Identification of potential hydrophobic properties of carbon layer from the coffee bean waste

D Fitria¹, L A Al Baroroh¹, F Destyorini¹, W B Widayatno¹, M I Amal² and A S Wismogroho¹

¹Research Center for Physics, Indonesian Institute of Sciences, Tangerang Selatan, Indonesia
²Research Center for Metallurgy and Materials, Indonesian Institute of Sciences, Tangerang Selatan, Indonesia

E-mail: fdytta24@gmail.com

Abstract. The significant increase of waste due to vast development of human civilization and industrialization has plunged humanity into various environmental issues. Nowadays, the concern on waste handling and conversion into more valuable material has become one of hot research topics. Biomass waste has great abundance with various types that can be utilized for many applications such as landfill, recycled-material, adsorbent, separation, catalysis, and so on. In this study, coffee bean waste (CBW) was used as a source to produce hydrophobic layer. The CBW was converted into amorphous carbon using simple carbonization method at 500 °C, dispersed in acetic acid and then mixed with polyvinyl alcohol (PVA) at low temperature heating. In order to investigate effects of composition on hydrophobicity properties, ratio of carbon and PVA was varied. In addition, acetic acid was used to evaluate effect of dispersant on hydrophobic properties. SEM analysis reveals unique morphology of carbon layer. The measurement of contact angle demonstrates that this unique morphology possesses comparable hydrophobicity with that of some well-known materials. Fourier transform infrared spectroscopy (FTIR) analysis confirms the effect of PVA bonding and carbon layer on its hydrophobicity.

1. Introduction

Million tons of coffee beans are produced and consumed by people and health industry each year and most of it is discarded as coffee bean waste. Coffee bean waste (CBW) is mainly composed of cellulose and lignocellulose which contains many heteroatoms such as carbon, oxygen, and nitrogen [1, 2]. Biomass waste is a promising material to be converted as carbon precursor due to its abundance and long term storage potential [3, 4]. Developing carbon precursor from CBW via carbonization may lead to economical, environmental, and efficient benefits. The weight loss of pyrolysed CBW at the temperature of 600 °C is very slow, so carbonization in low thermal process (500 °C) has attracted researchers' interest [5].

Most carbon-based material is generally hydrophobic which is purely based on aromatic, non-polar and sheet structure, so that interaction with extremely polar molecules such as water is very weak [6]. Hydrophobic surface has value of water contact angle of $90^\circ < \theta < 150^\circ$. Surfaces with hydrophobic properties have many applications such as catalyst, anti-corrosion coating, textiles, and self-cleaning [7 - 9]. Unfortunately, materials with hydrophobic properties are relatively expensive and limited.
Therefore, the development of carbon from CBW as hydrophobic material is in great demand because it is very economical and it triggers unlimited development.

In this study, a potential hydrophobic property of CBW with variation of binder is identified. CBW was carbonized at low temperature to obtain carbon precursor which was then dispersed with acetic acid. Carbon layer was fabricated by using a simple coating method on an aluminum plate where PVA was used as the binder. To see the effect of acetic acid on the hydrophobic properties, the carbon layer was also fabricated without using dispersant.

2. Materials and methods

2.1. Carbon layer preparation and characterization

0.24 g CBW was ground until it passed through 100 meshes. CBW was carbonized at 500 °C and held for 1 hour. 20 ml of technical acetic acid with pH of 4 was added to the carbon. The mixture was sonicated for 30 min then dried at 90 °C. In different glasses, 0.03 g of polyvinyl alcohol (PVA) was dissolved homogeneously into distilled water. The dispersed carbon was added to the PVA solution while stirred with stirrer and heated to 90 °C until the mixture turned into slurry. The slurry was casted on aluminium plate using simple coating method. The formed layer was dried at room temperature. PVA and CBW with mass ratio of 1:6, 1:10, and 1:12 were made as other variation. The effect of dispersants was evaluated by fabricating samples with an addition of acetic acid and sonication process. Synthesis of carbon layers using commercial activated carbon with a ratio of 1:8 was used as control.

Functional groups of samples were evaluated using Fourier transform infrared spectroscopy (FTIR) by Nicolet iS10. Samples were characterized by Scanning Electron Microscopy (SEM) to identify surface morphology and justify the existence of PVA in the samples.

2.2. Contact angle measurement

The contact angle measurements were carried out using SLR Camera fitted to macro lens (Canon). 25 µl distilled water was delivered from micropipettes to form sessile drop on the substrate. The measurement was supported by ImageJ software. The average angle was measured four times by averaging left and right angle of the droplets on the substrate.

\[ Contact \ Angle = \frac{\alpha^\ast + \alpha^\ast\ast}{2} \]  

(1)

Figure 1. Contact Angle Illustration.

3. Results and discussion

3.1. Functional groups of carbon layer

FTIR spectra of the samples are presented in figures 2 and 3. Figure 2 shows a comparison of the use of acetic acid as a dispersant and the interaction response with PVA in carbon layer formation. In
figures 2a and 2b, CBW 500 °C spectrum has significant peak at 1400 - 1600 cm\(^{-1}\) corresponding to the stretching vibration of the C-C bond (in ring) and around 2500 – 3500 cm\(^{-1}\) attributed to the stretching vibration of the hydrogen-bonded OH groups [10]. It indicates carbonized CBW is not pure due to the existence of other functional groups beside aromatics. Dispersed CBW has peak with strong intensity at 1402 cm\(^{-1}\) and 1262 cm\(^{-1}\) that are identified as C-H bond and C-O bond formed by interaction of acetic acid at the surface of CBW (figure 2c). Those functional groups will enhance the interaction of CBW and PVA to increase hydrophobic properties of carbon layer. In addition, strong peak at 1500 - 1700 cm\(^{-1}\) shows intensity increase compared to CBW 500 °C. It is because acetic acid successfully functionalized C-C bond in surface of CBW [11]. The peak of carbon layer at 1616 cm\(^{-1}\) is C-C bond as can be seen in figures 2d and 2e. It provides a shift and intensity decrease due to the effect of interaction between π-bond in the CBW surface and open double bond on PVA [12].

The FTIR spectra of Carbon layer with PVA variation are presented in figure 3. Carbon layer 1:6, 1:10, and 1:12 have strong intensity around 1400 cm\(^{-1}\) while carbon layer 1:8 is weak due to strong interaction between CBW and PVA.

![Figure 2. FTIR spectra (a) CBW, (b) CBW 500 °C, (c) dispersed carbon CBW with acetic acid, (d) carbon layer 1:8 with dispersant (acetic acid), and (e) carbon layer without dispersant.](image1)

![Figure 3. FTIR spectra of carbon layer with PVA variation (a) 1:6, (b) 1:8, (c) 1:10, and (d) 1:12.](image2)

3.2. Morphology of carbon layer

Figure 4 shows SEM images of carbon layer made from dispersed CBW and non dispersed CBW, raw material, and the activated carbon. SEM images show that carbon layer from non dispersed CBW has greater surface roughness compare to the dispersed CBW in spite of both samples having impurities (undissolved PVA). The particles of carbon layer from CBW have aggregate structure due to agglomeration with PVA binder as shown in figures 4a and 4b. Carbon layer from activated carbon clearly reveals greater surface roughness compare to CBW carbon based due to uniform size and purity of activated carbon (see figures 4c and 4e). Another phase is also identified in CBW 500 °C image besides carbon phase as observed from figure 4d.
Figure 4. SEM Images of (a) carbon layer 1:8 from dispersed CBW, (b) carbon layer 1:8 from non dispersed CBW, (c) carbon layer 1:8 from activated carbon, (d) CBW 500 °C, and (e) activated carbon.

3.3. Contact angle of carbon layer
Carbon layers were fabricated using simple coating method with weight percentage (wt.%) variation of PVA binder. The effect of acetic acid as dispersant and PVA as binder on carbon layer are presented in table 1. Contact angle of carbon layers from CBW 500 °C are larger than 90°. The results suggest that CBW 500 °C has potential hydrophobic properties and it is comparable with commercial
activated carbon. Carbon layer from CBW 500 °C has lower contact angle than carbon layer from commercial activated carbon (114.334°) because CBW 500 °C has hydrophilic functional groups on its surface as detected using FTIR [13] which decrease the potential hydrophobic properties [14]. Table 1 shows that acetic acid affects the contact angle. Carbon layer from dispersed CBW has lower contact angle compared to carbon layer from non dispersed CBW because acetic acid increases agglomeration with the results that decrease the roughness as provided by SEM images. The highest contact angle of carbon layer from non dispersed CBW is 117.414° with variation of PVA 1:10, whereas carbon layer 1:10 from dispersed CBW is 108.527°. Contact angle of carbon layer 1:10 with or without dispersed carbon is better than 1:6, 1:18, and 1:12 variation. It suggests that the optimal weight percentage ratio of PVA to CBW is 1:10. Contact angle increases with increasing of PVA binder because PVA has high permeability that decreases potential hydrophobic properties of carbon layer [11]. However, only potential hydrophobic properties of CBW is detected in the measurement.

Table 1. Contact angle measurement.

| Name of Sample | Variation | Contact Angle Measurement |
|----------------|-----------|---------------------------|
|                |           | Dispersed in Acetic Acid  | Non Dispersed |
| PVA : CBW 500°C | 1:6       | 104.502°                  | 112.734°      |
| PVA : CBW 500°C | 1:8       | 105.935°                  | 108.719°      |
| PVA : Activated Carbon | -       |                           | 114.334°      |
| PVA : CBW 500°C | 1:10      | 108.527°                  | 117.414°      |
| PVA : CBW 500°C | 1:12      | 107.661°                  | 111.262°      |

4. Conclusion
Carbon layer from CBW with and without dispersion of acetic acid have been successfully fabricated using simple coating method. Potential hydrophobic properties of CBW 500 °C was successfully optimized using PVA binder. Acetic acid as dispersant controlled the contact angle due to interaction with PVA, but unfortunately decreased the contact angle when compared to non dispersed CBW. The
optimal PVA variation (wt.%) for fabrication carbon layer from CBW 500 °C was 1:10 (117.414°) due to its suitable interaction with open double bond on PVA.

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