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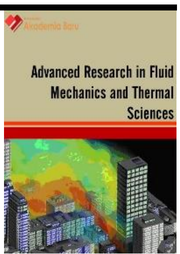

Structural, Thermal, and Mechanical Properties of Spent Mushroom Substrate (SMS) and Rubberwood Sawdust (RWS) Binderless Particleboards

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ABSTRACT

The aim of this study is to examine the chemical compositions (extractive, alpha-cellulose, hemicellulose, and lignin) of the spent mushroom substrate (SMS) and rubberwood sawdust (RWS) to evaluate its suitability in the production of binderless particleboard. In this study, SMS fiber and RWS fiber were used to produce experimental binderless particleboard panels. Binderless particleboards were made with a target density of 0.80 g/cm^3 at temperature 130 °C and a pressure of 5 MPa under the hot press. The chemical composition of the SMS fiber was found to be slightly lower than that of the RWS fiber. The degradation of the chemical composition can cause reduction of particle size and discoloration of fibers. Binderless particleboard made from SMS fiber also shows slightly lower mechanical properties as compared to the RWS fiber. The reaction and thermal profiles show almost similar characteristics for both SMS and RWS samples. However, the spent mushroom substrate (SMS) shows slightly lower chemical, thermal, and mechanical properties as compared to the rubberwood sawdust (RWS).

Keywords:
Cellulose; Thermal; Binderless; particleboard

1. Introduction

Mushroom is a fleshy body of some fungi (mostly *basidiomycotina* and *ascomycotina*) which is formed from a group of mycelium buried in substratum [1]. Various types of mushrooms have been artificially cultivated, but only six mushrooms are widely preferred for large-scale cultivation and

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commercialization. Paddy straw mushroom, oyster mushroom, button mushroom, milky mushroom, Shiitake mushroom, and Jew's ear mushroom are the most cultivated mushrooms [2,3].

The spent mushroom substrate (SMS) is a valuable by-product from the mushroom industries. It consists of partially degraded-lignocellulose material such as rubberwood sawdust [4,5]. At a global scale, mushroom cultivation and its respective waste production have been increased over the last few decades [6,7]. One kilogram of mushroom requires approximately five kilograms of substrate in order to turn into the waste products [8].

A huge amount of SMS in the mushroom farms is one of the most serious challenges in terms of environmental concerns such as soil, water, and air pollutions [9-12]. Recycling of SMS into the secondary substrate for mushroom cultivation is not economically feasible, since it no longer works as an appropriate mushroom cultivation medium, and also the production of fresh new mushroom substrate is much cheaper [13,14].

Oyster mushroom, or white-rot fungi, is the most commonly cultivated mushroom in Malaysia [5,6], due to its strong enzymatic action towards various kinds of organic substrates. Substrate inoculated with white-rot fungi has a tendency to discolor from brown to white due to degradation of lignin [5,15]. The wood-degrading mushroom is a waste material from mushroom cultivation and a product of natural lignocellulosic enzymatic systems [16,17]. Enzymatic pre-treatment during mushroom cultivation can improve the properties of wood fiber. In addition, the laccase enzyme in the mushroom production can enhance degradation of the phenolic molecules in wood fiber. The term "binderless particleboard" refers to the panel of wood particles formed in the presence of three main elements; water, heat, pressure without any adhesives or binders. The binderless particleboard fabricated from wood fiber has exhibited improved mechanical properties [18].

Oyster mushroom species can secrete an enzyme which is potential for digestion of lignocellulosic component. This enzyme can breakdown the polysaccharides backbone into lower molecular weight monomers [14,19,20]. The degradation of the structural backbone such as cellulose and hemicelluloses might give a negative or positive effect on the wood fiber during the production of binderless particleboard. The breakdown of hemicelluloses into small sugar monomers, and also degradation of lignin during enzymatic pre-treatment can contribute to the self-bonding between the fibers [21-23]. The current can improve the mechanical properties of the particleboard [21,24]. The determination amount of lignocelluloses component that undergoes degradation during mushroom growth activity is important.

Previous studies report that the chemical composition of wood fiber is important as it will affect the mechanical performance of the board [21,24]. The determination amount of lignocelluloses component that undergoes degradation during mushroom growth activity is important. In the current study, spent mushroom substrate (SMS) and rubberwood sawdust (RWS) were successfully fabricated and examined for the production of binderless particleboard. The SMS was an abundance material and considered as secondary waste fiber that was not being utilized completely. Thus, using SMS as raw material for the production of binderless particleboard would be much more economical than RWS. Thus, various properties (chemical, thermal, mechanical) of SMS were analyzed in order to replace with the current RWS as a raw material in the binderless particleboard.

2. Methodology

2.1 Materials

The SMS and RWS fibers were obtained from a mushroom farm in Lahar Bubu mushroom farms, Pulau Pinang, Malaysia (Figure 1). As mentioned before, SMS fiber is a waste product of mushroom substrate made from RWS. The SMS fiber is used as a substrate for mushroom production for about

3 months, while the RWS fiber is unused raw material before the preparation of a fresh mushroom substrate.

Fig. 1. Spent mushroom substrate block

2.2 Fabrication of Binderless Particleboard

The SMS and RWS fibers were first obtained and disintegrated homogenously. The fabrication of the particleboard was followed from previous studies [25]. However, there was no binder used in this fabrication process and the moisture content of the fibers was at 60 %. Thus, the pressing method was followed with a slight change from the mentioned previous studies. The fibers were placed and dispersed in a steel mold with the dimension of 21 cm × 15 cm × 0.6 cm at target density 0.80 g/cm^3. The fabrication process was continued by heating using a hot-press machine at 130 ^{o}C with 5 MPa pressure for 20 min. Then the heat from the hot press machine was turned off. The board was pressed continuously with the remaining heat from the hot press machine for another 20 minutes to complete the process [26,27].

2.3 Characterization

2.3.1 Chemical composition analysis

The SMS and RWS fibers were dried and disintegrated into powders in order to study their chemical compositions. The extraction of the samples was followed by continuous refluxing for 6 hours in a mixture of ethanol and toluene (2:1, v/v). Hollocellulose and lignin contents were determined using Wise Methods and TAPPI standard 22 os-74, respectively [21,28,29]. Moreover, the alpha-cellulose content was identified by the extraction of hollocelulose with 17.5 % NaOH solution. Finally, the hemicellulose content was calculated by subtracting the alpha-cellulose content from the hollocellulose content. All analyses were carried out in triplicate.

2.3.2 Particle size distribution analysis

The particle size distribution of micro-sawdust particles was measured by the dry sieving method using dry laser diffraction (Malvern Sciro2000 Mastersizer). The fibers were dried at 50^{o}C for 24 hours in order to ensure a narrow and homogeneous distribution of the fibers. The refractive index for the fiber was set at 1.53, and the particle size distribution of the fibers was obtained.

2.3.3 Structural and thermal analysis

The functional groups existing in fibers were analyzed using a Fourier Transform Infrared Spectroscopy (FTIR) - Nicole infrared spectrophotometer, Avatar 360 FTIR E.S.P - in the range of 4000

- 470 cm^{-1} with a resolution of 4 cm^{-1}. Approximately, 5 mg of fibers with 95 mg of finely ground potassium bromide (KBr) were mixed and pressed into pellets of about 1 mm thickness. Significant transmittance peaks at particular wavenumbers were measured using the "find peak tool" provided by the Nicolet OMNIC 5.01 software. The thermal stability of the fibers was measured using a Perkin Elmer-7 thermogravimetry. The thermal profiles were recorded from 30 °C to 800 °C, where around 5-10 mg of the sample was placed in an aluminum pan at a heating rate of 20 °C min^{-1} under a nitrogen atmosphere. It is noted that, the SMS and RWS fibers before hot press were used in this analysis in order to characterize their functional groups and thermal properties, respectively. The analysis on the properties of fibers before hot press might reveal a potential outcome of functional group and thermal stability that contributes on fiber bonding during board formation.

2.3.4 Dimensional stability analysis

Five replicate specimens for water absorption and thickness swelling test with a dimension of 5 cm × 5 cm were prepared, from particleboard. The water absorption and thickness swelling were followed according to Japanese Industrial Standard JIS A 5908:2003 [30].

2.3.5 Mechanical strength analysis

Five replicate specimens for the flexural strength test and tensile strength test with a dimension of 5 cm × 15 cm and 2.5 cm × 25 cm were prepared, from particleboard, respectively. The flexural strength was followed according to Japanese Industrial Standard JIS A 5908:2003 [30], while for tensile strength, the test was followed according to ASTM D3039 [31]. An Instron Testing System Model UTM-5582 equipped with a load cell capacity of 1000kg was used for the mechanical analysis.

3. Results and Discussion

3.1 Chemical Composition

The chemical constituents of SMS and RWS fibers are both structural (cellulose, hemicelluloses, and lignin) and non-structural substances (mostly low-molecular-mass compounds). The chemical composition (non-structural) of the SMS and RWS fibers were obtained to be extractive, cellulose, hemicellulose, and lignin (Figure 2). From the results, it is obvious that the chemical composition of both SMS and RWS fibers are almost similar, however there are a few differences in the overall concentration of the existing constitutions. In the production of particleboard, the chemical compositions of the raw materials are important as it might give a negative or positive effect in the performance of the board [32].

Extractives are a minor fraction in the wood-based materials. In the current study, 13.81 % of the extractives were measured from the SMS fiber, while 4.46 % from the RWS. Higher concentration of extractives in SMS can be due to the presence of a larger amount of sugar content in the fiber [24]. As mentioned before, lignocellulose-degrading enzymes play a crucial role in converting lignocellulose into carbohydrates and noncarbohydrates components [33]. The enzymatic reactions during mushroom growth from SMS fiber enhance the degradation of wood polysaccharides such as α-cellulose and hemicellulose into sugar for energy uptake [22,23]. A large amount of extractives remaining in the SMS fiber can be considered as an inefficient uptake of sugar-based monomers and oligomers during mushroom growth [21].

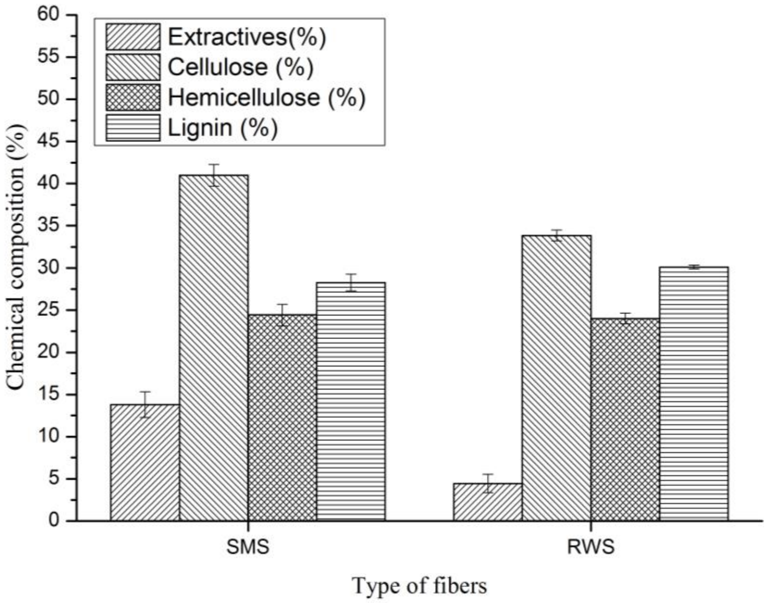

Fig. 2. Chemical composition of SMS fiber and RWS fiber

By comparing the chemical compositions of SMS and RWS fibers, it can be observed that the overall concentration of α-cellulose and hemicellulose decreased from 41 % to 33.87 %, and from 24.43 % to 24.04 %, respectively. Lignin is reported as a natural self-bonding binder, and an important constituent in the production of particleboard [28]. The lignin contents of the samples were obtained to be around 28.28 % and 30.11 % for SMS and RWS, respectively. Based on the analysis, it was revealed that the degradation of chemical composition of SMS was slightly high and might probably result in a small reduction on particleboard performances.

The white-rot fungi are more likely tend to consume lignin as an energy source during growth. It can easily metabolize carbon sources to degrade lignin from fiber substrates [2,12]. Decolorization of the fibers from brownish to yellowish can be due to the degradation of lignin (i.e. reduction of the lignin content) [34]. It also is reported that, the presence of glucose can be one of the factors that will cause a brownish color. During the production process as a mushroom substrate, the SMS fiber underwent a heating treatment for sterilization. The heating treatment can initiate the discoloration mechanism of the glucose, which is called the non-enzymatic browning. Thus, it is also possible that the discoloration of the SMS fiber was attributed to glucose caramelizing during the process [35]. Figure 3 clearly shows the color of SMS and RWS samples, where the color of SMS is brighter than RWS.

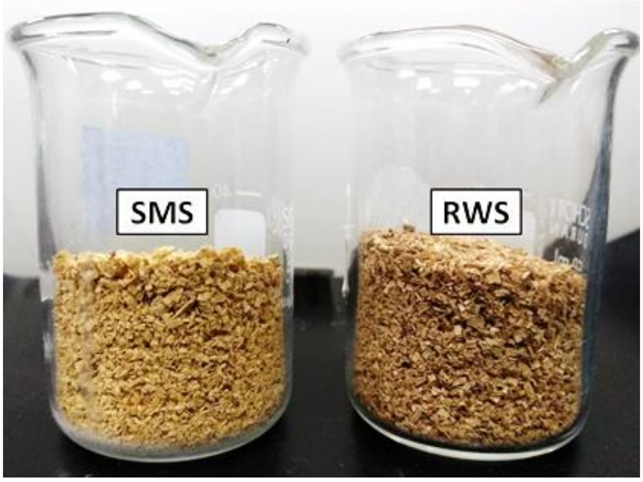

Fig. 3. The color of SMS and RWS fibers

Lignocellulose degradation can affect the average particle size of the sample (Figure 4). It is obvious that the average particle size of SMS (~686.7 µm) is smaller than RWS (~852.6 µm). This observation can be supported by Liu *et al.,* [24] in a study on various properties of binderless boards made from oak logs degraded by fungi. It was also reported that the reduction of the particle size can influence the mechanical properties of the binderless particleboard [36].

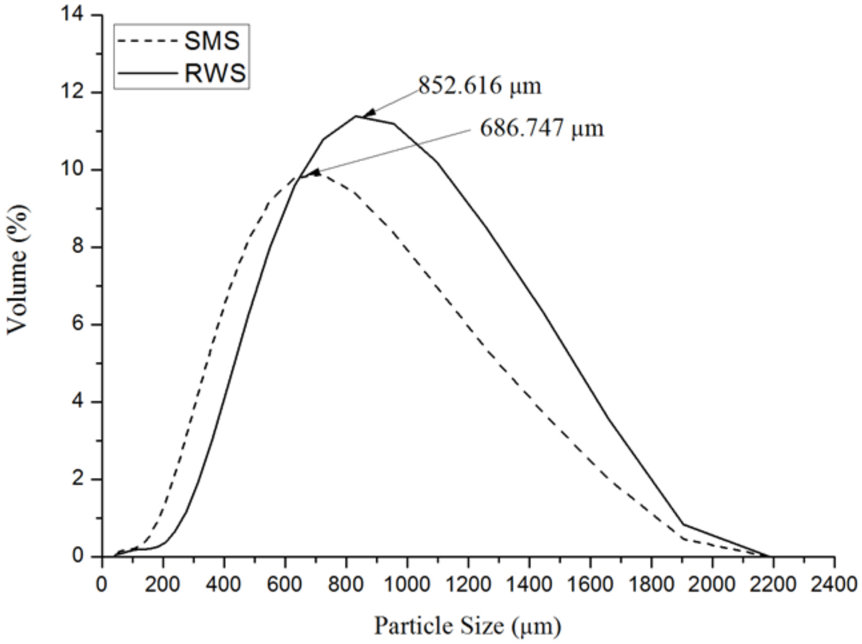

Fig. 4. Average particle size of SMS and RWS fibers

3.2 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analysis was used in order to study the structural units (functional groups) present within the SMS and RWS fibers (Figure 5). The FTIR spectra of both SMS and RWS are almost similar. A single and broad band at around 3400 cm^{-1} (3600 – 3200 cm^{-1}) is assigned to the vibration frequencies of -OH groups. The strong intensity of this band is most probably due to the abundance of hydroxyl groups present on the cellulosic constituents of SMS and RWS fibers [37]. In addition, a small band at around 2900 cm^{-1} (2800 - 3000 cm^{-1}) corresponds to the -C-H stretching vibrations of methoxyl, methylene, and methyl groups [32]. A very small reduction of this band in SMS fiber can be assumed as a cellulose degradation during mushroom growth. An intense band at around 1670 cm^{-1} can be assigned to the vibrational frequencies of -C=O groups originating from the unconjugated carbonyl/carboxyl stretching presents in the structural backbones of SMS and RWS samples [2]. The existence of this peak in the SMS fiber indicates an inefficient energy uptake during the growth activity of mushroom, which further reflects in a defective degradation of hemicellulose into sugar monomers. Two spectral regions between 1600-1200 cm^{-1} (aromatic skeleton vibrations) and 1200 to 800 cm^{-1} are assigned to the vibrational frequencies of lignin constituents. Since the type of mushroom used in this study is the white-rot fungi, lignin remains intact before or after the mushroom growth activity [38].

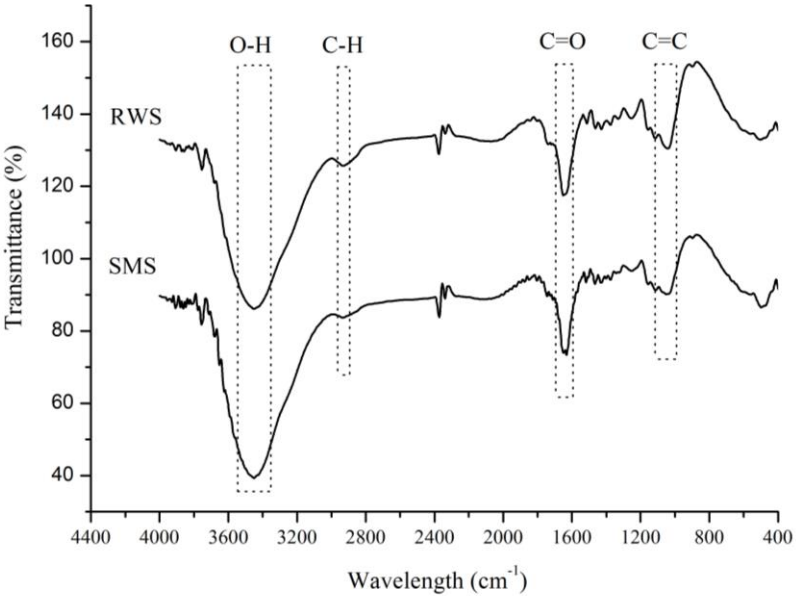

Fig. 5. FTIR spectra of SMS and RWS fiber

3.3 Thermal Stability

Figure 6 represents the TG and DTG thermograms of SMS and RWS fibers. The thermograms are quite similar and exhibit three decomposition steps. The first weight loss can be observed in the range of 30 °C to 100 °C, attributed to the evaporation of surface water [39]. This is because fibers are a hygroscopic material that tends to absorb moisture when exposed to the open air [36,40]. The second weight between 250 °C to 390 °C corresponds to the partial degradation of lignocelluloses constituents like hemicelluloses and cellulose [41]. However, the degradation is incomplete below 350 °C due to the presence of lignin. Thus, compared to the other lignocelluloses components, lignin requires a more extended period of time and higher temperature to ensure complete degradation [25]. The third step of degradation (390 °C to 550 °C) is attributed to the complete degradation of lignocelluloses. Comparison between these two thermograms (i.e. SMS and RWS fibers) indicated a slightly lower thermal stability of SMS as compared to the RWS fiber.

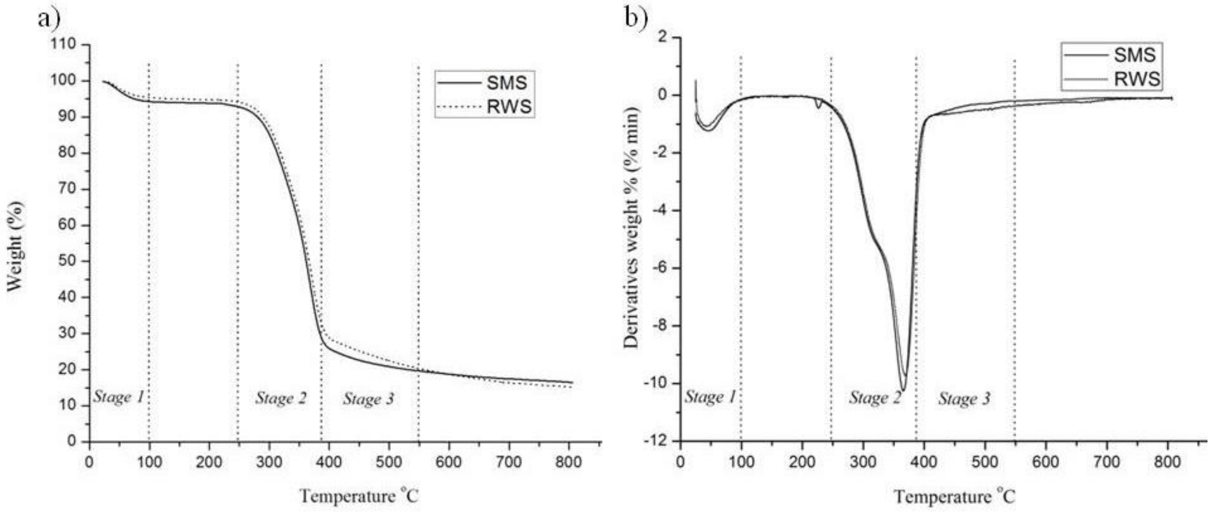

Fig. 6. (a) TG and (b) DTG thermogram of SMS and RWS fibers

3.5 Dimensional Stability Properties

The average values of the water absorption and thickness of the SMS and RWS based binderless particleboard are shown in Figure 7. From the figures, it can be observed that the particleboard made from SMS fiber has slightly lower water absorption but almost similar with particleboard from RWS fiber. The water absorption of the SMS and RWS fiber particleboards were measured to be around 161.94 % and 167.00 %, respectively. From the result, it is revealed that both particleboards have high water absorption due to penetration of water into the capillaries and void in the boards [42]. The reduction of the rate and amount of water absorbed can be achieved by optimization of interfacial adhesion between fiber and binder [43,44]. Meanwhile, the thickness swelling of board made from SMS fiber is much lower by 14.85 %, while RWS fiber was 69.04 %. The thickness swelling for SMS binderless particleboard has met the requirement of the Japanese Industrial Standard. As mentioned in the chemical analysis, the SMS fiber contained a large amount of extractives remaining due to an inefficient uptake of sugar-based monomers [21]. The sugar can undergo polymerization during hot pressing resulting in the formation of adhesive to increase the bonding between fibers in particleboard [36]. As the result, the thickness swelling for particleboard from SMS fiber was reduced.

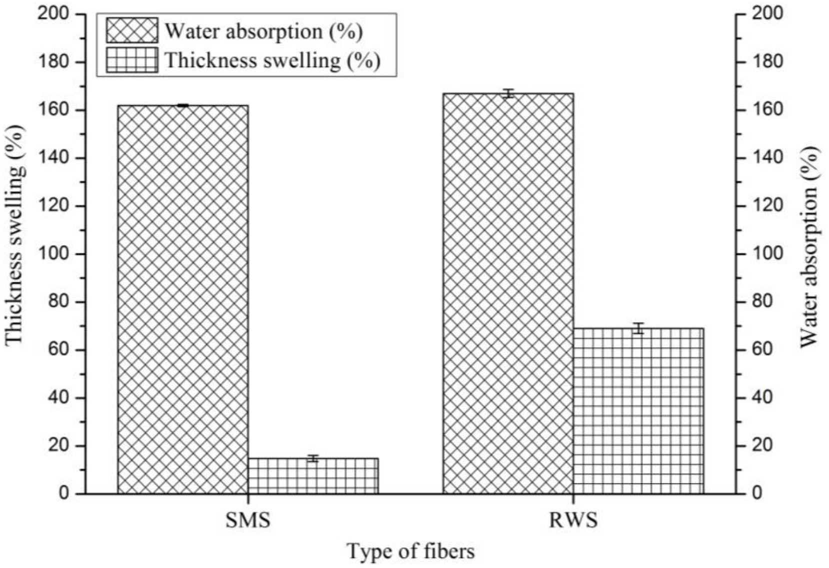

Fig. 7. Changes of dimensional stability at different types of fibers

3.4 Mechanical Properties

The average value of the flexural strength and the tensile strength of the SMS and RWS based binderless particleboard are shown in Figure 8. From the figure, it can be observed that the particleboard made from SMS fiber has slightly lower mechanical strength. The flexural strength of the SMS particleboard was measured to be around 5.98 MPa with the tensile strength of 2.08 MPa. Similarly, for the RWS, 6.2 MPa flexural strength and 3.16 MPa tensile strength were obtained. The flexural strengths for both particleboards do not meet the requirement of the Japanese Industrial Standard. This is due to the fabrication of particleboards without any binders, i.e. by self-hydrogen bonding between fibers [25]. As we discussed before, the total amount of lignocelluloses content in the SMS fiber is lower than RWS fiber which can be directly reflected into the mechanical properties of the boards [21,36].

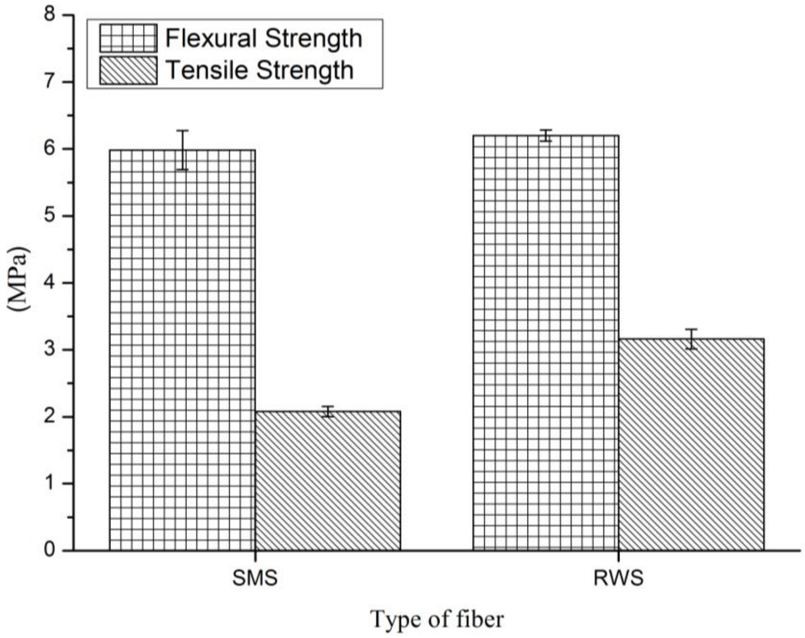

Fig. 8. Changes of mechanical strength at different types of fibers

4. Conclusions

Chemical compositions, structural unites, and thermomechanical properties of the SMS and RWS binderless particleboards were compared in order to provide an alternative for RWS particleboard. The results revealed that the SMS fiber (which is a mushroom waste) has a potential to replace RWS fiber as a raw material for the production of binderless particleboard. The non-structural chemical compositions of the SMS (alpha cellulose, hemicelluloses, and lignin) approximately exhibited a similar trend as compared to the RWS *i.e.* an incomplete enzymatic degradation profile. This can be further reflected in the mechanical properties of the board. However, the degradation of lignocelluloses had reduced the particle size of the SMS and decolorized the wood fiber. The structural and thermal analyses of the samples indicated almost similar properties of the SMS and RWS fibers. It can be concluded that owing to the similar properties of the SMS and RWS, the SMS can be potentially utilized as an alternative to RWS in the production of binderless particleboard since a slight reduction in the lignocelluloses component in SMS fiber does not significantly affect the mechanical performances of the board. The SMS, as a waste product, can be potentially commercialized and replaced with RWS fiber, which is economically more feasible and environmentally friendly. In order to meet the required standard, it is recommended that the SMS fiber needs to be reinforced or mixed with other waste natural fibers with suitable processing and fabrication methods in order to improve the mechanical performance of the binderless particleboard.

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