Microfibril Cellulose Filler Contributes to Thermal Stability and Morphology of Bioplastics Characteristics of Sorghum-Based

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Abstract. This research aimed to examine the effect of cellulose microfibrils filler to thermal characteristic and morphology of bioplastic. Sorghum starch and chitosan, of which 63 micron particle size, were varied by starch to chitosan ratio (g/g) of 10:0; 9.5:0.5; 8.5:1.5; 7.5:2.5; 6.5:3.5; and 5.5:4.5 respectively. The cellulose microfibrils as a filler were added, and its concentration varied of 0; 1; 2; and 3% based on the total dry weight of the combined biomaterials. Glycerol as a plasticizer was also appended to about 10% based on the total dry weight of the combined biomaterials. The combination of 8.5 g sorghum starch and 1.5 g chitosan gave the best results and revealed the enhance of the thermal characteristic of bioplastic due to the increase of the filler. This phenomenon was expressed in glass transition temperature and melting temperature of bioplastic. The SEM analysis on the morphology structure of bioplastic surface showed that the increase of the filler contributes to dense of bioplastic structure.

Keywords: Bioplastics, cellulose microfibrils, thermal stability.

1. Introduction

Synthetic plastics made from petroleum is one of the materials used to facilitate human life because it is lightweight and economical. However, the use of such plastics on an ongoing basis can increase environmental problems because it has a low level of degradability. This plastic will be difficult to degrade by decomposing bacteria so that there is an accumulation of plastic that causes environmental problems. Observing, the magnitude of the negative impact on the environment that can occur, it takes innovation in making plastics that can be biologically degraded. One innovation to be realized is the making of biodegradable or bioplastic plastics that can match the characteristics of synthetic plastics[1].

Bioplastics preparation utilize renewable natural materials, so they are easily degraded naturally[2]. These material feedstocks retrieve from natural polymers, namely polysaccharides and proteins[3]. Sorghum starch is one of the natural polysaccharides potentially used for this purpose. It is derived from the Sorghum plant (Sorghum bicolor L.), a type of cereal plant which has promisingly to develop and cultivate, especially in dry areas with 80.42% starch content[4]. However, starch-based bioplastics have the disadvantages of the low mechanical properties and the high rate of water absorption. Therefore, the presence of additives is needed in order to enhance its properties. Addition of chitosan in the starch-based bioplastics can reduce the rate of water absorption due to its hydrophobic nature.
The mechanical properties can also improve by means of a filler. The added filler will occupy the cavity between the bioplastic constituents and make it denser. The difference in the size of the filler can also influence its density. The smaller the size of the filler used, the bioplastic surface produced will be denser and have a greater surface contact.

This study will examine the exact formulation of constituents that form bioplastics, namely sorghum starch, chitosan, and cellulose microfibrils (CMF) derived from sorghum stem.

2. Research Methodology

2.1. Materials and tools
The main ingredients in bioplastics synthesis are sorghum starch and glycerol, and as a filler used microfibril cellulose extracted from sorghum stem. Sorghum starch and sorghum stem were obtained from BPTP Lampung. The chemicals involved during bioplastics preparation are potassium hydroxide (KOH), hydrogen peroxide (H2O2), acetic acid (CH3COOH) and demineralized water. Morphological testing using Scanning Electron Microscope (ZEIZZ EVO MA 10). Meanwhile, observation of thermal characteristics used the Differential Scanning Calorimetry (Q20) method.

2.2. Synthesis of cellulose microfibrils (CMF)
The method of CMF processing is a semi-mechanical method that refers to previous research. Sorghum stem powder, which has reduced to 100 mesh size, is weighed as much as 10 grams and then placed in a 500 ml volume measuring cup. The sorghum stem is then soaked and stirred with a 4% KOH solution at 80°C for 1 hour. Then the sorghum stems are washed and bleached twice using 6% H2O2 at 70°C each for 1 hour while stirring. Material that has been washed soaked and stirred with 4% KOH solution at 80°C for 1 hour. For the final stage, the material is washed to produce a pH of washing water nearly seven from the initial pH of 12. After washing, sorghum powder in the oven at 100°C for 3 hours. Dry sorghum stem powder is put into the dish mill for 90 minutes to reduce its size.

2.3. Synthesis of bioplastics
The bioplastic synthesis referred to Weiping Ban with some modification. Starch and chitosan were weighed at 9.5; 0.5 g / g. Then chitosan was dissolved with 90% acetic acid with a chitosan concentration of 20% so that the volume of chitosan was 2.5 ml. After that, starch is mixed in 196.7 ml of distilled water and then mixed with a chitosan solution in a 500 ml measuring cup. Starch solution: chitosan is placed on a hot plate at a temperature of 95°C while stirring at 375 rpm. About 0.8 ml Glycerol was mixed into a solution of starch and chitosan. This mixture stirred until the mixture is homogeneous, then add 1% by weight CMF to the mixture. The bioplastic mixture then stirred for 35 minutes. The bioplastic solution removed from the hot plate and allowed to stand until the temperature drops to 35°C. The bioplastic solution was then poured as much as 100 ml into a mold and dried in an oven at 60°C for 10 hours. The plastic removed from the mold and put into a ziplock and stored in a desiccator before being analyzed. These steps are repeated with variations in the formulation of starch; chitosan10; 0, 9.5, 0.5, 8.5, 1.5, 7.5, 2.5, 6.5, 3.5, and 5.5 ; 4.5 (gr; gr) and 0%, 2% and 3% wt CMF concentrations.

The bioplastic sheets were analyzed thermally with differential Scanning Calorimetry (DSC) and morphological tests with Scanning Electron micrograph (SEM).

3. Results and discussion

3.1. The morphology of CMF
The morphology of CMF as it is shown in Figure 1, informed that the cellulose filler has 2-8 μm diameter. This value is smaller when compared to the previous study, that is 63 μm. Differences in solvents used can affect the fibers formed. Removing lignin and hemicellulose levels also affects the
quality of extracted CMF. Delignification using KOH solution drastically decrease in hemicellulose and lignin content, about 81 to 86%.

The alkaline pretreatment causes hemicellulose hydrolyzed and dissolved in aqueous solution while, the bleaching process eliminated most of the lignin [5]. Mechanical treatment will split the fibers to give a smaller diameter. As a result, the cellulose content in the fiber after treatment increase to about 50%.

![Figure 1](image)

**Figure 1.** The effect of addition of filler and plasticizer on tensile strength of the bioplasics.

### 3.2. The thermal analysis of bioplastics

The result of DSC analysis for a polymer material will provide information on the glass transition point (Tg), the crystallization point (Tc), and the melting point (Tm). The glass transition point (Tg) is the temperature at which the material changes from a glassy to rubbery. The crystallization temperature (Tc) is the temperature when the polymer is crystalline. Meanwhile, the melting point (Tm) is the parameter when the polymer starts to melt to form a liquid. On the other hand, the decomposition point (Td) is the point when the polymer begins to break down or degrade[8].

<table>
<thead>
<tr>
<th>CMF concentration, wt%</th>
<th>Tg, °C</th>
<th>Tc, °C</th>
<th>Tm, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>47.44</td>
<td>112.92</td>
<td>175.56</td>
</tr>
<tr>
<td>1</td>
<td>47.40</td>
<td>101.25</td>
<td>159.27</td>
</tr>
<tr>
<td>2</td>
<td>37.21</td>
<td>104.19</td>
<td>155.04</td>
</tr>
<tr>
<td>3</td>
<td>38.46</td>
<td>92.72</td>
<td>144.66</td>
</tr>
</tbody>
</table>

DSC analysis performed in one warm-up. The results of the analysis are shown in Figures 2A, 2B, 2C, and 2D and the values are tabulated in Table 1. It can be seen that the bioplastics Tg values decrease as the addition of CMF filler, namely 47.44°C (without CMF), 40.70°C (1% CMF), 37.21°C (2% CMF), and 38.46°C (3% CMF) respectively. These results were owing to the elevation of the stiffness of the polymer on the filler addition. Likewise, transition crystallinity temperature (Tc) generally decrease because of filler addition, 112.92°C (without CMF), 101.25°C (1% CMF), 104.19°C (2% CMF), and 92.72°C (3% CMF). The increase in crystallinity corresponds to the interaction between bioplastics in the hydroxyl part at the end terminal of the bioplastic chain to form hydrogen bonds which can induce the bioplastic crystallization process, thereby increasing the bioplastic crystallinity. The addition of filler also affected to the diminishing of transition melting temperature (Tm) in bioplastics, 175.56°C (without CMF), 159.27°C (1% CMF), 155.04°C (2% CMF) and 144.66°C (3% CMF). A decrease in Tm is due to the positive charge of the hydrogen atoms.
in the CH-group to the negatively charged oxygen group in the weakened C = O group. Weak hydrogen bonds lessen the melting point[8].

Figure 2. DSC analysis of bioplastics formulated from 8.5 grams of starch and 1.5 grams of chitosan without filler addition (a), 1% filler (b), 2% filler (c), and 3% filler (d).

3.3. The morphology of bioplastics
Analysis of SEM on bioplastics comprises of 8.5 grams sorghum starch and 1.5 grams chitosan on filler addition incremental are shown in Figure 3. It is examined that the more CMF filler added, the higher of the homogeneity of bioplastics resulted. Moreover, this additive could also increase the smoothness of the matrix. It is because the trapped MFC fills the empty cavity on the bioplastic surface that contributes to improving the bioplastic density[2].
Figure 3. Surface profiles of bioplastics comprising of 8.5 g sorghum starch and 1.5 g chitosan on various CMF filler concentrations: (a) without filler addition, (b) 1% filler addition, (c) 2% filler addition, and (d) 3% filler addition.

4. Conclusion
The addition of CMF as an additive filler in the manufacture of sorghum-based bioplastics influences the morphology and thermal characteristics of the biocomposite products. Increasing the filler concentration by up to 3% can reduce the glass transition point (Tg), the crystallization point (Tc), the melting point (Tm). Also, the addition of filler in the mixture for this concentration range can increase the density and improve the surface profile of the resulting bioplastics.

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References


