Starch-based biofoams reinforced with microcrystalline cellulose from banana stem: Hydrophobicity and Biodegradability.

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Abstract. Microcrystalline cellulose was isolated from the banana stem, an abundant but underutilized bioresource, by using three main steps, specifically bleaching, alkaline treatment and acid hydrolysis. The isolated MC was used to reinforce starch-based biofoams with different loadings of 0%, 2%, 4%, and 6%. The result of contact angle measurement using the LB-ADSA method achieved remarkable increases of contact angle value as the MC loading increased from 0% to 6%. In addition, compared to starch-based biofoams, starch/MC composite biofoams showed improved biodegradability. The starch/MC composite biofoams displayed good hydrophobicity properties that can potentially represent a sustainable and green alternative for packaging and insulation materials.

1. Introduction
Indonesian banana trees are abundant but are underutilized and just to be waste because only the fruit is taken. Therefore, the integrated utilization of banana tree residues is a necessity. Banana stems have a substance of fibers that are suitable for textiles, composite materials, paper, and adsorbent materials [1]. Its have a good fiber contains several compounds such as lignin, alpha-cellulose, hemicellulose, and water [2]. This supported by [3] where the banana tree has a specific gravity of 0.29 g/cm and fiber size of 4.20 - 5.46 mm and lignin of 33.51%. In the previous study [4], reported natural fiber, essential oils, and also use enzymes can be improved the characteristic of biofoam as a filler. Then, according to Averous [5], the addition of cellulose fibers up to 15% can increase water resistance while increasing its tensile strength. The addition of fiber also affects increasing the hydrophobic nature of Biofoam due to the ability of the fiber to absorb water that is smaller than starch [6].

Given their characteristics, cellulose fibers can reinforce biofoam materials [7]. Biofoam based on starch, in reality, are porous materials which in wet conditions had poor mechanical strength. Such weaknesses can be addressed through the incorporation of cellulosic fiber, particularly when converted as microcrystalline cellulose, which can improve water resistance. Moreover, microcrystalline cellulose in combination with starch is supposed to be fully biodegradable, enhancing its potential packaging ability. In the study, the synthesis new class of biofoam consisting of starch-based biofoam

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with microcrystalline cellulose from the banana stem, which was tested for their hydrophobicity and biodegradability.

2. Materials and Methods

2.1 Materials

Microcrystalline cellulose (MC) was obtained from banana stem (*Musa paradisiaca* L) waste. The chemicals were purchased from Merck and Bratachem, polyvinyl alcohol (PVA) (Merck) Technical grade cassava starch (Bratachem), and Mg Stearate (Bratachem).

2.2 Preparation of biofoam

Various biofoam formulations (Table 1) were prepared using a conventional molding machine for compression. Starch, PVA, Magnesium stearate, distilled water, a varied amount of MC were mixed until a homogenous mixture was obtained. The mixture was poured into a 170 mm × 110 mm x 2 mm mold, which was placed in the compression molding machine. The mold temperature was set at 150°C. The process was carried out at a load pressure of 100 bar for 4 mins of holding time. The variables in this paper was MC content (0%; 2%; 4% and 6% MC) for 30 g of Starch content (in weight) each variation contain 100 mL of water.

| Formulas                        | Code | Composition (%) | Starch | MC | PVA | Mg stearate |
|--------------------------------|------|-----------------|--------|----|-----|-------------|
| Starch/PVA/Mg Stearate/MC 0%   | M0   | 85              | 0      | 10 | 5   |             |
| Starch/PVA/Mg Stearate/MC 2%   | M1   | 82              | 2      | 10 | 5   |             |
| Starch/PVA/Mg Stearate/MC 4%   | M2   | 80              | 4      | 10 | 5   |             |
| Starch/PVA/Mg Stearate/MC 6%   | M3   | 78              | 6      | 10 | 5   |             |

2.3 Water-Contact Angle

The water-contact angle value was measured using ImageJ ver-1.52a (Wayne Rasband, National Institute of Health, USA) software with Low Bond-Axisymetri Drop Shape Analysis (LB-ADSA) method.

2.4 Water Sorption

The Starch/PVA/Mg Stearate/MC biofoam water sorption was measured according to ABNT NBR NM-ISO 535. Four composites were cut into 2x2 cm specimens and conditioned at room temperature by using a chamber containing water. After 1 minute immersion time the average value of biofoam water sorption was calculated:

\[
\text{Water absorption} \ (\%) = \frac{W_a - W_0}{W_0} \times 100\%
\]

where \(W_0\) and \(W_a\) respectively, are the specimen mass before and after water absorption. The tests are performed for each specimen by triplicate.

2.5 Differential Scanning Calorimetry

Differential Scanning Calorimetry analysis of Starch/PVA/Mg Stearate/MC biofoam was performed using Linssesis type STA PT 1600 at a heating rate of 10 C/min under nitrogen atmosphere.

2.6 Biodegradability test

In biodegradability analysis, the biofoam composite ware was cut into rectangular samples of 30-40 mm. The biodegradability of the samples buried in compost soil was determined by calculating weight
loss. Every sample was buried in the soil of compost and each specimen was dug out of the soil of compost after being buried for 30 days. The proportion of weight loss $W$ (%) was determined using the formula:

$$\text{Weight loss (\%)} = \frac{W_{\text{initial}} - W_{\text{final}}}{W_{\text{initial}}} \times 100\%$$

(2)

Where $W_{\text{initial}}$ and $W_{\text{final}}$ are the weights of specimen before and after buried in compost soil.

3. Results and Discussion

3.1 Water-Contact Angle

The hydrophobicity of biofoam can be obtained by measuring the contact angle ($\theta$) of the water droplets on the biofoam surface. The results obtained show the addition of MC will have a significant influence on the contact angle (Table 2). The difference in contact angle between biofoam with 0% MC and biofoam with 2% MC is around 15°, indicates that the addition of MC enhances the hydrophobic nature of biofoam. Meanwhile, as shown in Table 2, no significant differences between biofoam that contain MC.

| Composites     | Contact angle (°) |
|----------------|-------------------|
| Biofoam, 0% MC | 74.27             |
| Biofoam, 2% MC | 89.19             |
| Biofoam, 4% MC | 90.70             |
| Biofoam, 6% MC | 94.97             |

The difference contact angle may be related to surface roughness and / or availability OH on biofoam surfaces [8]. In this case, the difference between the contact angles may be related with OH availability. Starch and MC have strong hydrogen bond interactions so that it will reduce water interactions. An increase in the hydrophobic nature of biofoam will occur with increasing MC content due to the hydrophobic nature of MC [9].

Figure 1. Water-contact angle image of (a) Biofoam with 0% MC, (b) Biofoam with 2% MC, (c) Biofoam with 4% MC, and (d) Biofoam with 6% MC.
3.2 Water Sorption
In the equilibrium moisture environment, water sorption per unit mass (percent) of the composite biofoams were examined. For increased MC content, lower water sorption occurs. The biofoam/0% MC absorbed approximately ~11% of water, while the absorption was decreased almost linearly with the addition of MC to a minimum of 7%. The value obtained in this study is lower than previous studies which range from 23-35% [10]. The decrease in water absorption can be caused by the interaction of strong hydrogen bonds between starch and MC, in addition to the presence of crystalline PVA which can also affect [11]. Optimum water absorption ability on Biofoam/6% MC content.

![Water sorption graph of biofoam](image)

Figure 2. Water sorption graph of biofoam

3.3 Differential Scanning Calorimetry
Biofoam thermal stability is characterized by DSC [12]. The interaction between MC polymer chains and starch is influenced by moisture concentration. Decreasing the water content in the composite will increase the interaction between the MC polymer chain and starch which will cause the structure to become more rigid [13]. The heating process up to 150°C is accompanied by applying pressure of 100 bar causing the water content in the composite is lost so that a rigid biofoam is obtained. Figure 3 shows the DSC curve of biofoam, the glass transition temperature of biofoam was found to increase around 270°C to 287°C. The glass transition temperature is highly dependent on the mobility of the polymer chain [14].

It has been reported that strong interactions between polymer chains will cause an increase in Tg because the mobility of the polymer chains will decrease [14]. Figure 3 shows that in the presence of MC, glass transitions occur at higher temperatures due to the interaction of strong hydrogen bonds thereby reducing the mobility of the cellulose chain and the starch chain. The high Tg indicates that the material has good thermal stability properties and can include several aspects for packaging materials such as resistance to degradation by high storage temperatures [15].
3. **Biodegradable Test**

The weight loss of biofoam is illustrated in Figure 4. The composite of Biofoam/6% MC has the highest weight loss followed by that of Biofoam/4% MC, Biofoam/2% MC and Biofoam/0% MC, respectively. The reasons for this are the uniformity of the distribution of MC in the composite and the interfacial compatibility of MC and composite. The composite reinforced with MC has many inner defects and poor compatibility, leaving the composite vulnerable to the outer microorganism leading to the lowest weight loss.

![DSC graph of biofoam with 0% MC and biofoam with 6% MC](image1)

**Figure 3.** DSC graph of biofoam with 0% MC and biofoam with 6% MC

![Biodegradable graph of styrofoam (PS) and biofoam](image2)

**Figure 4.** Biodegradable graph of styrofoam (PS) and biofoam
The linear polymers in chemical degradation reactions cause a decrease in molecular weight or length chain reducting. Starch has acetal bonds which are very easy to degrade. The amount of mass reduction is caused by the composition of biofoam which consists of natural materials that are easily digested by microbes. The main factor of a polymer that can be degraded naturally was a natural polymer containing a hydroxyl group (-OH), this group was easily degraded microbially [16].

4. Conclusion
Microcrystalline Cellulose (MC) obtained from banana stem were prepared and used to reinforce starch biofoam. The incorporation of MC into the starch biofoam improved hydrophobicity and Biodegradability properties. Starch and MC interact strongly through hydrogen bonds which causes an increase in the water contact angle and reduces water absorption, the results obtained are close to the performance of PS foam. In addition, high Tg values and better biodegradability properties than PS foam indicate that this material has potential as a packaging material.

Acknowledgment
We gratefully acknowledge financial support from the Higher Education Directorate, Ministry of Education, the Republic of Indonesia for this research (PKM budget).

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