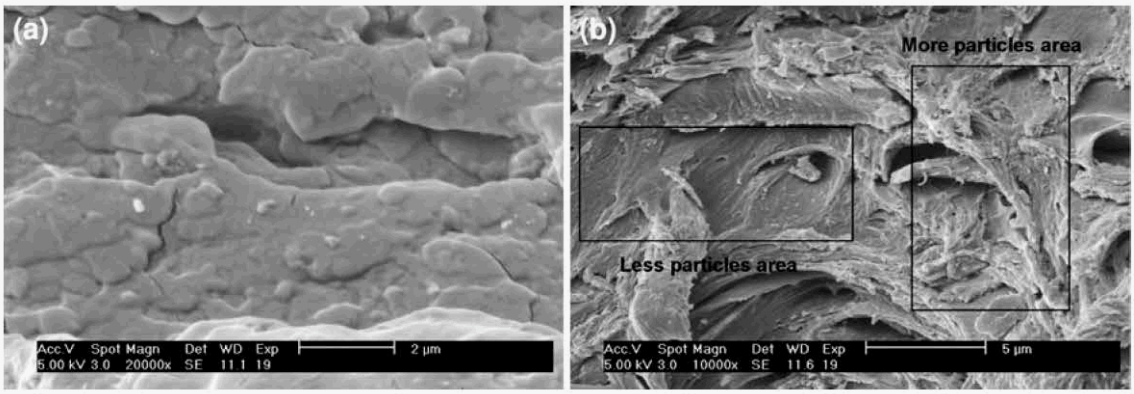

Fig. 10 SEM images of the fractured cross sectmns of 2 % DR + US (a Scale = 2 µm) and 10 % DR + US (b Scale = 5 µm) bagasse residues

SEM Observation of the Composites Fracture Surfaces

The SEM images of the fractured cross-sections of neat PVA and PVA composites reinforced with 5 % DR treated and 5 % DR + US treated bagasse residues are shown in Fig. 9. The fracture surfaces of neat PVA film were relatively smooth (Fig. 9a, b), while those of PVA composites with DR (Fig. 9c, d) and DR + US (Fig. 9e, f) treated bagasse residues were very rough. There were clear gaps between the larger bagasse particles and the polymer matrix for both DR and DR + US composites (Fig. 9d, f). The fractured surfaces also revealed that some particles and fibrils were aggregated, more significant for DR + US treated bagasse composites. Figure 10 shows the SEM images of the fractured cross-sections of PVA composites reinforced with 2 and 10 % DR + US treated bagasse residues. The particles were dispersed well at 2 % loading (Fig. 10a), while particle aggregations were observed at 10 % loading (Fig 10b). The non-uniform dispersion and aggregation of DR + US treated particles in the PVA matrix could explain that even the DR + US treated residues had smaller particles than DR treated residues, there are no significant difference in most of the tensile properties (Fig. 5,6)[15].

Conclusions

The preparation of PVA composites through the combination of biodegradable plastic PVA and a low-value fermentation residue reclaimed from the waste stream of bioethanol process was described. The residue had a high content of lignin and a low aspect ratio of residue fibers due to the multiple hydrolysis steps in the bioethanol process. At first, the residues were broken down to hundreds of nanometers to tens of microns after disk refining (DR) treatment and tens of nanometers to several microns after further ultrasonication (US) treatment in order to increase their surface areas and aspect ratios. The morphologies of these treated residues illustrated that most particles still had a low aspect ratio compared with cellulose fibrils reported in the literature. The results indicated that the PVA tensile modulus was significantly improved with the substitution of DR and DR + US treated bagasse residues, and the PVA tensile strength and maximal strain were slightly increased at 2 % DR + US substitution. Thermal property data revealed that the composites had higher thermal degradation temperature compared to neat PVA, and that decomposition temperature increased with the increase in the amount of residues used for substitution.

Acknowledgments This project was supported by Biomass Research & Development Initiative Competitive Grant no. 2011-10006-30358 from the USDA National Institute of Food and Agiculture and Institute of Food and Agricultural Sciences (IFAS) Startup funding at the University of Florida. The authors also thank the experimental help from Dr. Wade Yang about ultrasonication process at the Department of Food Science and Human Nutrition, Dr. Eric McLamore about Multisizer analysis at the Department of Agicultural and Biological Engineering, and SEM measurements at the Major Analytical Instrumentation Center, University of Florida. We also would like to acknowledge Qianqian Wang, a visiting Ph.D. student at US Forest Service, Forest Products Laboratory, from South China University of Technology, for carrying out disk refining of the bagasse residue.

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