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# Effect of ZnO and Annealing on the Hydrophobic Performance of x(ZnO)-CA-PLA

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Abstract. The advantages of hydrophobic surface are keeping the surface always dry, clean, and reducing fluid friction. The maintenance cost could be reduced significantly due to its naturally self-cleaning properties. Although many studies have been performed, the use of metal oxide combined cellulose acetate PLA has rarely informed. The purpose of this research was to fabricate a hydrophobic coating on a glass surface of ZnO-CA-PLA with various compositions of ZnO nanoparticles (ZnO NPs), annealing temperature, the temperature of measuring condition, and time exposure on its hydrophobicity which represented by the contact angle. The film was prepared using the spin-coating method. The crystallinity and morphology of ZnO-CA-PLA films were characterized using XRD, SEM-EDAX, and FTIR. The contact angle of hydrophobicity was measured using a digital microscope. It was revealed that the ZnO-CA-PLA composite film shows an excellent hydrophobic character. The increase of ZnO NPs gives rise to increase contact angle. A similar trend also achieved by increasing of annealing time. In contrary, the contact angle of hydrophobicity may reduce by prolonged exposure time and the increase of measuring temperature.

Keywords: ZnO-CA-PLA, dopant, annealing, time exposure, hydrophobic

### 1. Introduction

Biodegradable polymers are an area of interest for scientists to develop. PLA has attracted the considerable attention of many research groups due to produce from renewable resources, which make them biodegradable and compostable [1]. Poly Lactic acid (PLA) as a biodegradable material with excellent mechanical and biocompatibility properties, but it shows weak hydrophobic, low thermal stability, cannot withstand high temperatures, and sensitive to moisture [2].

Many efforts have been reported on the work of hydrophobic materials. Some previous researchers also use one or two components of ZnO-CA-PLA. The research studies of PLA biocomposites coupled with cellulose nanowhiskers show an increase in temperature stability [3,4]. CA has a good potential for electronic application with specific modifications such as inducing metal oxide [5]. Some

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elements in the transition group such as Mn, Fe, Cu, Zn, Pt, Au, Ag has been used to modify the properties of the material [6]. The research studies of metal oxide additions such as ZnO show a change of morphology, structures, increased hydrophobic properties, antibacterial used as applications in medical [7,8]. ZnO as a semiconductor material that has unique electrical properties, optical and biocompatible can be used as a dopant in preparing a composite material. It is found that the biocomposite films are characterized by a good dispersion of the ZnO particles in the PLA matrix. It was also rarely reported that no pre-treatment was performed on ZnO particles, such as silanization, to decrease its incompatibility with the polymer, excellent mechanical properties, decrease of permeability to  $CO_2$  and  $O_2$  [2], [9].

We propose to optimize the use of three materials consist of ZnO-CA-PLA with various composition, annealing temperature and time exposure. It is expected to achieve superior properties and excellent performance on the films for the application. This research was conducted to obtain the information of the effect of ZnO dopant and annealing on the performance of ZnO-CA-PLA hydrophobic.

A surface with hydrophobic properties can keep the surface dry, clean, reducing fluid friction with the surface. When it applied to the glass, then it can clean by itself naturally (self-cleaning), so the cost of maintenance is cheaper. The potential of hydrophobic films produced by this study can be applied as waterproof coating paint for marine shipyard paint, and ponds paint.

#### 2. Materials and Methods

The raw materials used in the synthesizing process were Zinc Acetate Dihydrate (p.a.) Cellulose Acetate (p.a.), Poly Lactic Acid, DMF (dimethylformamide) 99,8%, Aceton (p. a.) Chloroform, Deionized water, and Methanol. The materials were provided by Merck and Sigma-Aldrich. The instruments used were, ultrasonic cleaner power sonic 405 model LUC, SCILOGEX MS-H280-Pro hotplate stirrer, furnace 48000 Thermolyne, and Spincoater TC100 precision.

The fabricating of ZnO-CA-PLA/glass film is briefly described as follows. Firstly, a blend of 0.03 g CA and 0.25 g PLA were dissolved in chloroform and various amount of ZnO of 0, 0.1, 0.2, 0.3, and 0.4 g to a solvent of DMF: Aceton. Every solution was mixed for 2 hours at 80 °C with the speed of 600 rpm. The yielded solution was deposited on a glass substrate by a using a spin coating method using 2000 rpm for 30 seconds. Subsequently, ZnO-CA-PLA/glass film was annealed at 50°C for 2 hours. The ZnO-CA-PLA/glass film properties were characterized by means of XRD, FTIR, SEM-EDX, and Digital Microscope.

### 3. Results and Discussion

### 3.1. Functional Group of CA-PLA-ZnO by FTIR

IR Spectra is one of the ways to obtain information about a functional group of organic material existing in the system. By using IR spectra, one could obtain the information what was the mechanism in the process of synthesis. One may result in a new compound, a doped compound, or just composite systems. The effect of ZnO NPs of CA-ZnO NPs-PLA IR spectra is shown in Figure 1.

CA has a specific functional group which is shown by chain structure. The transmittance peaks on wavenumber of 1732, 1239 and 1367 cm<sup>-1</sup> indicate the appearance of carbonyl bonding of C=O *stretching*, acetyl –C-O *stretching* from acetate [9], and a bond of methyl group which stating of acetate group. IR spectra show the adding of ZnO in CA-ZnO-PLA at 1141 cm<sup>-1</sup>. It means that introducing ZnO on the CA-PLA showing a composite system of the film.

#### 3.2. Crystal Structure of CA-PLA-ZnO Analysis.

XRD analysis informs that there is a higher PLA composition than ZnO. The portion of PLA to ZnO is supported by EDAX analysis.

From the patterns of Figure 2, we calculate crystal size using Scherrer formula and also calculate the associated crystallinity. The crystallinity was calculated by area based on the X-RD patterns. The results are presented in Table 1.



Figure 1. IR Spectra of (a) CA-PLA and CA-ZnO-PLA with variation of ZnO (b) 0.1, (c) 0.2, (d) 0.3, and (e) 0.4.

Based on Table 1, it is obtained that the introducing of ZnO make the ZnO-CA-PLA has the crystal size between 12.97- 19.01 nm. The crystal size may be insignificantly affected by the amount of ZnO NPs in the films. The size of crystal at the nanometer scale, it indicated that the film shows a large surface area. The grain size or surface area can be associated with the performance of hydrophobic properties of water on the surface. The crystallinity is in the range of 2.11% - 8.57%. The crystallinity increases with increasing ZnO concentration. The increase of crystallinity in the ZnO/CA/PLA film indicates that ZnO contributes to crystallinity in the ZnO-CA-PLA film.



Figure 2. Diffraction pattern of ZnO-CA-PLA/glass composite film for various ZnO.

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Table 1. Crystal Size of the variation ZnO mass on ZnO-CA-PLA.			
Sample	Crystal size (nm)	Crystallinity (%)	
CA-PLA	15.89	2.11	
0,1 ZnO-CA-PLA	19.01	3.49	
0,2 ZnO-CA-PLA	14.93	2.92	
0,3 ZnO-CA-PLA	12.97	6.90	
0,4 ZnO-CA-PLA	15.04	8.57	

## 3.3 The Morphology of ZnO-CA-PLA/glass film

The images of SEM show that nano ZnO-CA-PLA/glass is the porous film. Based on Figure 3, it is shown that the morphology of cellulose acetate (CA) slightly smooth on its surface. It means that the film has less porous. The introducing PLA is on CA, provide the surface more porous as indicated by Fig. 3b. The introducing of ZnO made the films more porous and agglomerate between ZnO and CA-PLA. More ZnO added on CA- PLA gives more agglomeration of its surface which is shown in Fig. 3c to 3f. The average size of the porous is in the range micrometer.



Figure 3. The morphology of (a) CA; (b) CA-PLA; and ZnO-CA-PLA with variation of ZnO for 0.1 (c); 0.2 (d); 0.3 (e); and 0.4 (f).

## 3.4 Hydrophobicity of CA-ZnO-PLA

Contact angle measurement can be used to show the hydrophobic properties [10]. Figure 4, shows that the addition of ZnO significantly increases its contact angle. The highest contact angle was obtained by the sample with 0.3 grams of ZnO.



Figure 4. The effect of ZnO addition at annealing 1 hours on contact angle.

We also obtained a significant improvement of the annealing effect on contact angle. The longer annealing times led to the more hydrophobic surface as depicted in Figure 5 and Table 2. The increase of hydrophobicity is depended on the annealing time. This trend is occurring at all ranges of ZnO dopant. The optimum value does not change by the annealing time.



Figure 5. The effect of annealing times to the contact angle

ZnO (g)	1 (h)	2 (h)
0.1	103.4	106.4
0.2	117.3	120.3
0.3	133.4	135.0
0.4	124.1	128.1

**Table 2.** The contact angle of water as a function of ZnO annealing time.

Other impressive results show by the contact angle of water droplet on the film as a variation of temperature measuring condition. As indicated in Figure 7, the room temperature contact angle is slightly declined while exposing up to 1 minute. The contact angle still exhibits a superhydrophobic performance



**Figure 6.** The visual contact angle of water drop on ZnO-CA-PLA film with various ZnO of (a) 0.1, (b) 0.2, (c) 0.3, and (d) 0.4 grams.



Figure 7. The effect of exposure time on the contact angle

A further experiment for the same films, we measured the influence of temperature measuring condition while exposed in different duration. As expected, we found that the higher temperature tends to decrease its contact angle. On the other hand, the time exposure also slightly reduce the contact angle. The performance of hydrophobic water on the films under the influence of time exposure and temperature condition is shown in Figure 8.



Figure 8. The effect of temperature on the contact angle of water



Figure 9. The contact angle of water droplet on ZnO-CA-PLA film at various temperatures.

A visual of the contact angle of water droplet on the films as a function of temperature condition and time exposure is depicted in Figure 9. Several aspects which influencing the hydrophobic performance of ZnONPs-CA-PLA has been studied. There two categories of the factors. One type may improve the hydrophobic performance, and the other one is a group of factors which could reduce the contact angle. Although these results are relatively similar to other report [11], this work shows more comprehensive results than other published works. It is known that ZnO-CA is an excellent potential material for electrical properties [12]. It would be good when the electronic device to fabricate also showing a good of hydrophobic performance.

### 4. Conclusion

ZnO-CA-PLA hydrophobic film has been successfully prepared through the use of spin coating methods. Contact angle represents the performance of hydrophobicity of the films. The introducing of ZnO NPs and increase of annealing time give rise to increase the contact angle. On the other hand, the rise in time exposure and the rise in the temperature measurement tend to decrease the contact angle.

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