Microfibrillated cellulose from sweet sorghum (*Shorghum Bicolor* (L.) Moench) fiber by twin screw extruder and its characteristics on polylactic acid biocomposites

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Abstract. High tensile strength and modulus could be obtained by microfibrillated cellulose (MFC) addition into PLA matrix. MFC production from sweet sorghum fiber with twin screw extruder (TSE) could be an effective mechanical treatment. The objective of this research is to study the effectivity of twin screw extruders for MFC production from sweet sorghum fiber and to analyze its effect on PLA biocomposites properties. Sorghum fiber was firstly delignificated with alkaline treatments and bleached with sodium peroxide solution to produce high cellulose content of fiber. Bleached sorghum fiber was then passed through into TSE for 1, 3, and 5 passes. Afterward, PLA biocomposites with MFC from TSE process were produced by the solvent casting method. Twin screw extruder with co-rotating intermeshing flow is effective for defibrillation and size reduction of cellulose fibers which could achieve 1-10 µm in diameter and millimeters in length. The tensile strength of PLAM\(_{\text{TSE5}}\) increase 4.54% in 50.60 Mpa and modulus of elasticity increase 40.36% in 2.82 Gpa. Storage modulus of PLAM\(_{\text{TSE5}}\) also increases 10.64% in 3.088 Mpa compare to pure PLA.

1. Introduction
Polylactic acid (PLA) is a linier aliphatic from acetic acid monomer. Commercial PLA produces in amorphous and semicrystalline depend on L-lactide and D-lactic acid content which contributes to different properties [1,2]. PLA is one of the biodegradable polymers which become widely developed in the last decade to consider environmental and green movement issues. Some excellencies of PLA include are high tensile and modulus of elasticity than polypropylene, biodegradable, biocompatible, good clarity, good oil resistance, and good oxygen barrier [1,3,4]. With these properties, PLA could be able for some applications in biomedical, food packaging, and automotive industry [1,5]. However, the weaknesses which are high glass transition temperature (Tg), brittle, low degradation, and low crystallization rate limit the application of PLA [1,2,5]. Modification of PLA whether intramolecular and intermolecular could be as an effective method by the nucleating agent or reinforcing agent addition to overcoming these drawbacks [1,5,6].
Modification via nucleating agent mechanism has been done with various types of organic and inorganic materials. Consider full biodegradability and environmental friendly material, bio-based nucleating agent such as starch, organic plasticizer, and cellulose more preferable than minerals [1, 5]. Cellulose is abundantly available which could be derived from lignocellulosic materials such us stalk, fiber, leaf, and stem [1]. One of potential lignocellulosic fiber is sweet sorghum with high biomass waste because sorghum could be regularly harvested in 3-4 months. In Indonesia, sweet sorghum plantation is cultivated mostly in Java and Nusa Tenggara. Cellulose resources from sweet sorghum could be derived from leaf and stalk part. The cellulose content in leaf part about 64.8% while in stalks is about 65.1% which close to commercial natural fiber such as flax, hemp, and coconut [2].

The preparation of cellulose as a reinforcing agent becomes a crucial role to produce good properties of biocomposites. The disintegration of cellulose into the fiber with a diameter in micro and nano scale has modulus of elasticity about 40-70 Gpa and tensile strength 400-700 MPa, while in crystal structure about 130-250 GPa and tensile strength about 800-10,000 MPa [3]. Microfibrillated cellulose (MFC) could produce by mechanical treatments using refiner, high pressure homogenizer, microfluidizer, grinder, and high intensity ultrasonicator [10,11]. Mechanical treatments enable cellulose fiber defibrillated in radially order so could produce high aspect ratio of MFC. Some studies suggest for twin screw extruders as low energy consumption and effective mechanical treatments to produce high solid content of MFC even in a single process [12,13,14] or combination with another process [15,16].

Some studies report for mechanical properties enhancement for PLA and MFC biocomposites. Kneading process of PLA and MFC from kenaf pulp by twin screw extruders could improve tensile strength about 21% and MOE about 34.5% [4]. The addition of fibrillated cellulose up to 1 to 3% enhances tensile strength up to 1.2 fold of PLA composites, but more than 3% result in agglomeration of MFC [5]. In addition, amorphous PLA with 20% of MFC improves tensile strength in 72.1% and modulus 57.6% [6]. Besides tensile strength and modulus enhancement, storage modulus up to 160 MPa under dynamic mechanical analysis resulted in higher value than fully crystallized PLA [7].

As the best know of authors, there is a limited study about PLA and sweet sorghum fiber biocomposites. The only research is PLA biocomposites reinforced with the modified fiber of sweet sorghum in particle form [8]. PLA biocomposites reinforced with MFC from sweet sorghum have not been done, especially MFC which isolated from twin screw extruder. The objective of this research is to study the effectivity of twin screw extruders for MFC production from sweet sorghum fiber and to analyze its effect on PLA biocomposites properties.

2. Materials and Methods

2.1. Materials

Sweet sorghum (Shorgum Bicolor (L.)Moench) was harvested from the Center of Innovation cultivation side, Cibinong. Particle production of sweet sorghum’s stem was conducted using hammer mill and disc mill until 40-60 mesh of particle size which could be as raw material for fiber. Acetone 90%, hydrogen peroxide 30%, and sodium hydroxide were used for cellulose isolation. Acetone and hydrogen peroxide (H₂O₂) is in technical grade while sodium hydroxide (NaOH) is in pure analysis grade. Amorphous PLA (polylactic acid) 4060 D was purchased from Natureworks, USA. PLA 4060 D has D-lactide content is about 12%, Tg (glass transition temperature) is about 55-60°C, density is 1.24 g/cm³, and MFR (melt flow rate) at 180°C is 3.89 g/10 min.

2.2. Methods

2.2.1. Isolation of cellulose from sorghum fiber

Prior to isolate, sorghum fiber was firstly passed through delignification process. As much 100 g of sorghum particle was cooked on 10% (v/v) of NaOH solution at 95°C for 120 min with 250 rpm of
magnetic stirring. Particle which transforms into fiber was washed using aquadest until neutral. Subsequently, sorghum fiber was bleached using combination of 30% (v/v) of H₂O₂ and 10% (v/v) of NaOH solution at 95°C for 60 min. Cellulose fiber was then washed using aquadest until neutral with pH in 6.2-6.5.

Chemical composition of cellulose derived from sorghum fiber was analyzed using FTIR (Fourier Transform Infra Red). Universal Attenuated total reflectance (UATR)-FTIR Perkin Elmer Spectrum Two was used for qualitative analysis with scanning operation in 4000-400 cm⁻¹ of wavelength with 15 times of repetition for each sample.

2.2.2. Preparation of microfibrillated cellulose
Mechanical fibrillation was conducted using TSE Haake Rheomix PTW 16. As much as 10 g of cellulose fibers was feed through sample hooper and then kneaded between two co-rotating screws. Rotational speed was 400 rpm and temperature condition at 26°C for all zone. The fibrillation process was conducted in 1, 3, and 5 passes.

2.2.3. Characterization of microfibrillated cellulose from sorghum fiber

2.2.3.1. Dispersion stability of microfibrillated cellulose
Microfibrillated cellulose by TSE process was then dispersibility tested on water. Some samples of MFC which collected on the edge of TSE in 1, 3, and 5 passes was placed in 50 mL vial bottles then observed the fiber stability after 5 min suspended in water.

2.2.3.2. Morphology of microfibrillated cellulose
Morphology of MFC from sorghum fiber was done using FE-SEM (Field Emission Scanning Microscopy) Quattro S Thermo Fisher Scientific. MFC was placed on the step without coating then observed in 1000 times of magnification with scanning electron emission in 2 kV.

2.2.4. Production of polylactic acid and microfibrillated sorghum fiber biocomposite
As much as 54 g of PLA 4060D was dissolved on 600 mL of acetone then stirred for 45 min at room temperature. Treated and untreated MFC in 1% (w/w) was blended into solution for 15 min. The blended compound was cast into 25 x 40 square mold then oven dried at 65°C for 12 hours to vaporize the solvent.

Sample specimens for mechanical properties were molded using a Mini jet Pro to obtain dog bone specimen test according to ASTM D 638 type V. PLA compound was cut into pieces then feed in minijet pro at 155°C of cylinder temperature, 600 bar of molding pressure, and 15 seconds of infection time.

2.2.5. Properties of polylactic acid biocomposites

2.2.5.1. Mechanical properties
Mechanical properties were analyzed using Universal Testing Machine (UTM) autograph 10 kN Shimadzu. The tensile test was conducted according to ASTM 638 for plastic composites with load cell 5 kN and crosshead speed 1 mm/min.

2.2.5.2. Thermal properties
Thermal analysis was conducted using Differential Scanning Calorymetry (DSC) 4000 Pyris 1 Perkin Elmer equipped with intercooler. 5 mg of PLA pieces were placed into a alununum pan. The sample was heated from 25°C to 200°C with heating rate 20°C/min, hold the sample at 200°C for 2 min, cooled from 200°C to 25°C with cooling rate 5°C/min, hold at 25°C for 2 min, then heated from 25 to 200°C with heating rate 5°C/min.

2.2.5.3. Dynamic mechanical properties. Rectangular sample
Dynamic mechanical properties were conducted using Dynamic Mechanical Analysis (DMA) 8000 Perkin Elmer. The specimens were prepared in rectangular with dimension in 30 x 6 x 2 mm. The analysis was undertaken from 0°C to 100°C with heating rate of 2°C/min and frequency in 1 Hz.
3. Results and Discussion

3.1. Characterization of cellulose from sorghum fiber

The main component of sorghum fiber is consist of cellulose, hemicellulose, and lignin. The Visual appearance of sorghum is similar to general natural fiber derived from stalk part of plant such as corn stalk and kenaf which classified as short fiber as seen in figure 1 (a). As a reinforcing agent in composite materials that purposed to enhance mechanical properties as well as thermal and optical properties, natural fibers should be prepared in high cellulose content. Cellulose in the crystalline part considers has better compatibilities to polymer matric than lignin and hemicellulose in amorphous part. Hemicellulose and lignin are interfered with physical bonding with polymer matric and have low ultraviolet degradation resilience [9]. In order to facilitate better properties of the composite, delignification process might be undertaken to isolate cellulose from fibers. Delignification followed with bleaching process result in brighter fibers than the original as seen in figure 1 (b) which could be termed as cellulose fibers. The chemical component of cellulose fibers is consisting of 88% of holocellulose and 3% of lignin. Lignin is still contained after the bleaching process even in small presence and bright appearance.

![Figure 1](image)

**Figure 1.** (a) Visual appearance of sorghum particle and (b) sorghum fiber after bleaching process

| Identified functional groups | Sorghum particle | Sorghum fiber after delignification process | Sorghum fiber after bleaching process |
|-----------------------------|-----------------|------------------------------------------|--------------------------------------|
| Stretching of –OH           | 3330            | 3330                                     | 3332                                 |
| Stretching of C-H           | 2922            | 2922                                     | 2922                                 |
| Stretching of C=O           | 1734            | 1734                                     | -                                    |
| Absorbed O-H conjugated C-O | 1644            | 1644                                     | 1637                                 |
| C-C aromatic vibration of lignin | 1510         | 1506                                     | -                                    |
| Deformation C-H in cellulose and hemicellulose | 1385 | 1377                                     | 1369                                 |
| Stretching C-O in cellulose | 1030            | 1027                                     | 1032                                 |
| β glicocidic linkage        | -               | 895                                      | 895                                  |

Identified functional groups on FTIR spectrogram for all cellulose isolation steps are represented in Table 1. FTIR Spectrogram identified the specific functional groups of cellulose in 3330 cm$^{-1}$, 2922 cm$^{-1}$ which are identified the stretching of –OH and C-H groups respectively for all fibers. These intensity of functional groups are higher for delignified and bleached fiber than particles as shown in
Figure 2. Consistent with these results, identified functional groups of β-(1-4)-glycosidic bond of cellulose in 895 cm\(^{-1}\) is obviously detected in delignified and bleached fiber which correspond to exposed cellulose part. The absence of aromatic ring vibration of lignin in 1515 cm\(^{-1}\) for bleached fiber indicate that lignin almost totally dissolved during the bleaching process and result in bright fiber. Furthermore, carbonyl groups that indicates for xylan on hemicellulose in 1734 cm\(^{-1}\) is not detected for bleached fibers as seen in Figure 2. In these cases, sorghum fiber that bleached through sodium peroxide solution could be as raw material for MFC with high cellulose content. Alkaline extraction allows for sugar degradation of hemicellulose and disruption of lignin macromolecules then by peroxide oxidation break up chromophore compound on lignin structure [10].

![FTIR spectrogram from sorghum particle, (b) sorghum fiber after delignification process, and (c) after bleaching process](image)

**Figure 2.** (a) FTIR spectrogram from sorghum particle, (b) sorghum fiber after delignification process, and (c) after bleaching process

3.2. Characterization of microfibrillated cellulose

3.2.1. Dispersion stability

The dispersion of cellulose in water or a particular solvent could be an indicator of the size reduction and fibrillation effectiveness of cellulose. The mechanism of kneading process by pass through the cellulose fibers between two rotors which moving forward in co rotating flow so could defibrillate and reduce the diameter of cellulose simultaneously. The dispersion stability of MFC in 1, 3, and 5 passes are present in Figure 4. The samples start with turbid suspension after the TSE process as shown in figure 3 (a), then after 5 minutes, the MFC with 1 and 3 passes of TSE becomes translucent while MFC with 5 passes remains turbid as shown in Figure 3 (b). These results indicate that smaller particle size is produced by 5 passes of TSE than 1 and 3 passes. Smaller particle size correspond to the wide surface area. The defibrillation process also could expose hydroxyl groups of cellulose which than facilitate hydrogen bonding with water. Therefore, cellulose with smaller particle size and more expose hydroxyl groups is more stable in suspension. MFC build a strong network by hydrogen bonding then well dispersed into the water [11]. MFC which processed minimal in 5 passes more stable in water because result in smaller fiber than 1 and 3 passes of the TSE process [12].
Figure 3. Dispersion stability of treated MFC with TSE in (A) 1 passes, (B) 3 passes, and (C) 5 passes.

3.2.2. Morphology
MFC which resulted by the TSE process performs in micrometers scale of fiber’s diameter with millimeters scale of length. Kneading mechanism by the co-rotating flow of TSE effectively produce MFC with high aspect ratio as presented in figure 4 (a, b). Sorghum fiber which has passed through the TSE in 5 passes has smaller fiber’s diameter with about 1 up to 10 µm (Figure 4b) than 1 passes with about 10 up to 20 µm (Figure 4a). Figure 4b also show defibrillation and size reduction could be achieved at the same time. Co rotating intermeshing flow of TSE minimize the fibers freely rotate so could hold the fibers remain between on two kneading screw without thrown up into the TSE chamber. Those results confirm for better dispersion stability for MFC with 5 passes than in 1 and 3 passes of TSE. Rol et al. [13] report significant size reduction on fibrillated fiber after 7 passes of TSE as high shear in the nip of the kneading part. The shearing force on the fiber creates a rough surface then exposed hydroxyl groups of cellulose so could be stable in water which correlated for stable dispersion stability. Ho et al. [12] discover of highly entangled and twisted morphology of MFC with diameters in nanoscale and also suggest for optimum TSE process not more than 6 passes because could encourage for cellulose crystallinity degradation on 10 passes.

Figure 4. Morphology of treated MFC by TSE in 1 passes (a) and 5 passes (b) with 1000 x of magnification.
3.3. Properties of polylactic acid biocomposites

3.3.1. Mechanical properties
PLA biocomposites were produced with MFC without treatment then denoted as PLAM and MFC with 5 passes of TSE then denoted as PLAM_TSE5. Mechanical properties of PLA biocomposites include tensile strength and modulus of elasticity are expressed in figure 5. The addition of MFC improves tensile strength up to 2.5% and 4.54% for PLAM and PLAM_TSE5 respectively. The high aspect ratio of MFC enables better bonding and wettability with PLA matrix because of wider surface area. Modulus of elasticity also increases about 38.34% and 40.36% for PLAM and PLAM_TSE5 respectively. MFC addition could enhance the toughness of PLA biocomposites and further with high aspect ratio result in better ductility than pure PLA and PLAM. Overall, MFC with higher aspect ratio, correspond to good interfacial adhesion, could produce PLA biocomposites with higher stiffness and toughness to hold some loads. These results agree with Joonoobi et al. [4] and Suryanegara et al. [6], MFC addition improves the interfacial adhesion and physical bond into amorphous PLA and semi-crystalline PLA that contribute to tensile strength and modulus enhancement.

![Figure 5](image-url) Mechanical properties of PLA biocomposites

3.3.2. Thermal properties
Thermal properties of PLA biocomposites are represented with glass transition temperature (Tg) and melting temperature (Tm). Consider that PLA 4060D is an amorphous PLA, there is no crystallization temperature (Tc) and cold crystallization temperature (Tcc) could be detected because of organized crystal structure that could not be formed. The addition of MFC could cause Tg and Tm shift for PLAM and PLAM_TSE5 even in slightly different as presented in Figure 6. These results indicate that MFC has interaction with PLA matrix. PLAM_TSE5 has a higher Tg than PLA and PLAM which correspond to the brittleness. These results were similar to Frone et al. [14] that higher Tg could be affected by lower chain mobility of PLA because of MFC addition. Different tendencies report by Johari et al. [15] that addition MFC together with plasticizer effective to lower the Tg because of accessible chain mobility. Figure 6 reveals only one endothermic peak performed for all biocomposites at around 129 up to 130°C which correlated for one form crystal structure for amorphous PLA. The Tm is affected by the form and perfection of crystal structure [14]. The endothermic peak of PLA with MFC (PLAM and
PLAM_TSE5) has broader peak than PLA which might indicate the change of PLA polymer chain by MFC addition.

![Figure 6. Thermal properties of PLA biocomposites](image)

**Figure 6.** Thermal properties of PLA biocomposites

3.3.3. Dynamic mechanical properties

Dynamic mechanical analysis allows some tensile force and thermal exposure simultaneously. The addition of MFC increase the storage modulus of PLA biocomposites even in amorphous state. Storage modulus of PLAM_TSE5 is 3.088 Mpa which increase about 10.64% from PLA in amorphous and glassy condition as shown in Figure 7. Contrary, storage modulus tends to be unchanged at the rubbery stage at 75°C. In these cases, MFC might limit the molecular chain mobility of PLA above the Tg [4]. Storage modulus enhancement indicates good interfacial adhesion between MFC and PLA [6]. Tg in dynamic condition tends to increase, similar to thermal analysis, for PLAM and PLAM_TSE5. These results emphasize that lower chain mobility might occur above the Tg than under the Tg with MFC addition.

![Figure 7. Thermomechanical properties of PLA biocomposites](image)

**Figure 7.** Thermomechanical properties of PLA biocomposites
4. Conclusion

Sorghum fibers which isolate by sodium peroxide solution could produce high cellulose content fiber. Twin screw extruder with co rotating internmeshing flow is effective for defibrillation and size reduction of cellulose fibers which could achieve 1-10 µm in diameter and millimeters in length. The high aspect ratio of MFC could facilitate bonding and wettability on PLA matrix which could improve some properties include mechanical, thermal, and dynamic mechanical. The tensile strength of PLAM_TSE5 increase 4.54% in 50.60 Mpa and modulus of elasticity increase 40.36% in 2.82 Gpa. Storage modulus of PLAM_TSE5 also increases 10.64% in 3.088 Mpa compare to PLA.

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