



The Effect of the Addition of Lactic Acid as a Modifier to the Morphology and Thermal Properties of Cellulose Nano Fiber Paper

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This study discusses on an attempt to create a transparent conductive paper made by a facile process and environmentally friendly cellulose-based sorghum as a substitute for glass coating in the display industry that has the advantage of being able to be formed and folded. Sorghum stems with a relatively high cellulose content of around 40% make it a potential material to be used as a conductive transparent paper. The isolation of microfibrillated cellulose from sorghum stem waste using chemicals and sonication methods to obtain cellulose nanofibril (CNF) within a nanometer size range are discussed in this research. Furthermore, lactic acid (LA) as a modifier is added with varying concentrations to explore the effect of its addition on the processing of the transparent paper made from the CNF. Characterization in this study includes several aspects: to investigate the morphology of the CNF paper is carried out by scanning electron microscope. In addition, thermal strength for the product is analyzed using thermal gravimetric analysis. It is found that the CNF paper with 0.5 wt% of LA able to increase paper drying time while still able to maintain the morphology of the transparent paper.

such as metal oxide semiconductors,^[2] conducting polymers,^[3] carbon,^[4] graphene,^[5] and metal nanowire.^[6-7]

The biggest composition for paper making is cellulose. The most natural cellulose-producing resources are in the stems of plants, trees, and agricultural residues such as rice husks, straw, etc. Cellulose has a great potential to replace glass fibers because cellulose has high mechanical properties such as stiffness, impact resistance, flexibility, and modulus.^[8] The weakness of paper, which is generally composed of cellulose is not transparent because the diameter of the cellulose fiber is greater than the wavelength of visible light.^[9] With that, the use of paper is very limited to be applied in the electronic world. In order to make the cellulose transparent, the fiber size can be made smaller by making nano cellulose. Many studies have stated that nanocellulose compare to its macro counterpart have increased crystallinity, aspect ratio,

surface area and increased dispersion and biodegradation capabilities.^[10-14]

In Indonesia, the potential to produce natural cellulose fibers is very high because this country has abundant plantation and forest products. One of the natural ingredients that are developing in its use in Indonesia is sorghum plants. In the world, sweet sorghum is the largest plantation product after wheat, rice, corn, and barley. Countries such as China, the United States, India, and even Africa, sweet sorghum commodities have been developed for food as well as bioenergy. So far, the use of sweet sorghum in Indonesia is only as animal feed and is still a favorite of bioethanol research materials. Thus, sorghum which has a high cellulose content has the potential to be used in making conductive paper.

This research is focusing on the synthesis of the mentioned conductive paper called cellulose nanofibril (CNF) paper, in which the nanocellulose was isolated from the bulk cellulose that came from sorghum waste using a crusher and further treated with alkali-bleach method and ultrasonication. To increase the rate of CNF paper fabrication, lactic acid (LA) was added to accelerate the drying process. LA is considered compatible with the cellulose fiber and able to create steric hindrance in between them, therefore it established spaces in the CNF morphology

1. Introduction

Conductive paper is a breakthrough in smart-paper technology that can be developed as an electronic material as well as applications in the field of renewable energy. The nature of paper that can be folded, easy to print, and environmentally friendly is needed to increase the flexibility of future electronic product such as a conductive film. Traditional transparent film layers such as indium thin oxide (ITO) is fragile and rigid,^[1] hence cannot be used as a part for flexible electronics. Therefore, in recent years research on making flexible films has been successfully carried out, for example using materials

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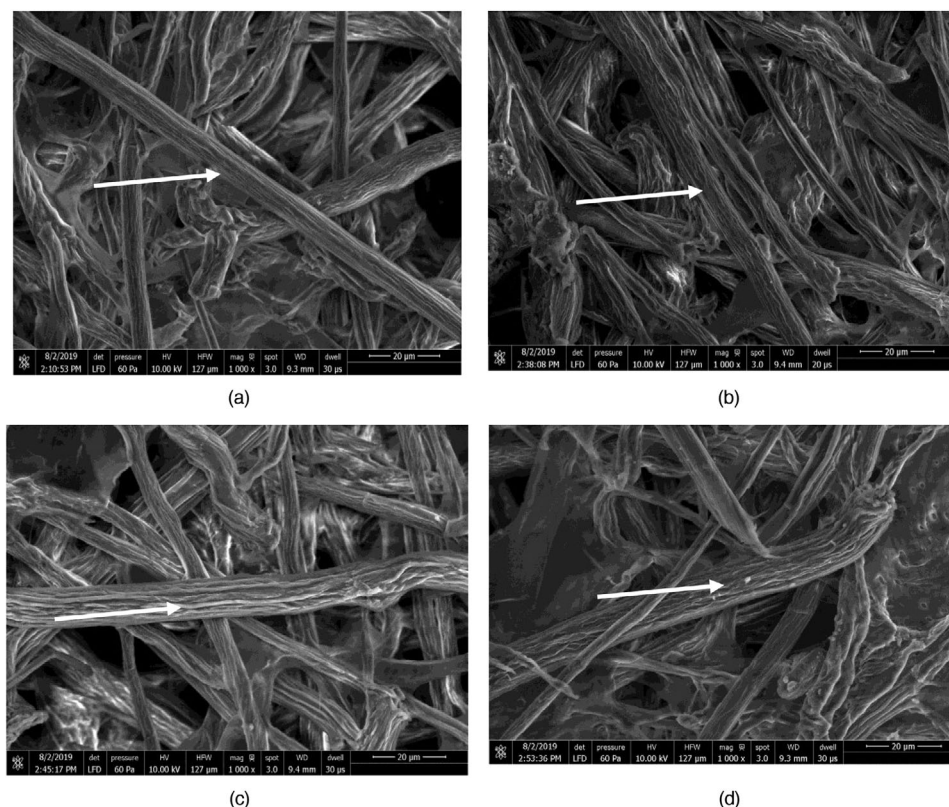


Figure 1. 1000× magnification of secondary electron (SE) images of nanocellulose paper a) without LA; b) with 0.3 wt% LA; c) with 0.5 wt% LA; d) with 0.8 wt% LA

which in return able to increase the overall drying time.^[15] In that case, new structure is created and therefore investigated thoroughly in this report.

2. Results and Discussions

2.1. CNF Morphology

Figure 1a–c shows the SEM images of the paper morphology at 1000× magnification. We can see that there is no effect of the LA to the morphologies of the paper, but there are some visible fibrillated celluloses of various sizes with an average diameter of 6 μm.^[17]

The biggest fibrils that are highlighted by white arrows consist of fibers lump, which forms into a larger fibril. It is suspected that from the process of making the CNF paper, the fibers that were originally nano-sized, agglomerated back into MFC.

2.2. Modified CNF Paper with LA

The addition of lactic acid to the CNF paper aims to reduce the drying time of paper fabrication.

From the results combine in **Table 1**, the addition of lactic acid has reduced the drying time. The reason is that the con-

Table 1. Drying time of each sample.

Sample	Draining time [min] in 80 °C
Reference	75
LA 0.3%	65
LA 0.5%	50
LA 0.8%	60

densation polymerization (oligomerization) occurs between LA and hydroxyl groups of the CNF under high temperature and pressure.^[18] The modification of the CNF with LA, then decrease the hydrophilic moieties and hence the water absorption is decreased. From the results obtained, the fastest drying time achieved by the CNF paper with LA composition of 0.5 wt%.

2.3. Thermal Properties

Thermal tests are carried out to identify the effect of adding LA to the thermal behavior of the CNF paper. This test is important to determine the degradation temperature and thermal resistance when the sample applied as a transparent conductive paper. Thermal stability of the CNF paper product is, therefore, studied by using TGA diagrams as indicated in **Figure 2** to investigate the

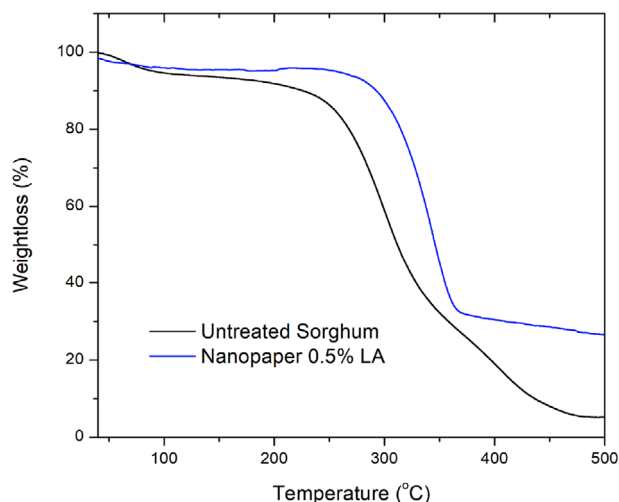


Figure 2. TGA curve of CNF and compare to the MFC extracted directly from sorghum stem

weight loss percentages in which correlated to its degradation temperature.

Figure 2 shows the thermal behavior characteristic of untreated sorghum and CNF paper with 0.5 wt % LA. In the literature, thermal degradation of sorghum occurs at 200–350 °C,^[19] while the graph shows that the MFC from sorghum without treatment begins slowly decompose from 250 to 450 °C and the CNF paper starts to decompose from 280 to 370 °C. In the Carvalho et al. trial,^[20] cellulose decomposed starting at around 310 °C. The increase in decomposition temperature is thought to be due to the reduced non-cellulose content in sorghum.

3. Conclusions

CNF paper that fabricated using ultrasonicated MFC obtained from sorghum stem was successfully produced. The addition of LA to the CNF did not cause any morphological changes from the paper. By adding as much as 0.5 wt% of LA to the CNF, it can reduce paper drying time up to 25 min. The thermal stability of the CNF paper was increased from the untreated sorghum, which indicated that the noncellulose content in the nanopaper was less than the reference.

4. Experimental Section

Materials: The sorghum stem was obtained from SEAMEO BIOTROP (Southeast Asian Regional Center for Tropical Biology)-Bogor. The lactic acid (LA) used was 88% industrial grade that synthesized locally in the University of Bhayangkara, whereas sodium hydroxide (NaOH), sodium hypochlorite (NaOCl), and technical quality acetic acid (CH₃COOH) were bought from Brataco.

Processing of the Sorghum Stem Waste into Nanocellulose: Dry sorghum stem waste was crushed with a crusher and then sieved with a 40-mesh sieve. Then the sample was treated with Alkali-bleach method developed by Aprilia et al.^[16] The result produced micro fibrillated cellulose (MFC) with a size of 100 μm. The MFC then dissolved in 300 mL of water in

a beaker glass and allowed to rise for 24 h. Then it is inserted into the ultrasonicator bath for 15 min with 1500 watts of power. After the ultrasonication, the colloid formed was centrifuged at a speed of 200 rpm in 10 min then 4000 rpm in 10 min. The floating part (supernatant) which was the CNF transferred into the freezer to dry then the dried sample was characterized and brought to the next stage.

Process of the Addition of LA to Modify the Nanocellulose: CNF and LA were dissolved in water then homogenized using magnetic stirrer for 10 min. The LA addition to the CNF paper has three variations, which were 0.3, 0.5, and 0.8 wt%. Colloids formed during the LA addition were then sonicated with sonication tips with 600 J mL⁻¹ energy for 10 min. Colloids formed after sonication were filtered with a PVDF membrane with a vacuum system to speed up the drying speed.

Fabrication of the Transparent Nanocellulose Paper: The CNF sample with the best drying speed was made into a transparent paper by adding water and homogenized by a magnetic stirrer for 15 min. The colloid was then poured into an acrylic board and dried in an oven at 80 °C for 1 h.

Characterizations: The final transparent nanocellulose paper morphology was analyzed using a scanning electron microscope (SEM) at PT Cipta Mikro Material (CMM). On the other hand, thermal properties were analyzed using thermal gravimetric analysis (TGA) at the Research Center for Physics of the Indonesian Institute of Sciences (LIPI-FISIKA).

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

lactic acid, nanocellulose, sorghum, transparent paper, ultrasonication

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