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Thermal stability evaluation of sweet sorghum fiber and degradation simulation during hot pressing of sweet sorghum–thermoplastic composite panels

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ABSTRACT

An understanding of the thermal behavior of natural fibers is critical in efficiently converting them into composites under heat and pressure. The objectives of this study were to evaluate the thermal stability of sweet sorghum fiber and simulate its thermal degradation during hot pressing into composite panels. Thermal stability of sweet sorghum was analyzed using thermogravimetric analysis, and its thermal degradation during the hot pressing process was simulated based on kinetic parameters calculated using the ASTM E1641 method, Friedman method, and independent parallel reaction model (IPRM). The results demonstrate that experimental testing data and IPRM prediction results are in accordance. Sorghum degradation ranged from 5.4% at the surface to 2.0% at the core of the panel after 10 min of hot pressing at a platen temperature of 160 °C. The results of this study will assist with consolidation of sorghum fibers into products under heat.

1. Introduction

Sweet sorghum (*Sorghum bicolor* (L.) Moench) is a high biomass yield crop, with one of the highest daily dry matter accumulation rates compared to other species (Billa et al., 1997). It only takes 3–5 months to mature, and one hectare of sweet sorghum yields 3–7 t of grain, 54–59 t of stalks and 6–8 t of sugar (Almodares and Hadi, 2009). Grain, leaves and stalks of sweet sorghum are commonly used as animal feed, among other uses. With increase in demand for biofuels, sweet sorghum is being diverted to ethanol production because of its high content of water-soluble sugars (Almodares and Hadi, 2009; Laopaiboon et al., 2009; Prasad et al., 2007; Wu et al., 2010). Producing composite panels using crushed sweet sorghum stalk is another option for sustainable and eco-conscious manufacturing.

Hot-pressing technology utilizes sorghum stalks effectively to produce an aesthetically pleasing and high-performance composite panel. Sweet sorghum and high-density polyethylene composites were fabricated by hot pressing, for example, in our previous study (Qi et al., 2013). Crushed sorghum composite panels can be fabricated by hot pressing technology with thermosetting or thermoplastic resins. Thermoplastic resins, being more hydrophobic, can assist in improving moisture resistance of the resulting composite panels (Qi et al., 2012). Because the thermal stability and degradation of fiber when subjected to high temperature influence the physical and mechanical properties of the resulting composite panel, it is crucial to fully understand the thermal stability and mass loss that occur during the hot pressing process in order to effectively set parameters such as platen temperature, furnish moisture content, and duration of hot-pressing. Thermogravimetric analysis (TGA) is one of the most commonly applied thermal analytical techniques in solid-phase thermal degradation studies (Ninan, 1989).

Activation energy and pre-exponential factor are two critical kinetic parameters, which can be obtained by analyzing and fitting the TGA testing data, for simulating thermal degradation of natural fiber according to fundamental Arrhenius rate expression. White et al. (2011) and Di Blasi (2008) reviewed methods of calculating thermal degradation kinetic parameters. Friedman method (Friedman, 1964) is based on a differential approach to the treatment of TGA data, and is a commonly used method to calculate activation energy, pre-exponential factor, and reaction

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order. Conversely, an integral method using Doyle's approximation equation was derived by Ozawa (1965) and Flynn and Wall (1966) (referred to as OFW method) to obtain activation energy and pre-exponential factor. Because both Friedman and OFW methods are global methods, which consider the reaction of natural fiber consisting of complex polymeric compounds as one component, these two methods can only provide a rough approximation for the overall rate of a complex process (Vyazovkin and Wight, 1998). The independent parallel reaction model (IPRM) separates each chemical component of natural fiber, and is often used to calculate the kinetic parameters of each pseudo component to precisely simulate their thermal degradation (Cardoso et al., 2011; Di Blasi, 2008; Sun et al., 2011). IPRM treats natural fibers as a composite of pseudo components where each pseudo component is one of its main chemical components as analyzed in this study.

Sweet sorghum has been used for manufacturing bio-based composites in the past (Yu et al., 2012), but there is a potential for thermal degradation under applied heat as water soluble sugars are a significant component of its chemical make up (~10%) (Qi et al., 2012). However, limited work has been conducted on the thermal stability and degradation properties of sweet sorghum fiber during composite manufacture under heat and pressure. The objectives of this study were to investigate the thermal stability of sweet sorghum fiber and its components, and to simulate thermal degradation of fiber and its pseudo components during the hot pressing process. Thermal stability of sweet sorghum fiber and its components was analyzed by TGA. Thermal degradation kinetic parameters of sweet sorghum and its pseudo components were determined using ASTM E1641, Friedman, and IPRM methods to simulate their mass loss caused by thermal degradation during the hot pressing process. The results will assist in determining appropriate process parameters for producing sorghum-based composite products by consolidating under heat.

2. Materials and methods

2.1. Materials

Sweet sorghum stalks were obtained from ChloroFill LLC in San Diego, California, with the grain and leaves removed, and majority of the water-soluble sugars extracted by crushing the stalks. The rind and pith of sweet sorghum stalks were manually separated (from here on referred to as simply rind and pith). All materials were milled into 60 mesh flour for TGA and chemical component analysis. Sweet sorghum specimens of combined rind and pith will be referred to as sorghum fiber from here on.

2.2. Chemical component analysis

Sorghum rind or pith was first extracted by Soxhlet with dichloromethane (DCM) for 16 h, followed by 48 h of warm water extraction (at 50 °C). Water-extractives were analyzed using high performance liquid chromatography (HPLC) to obtain their water-soluble sugar content. Sulfuric acid was added to the water-extractives free sample to remove Klason lignin (Sluiter et al., 2008). The supernatant of neutralized and centrifuged filtrate from the above sulfuric acid hydrolysis was passed through a small ion exchange cartridge (containing 0.5 mL of IR120H$^+$ and 0.5 mL IRA35 OH$^-$ resin) and filtrated through a 0.45 μm syringe filter into a HPLC vial. Carbohydrate HPLC analysis was performed using two Rezex RPM columns in series at 85 °C on elution with water (0.5 mL/min), 50 μL injection volume, and refractive index detection (ERMA). The DCM extractives, water extractives, and samples free of these extractives were later analyzed using TGA.

2.3. Thermogravimetric analysis

Thermogravimetric analysis was performed using a TA Q600 analyzer under a nitrogen purge at a flow rate of 100 mL/min. Approximately, 8-mg mass of sixty-mesh samples of sorghum fiber, rind and pith were analyzed using TGA. The materials were heated from room temperature to 600 °C, and the weight at 120 °C was set as zero mass loss in order to eliminate the influence of moisture. A heating rate of 20 °C/min was used to investigate thermal stability. Weight and time/temperature data were recorded and analyzed using TGA data acquisition software, yielding the weight loss (TG) and differential weight loss (DTG) curves. Each experiment was performed at least twice to ensure repeatability.

2.4. Thermal degradation kinetics

The complete reaction mechanism cannot be represented suitably by a single specific kinetic mode, due to the complicated chemical reaction (Brown and Galwey, 1979). Therefore, ASTM E1641-07, Friedman method, and IPRM were all applied to calculate the thermal degradation kinetics of sweet sorghum. Heating rates of 1, 2, 5, 10, 20 °C/min were employed to study thermal degradation kinetics.

2.4.1. ASTM E1641 method

The ASTM standard method E1641-07 for determination of kinetic parameters relies on a variant of the OFW method. A series of kinetic curves at different heating rates are tested, then the kinetics of biomass degradation is then expressed as the following fundamental Arrhenius rate expression:

$$\frac{d\alpha}{dt} = A\exp(-\frac{E}{RT})f(\alpha) \quad (1a)$$

where α denotes the conversion or extent of the reaction and t signifies time (min). A is the pre-exponential factor (min^{-1}), E is the activation energy (J/mol), R is the gas constant, and T is the absolute temperature (K). Conversion function $f(\alpha)$ represents the reaction model used, dependent on the controlling mechanism. The α can be defined as the mass fraction of biomass substrate that has decomposed, expressed as:

$$\alpha = \frac{w_0 - w}{w_0 - w_\infty} \quad (1b)$$

where w_0 is the initial weight at zero weight loss, w is the mass of substrate present at any time, and w_∞ is the final mass of solids. Eq. (1a) also can be transformed into the following equation, based on linear heating rate:

$$\frac{d\alpha}{dT} = \frac{d\alpha}{dt}\frac{dt}{dT} = \frac{A}{\beta}\exp(-\frac{E}{RT})f(\alpha) \quad (1c)$$

where β is heating rate (°C/min). Integrating Eq. (1c), the following relationship was established by Ozawa (1965) and Flynn and Wall (1966) using Doyle's empirical interpolation formula:

$$\log\beta = \log(A\frac{E}{Rg(\alpha)}) - 2.315 - 0.4567\frac{E}{RT} \quad (1d)$$

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} \quad (1e)$$

Plotting $\log\beta$ versus $1/T$ for different heating rates produces parallel lines at a fixed conversion. The slopes of these lines are $-0.4567E/R$. ASTM E1641 uses the slope factor 0.4567 as its initial value, and recalculates the slope factor using a given table of numerical integration constants to make Eq. (1d) more precise. The