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Microstructure and dielectric properties of cellulose acetate-ZnO/ITO composite films based on water hyacinth

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Abstract. The electrical properties of Cellulose Acetate (CA), especially extracted from water hyacinth, is rarely informed. CA is generally more stable compared to its cellulose. It has a good potential for electronic application with specific modifications such as inducing metal oxide. A combination of intrinsic properties of Zinc Oxide (ZnO) and CA is expected as a great potential for electrical and optical applications. CA-ZnO/ITO composite film was investigated in relation with its structure, dielectric constant, and the effect of light intensity on their dielectric constant. CA-ZnO composite films were prepared with different mass of ZnO i.e. 0; 0,02; 0,04; 0,06 and 0,08 grams. CA-ZnO solution was synthesized via the mixing method with PEG:DMF solvents by using a magnetic hotplate stirrer with the rotation rate of 1500 rpm at 80˚C. The CA-ZnO solution was then deposited onto ITO/glass substrate by using spin coating technique. The CA-ZnO/ITO films were annealed at 160 ˚C to remove the remaining solvents. The effects of ZnO composition on the structure (crystallinity and morphology) and dielectric constant properties were investigated by using X-Ray Diffractometer, Scanning Electron Microscopy, Fourier Transform Infrared Spectroscopy, and LCR meter. It was shown that cellulose can be isolated from water hyacinth with the yield of 67,72 % by Chesson method and can further be transformed into CA. The X-ray diffraction pattern showed that there are 2 phases formed i.e. CA and ZnO. Furthermore, greater ZnO amount increased the crystallinity of composite films. The CA-ZnO films exhibit porous films with ZnO distributed on the CA surface films. Therefore, ZnO increases the dielectric constant of CA-ZnO composite films.

1. Introduction

Water hyacinth is a common weed that grows rapidly in many areas of calm and shallow waters. The rapid growth of the weed can reduce its ecological functions such as silting rivers, decreasing biodiversity, inhibiting the flow of the river, and decreasing the solubility of oxygen in the water[1]. One way to overcome this problem is by using water hyacinth for traditional household products, such as traditional carpets, sacks, wallets and many other souvenirs. Water hyacinth may consist of 25-60% cellulose, 8–33% hemicellulose, and 10-17% lignin ([2];[3]). Cellulose can be used as emulsifier, adhesive, detergent, textile, cosmetic, paper materials, and drug releasing agent [4].

Cellulose has great mechanical and optical properties. On the other hand, cellulose is insoluble in many solvents, even in organic solvents. This characteristic limits its uses. However, it can be solved by a small modification which involves synthesizing the cellulose to its derivative called cellulose acetate (CA) [6]; [7].CA can be synthesized through acetylation process. CA exhibits dielectric

properties which are originated from hydrogen bond[8]. The properties of CA are biodegradable and biocompatible as cellulose. Nevertheless, CA shows better optical and mechanical properties than cellulose [9]. CA can be applied as a fibre, film, laminate, adhesive, coating, and raw material for plastic production. The development of physical properties of this material can be done by adding polymers, metals, or oxides such as AgNPs, AuNPs, ZnO, and hydroxy gallium. This procedure may change its morphology, structure, hydrophobicity, and antibacterial properties[10];[11]; [12];[13]; [6];[14]; [15].

Many researchers have been widely using ZnO for many diverse studies and applications. ZnO has more unique properties than other semiconductor compounds due to its optoelectronic properties. Nowadays, ZnO is applied as a photovoltaic, gas sensor, clinic application, solar cell, piezoelectric nanogenerator, electric transducer, and LED[12]; [16]. ZnO is being widely used for electronic applications and CA is commonly used for medical applications. Currently, there are still very few studies concerned with synthesizing nanoCA-ZnO/ITO composite film for electronic applications which have been reported comprehensively.

In the present work, nanoCA-ZnO/ITO composite film was synthesized through several steps. The general aim of this work is to explore the information related to electronic properties especially its dielectric constant which is induced by light intensity. Firstly, CA was synthesized by extracting cellulose from water hyacinth. Furthermore, cellulose was acetylated to produce nano CA. Nano CA and ZnO were mixed in a DMF:PEG solvent by using a magnetic stirrer at 80˚C. The Nano CA-ZnO solution was deposited onto ITO surface as a substrate by means of spin coating method. The Nano CA-ZnO/ITO composite film was characterized via FTIR, SEM-EDX, XRD, and LCR-meter which show its microstructure, morphology, and dielectric constant.

2. Materials And Methods

The raw materials used in the synthesizing process were water hyacinth, toluene 96%, ethanol 96%, sodium chloride 3 wt%, NaOH 4 wt%, acetic acid glacial p.a, sulphate acid p.a, DMF (dimethyl formamide) 99,8%, acetic anhydrate, zinc acetate dihydrate p.a, deionized water, methanol, and distilled water. The materials were provided by Merk and Aldrich, Germany. The instruments used were soxhlet apparatus, ultrasonic cleaner power sonic405 model LUC, SCILOGEX MS-H280-Pro hotplate stirrer, furnace 48000 thermolyne, and spincoater TC100 precision.

2.1. Synthesizing nano CA-ZnO/ITO composite film

CA-ZnO/ITO was synthesized with several steps. The process started with isolating cellulose from water hyacinth, transforming the cellulose into cellulose acetate, preparing nano-ZnO, and fabricating the CA-ZnO/ITO composite film.

2.2. Isolating cellulose from water hyacinth.

The water hyacinth was blended using a blender and was filtered by means of a 50-sized mesh filter. The dried water hyacinth is used as raw materials of isolating cellulose. Firstly, dewaxing process was done using toluene/ethanol (1:1) as solvent and used by soxhlet apparatus, followed by the bleaching 1 process which used $NaClO_2$ 3 wt% as the solvent for 4 hours at 50 ˚C. Then, the hemicellulose was removed by NaOH 4 wt% for 3 hours at the same temperature. The next process is de-lignification which uses NaClO 3 wt% for 4 hours and at the same temperature. Finally, the hydrolysis process was performed by using HCl. It was washed until the pH was neutral and dried at 80 ˚C.

2.3. Synthesizing cellulose acetate.

Cellulose acetate was synthesized through these following processes. Firstly, 10 gram of Cellulose and acetic acid glacial were mixed for 1 hour at 40˚C. Then, sulfate acid and acetic acid glacial were added and mixed for 40 minutes. This mixing process was possible at 18 ˚C and acetic anhydrate acid, sulfate acid, and acetic acid glacial were added at 40 ˚C. Furthermore, it was hydrolyzed for 15 hours at room temperature. Then, DI water was added gradually to result in a precipitate. It was washed to

neutral pH. Then, it was dried for 5 hours at 70 ˚C. Finally, this process produced cellulose acetate white powder.

Cellulose acetate was added to H_2SO_4 64 wt% and 200 mL distilled water at 45 ˚C for 20 minutes. This suspension was centrifuged at 4000 rpm. Finally, it was dried at 70 ˚C producing the nano CA.

2.4. Synthesizing ZnO.

ZnO was obtained through a 6.57 gram Zinc Acetate Dihydrate and DI water reaction. This solution was added by NaOH 3 M continually to reach the pH of 13 until it has a milky structure. Then, it was set aside for 30 minutes at 90 ˚C. Furthermore, it was washed by using methanol and then dried at room temperature. Finally, it produced ZnO white powder.

2.5. Fabricating CA-ZnO/ITO film.

CA-ZnO solution, the casting solution was synthesized by adding 0.3 gram CA powder and various amount of ZnO of 0; 0,02; 0,04; 0,06; and 0,08 gram to a solvent of PEG:DMF ratio (0,03 g: 3 mL). It was mixed for 5 hours at 80 ˚C with the speed of 1500 rpm. The casting solution was deposited on ITO/glass substrate via the spin coating method with the speed of 2500 rpm for 60 seconds. Finally, the CA-ZnO/ITO film was annealed at 160 ˚C.The CA-ZnO/ITO film properties were characterized by means of XRD, FTIR, SEM-EDX, and LCR-meter.

3. Result And Discussion

3.1. FTIR analysis

The result of the FTIR analysis was used to investigate the interaction between nano CA and ZnO. Figure 1 (a) shows the FTIR spectra of cellulose, nano CA film, and nano CA-ZnO/ITO. The main characteristic bands of cellulose are the hydroxyl group at 3271 cm-1 ([17]; [18]), C-H stretching at 2886 cm-1 ([19];[20]; [21]), and C-O-C stretching on β-glukosidic linkages at 1155, 1055, 896 cm-1 ([10]; [17]; [22]; [15]; [23]). The FTIR spectrum of the nano CA film on Figure1(a) shows the added peak at 1732 cm-1, 1239 cm-1 and 1367 cm-1 that respectively are –C=O stretching, acetyl –C-O stretching. In Figure1 (b), the Zn-O vibration confirms the formation of ZnO which is shown by the wave numbers of 400 - 1000 cm-1 on the nano CA-ZnO/ITO composite film.

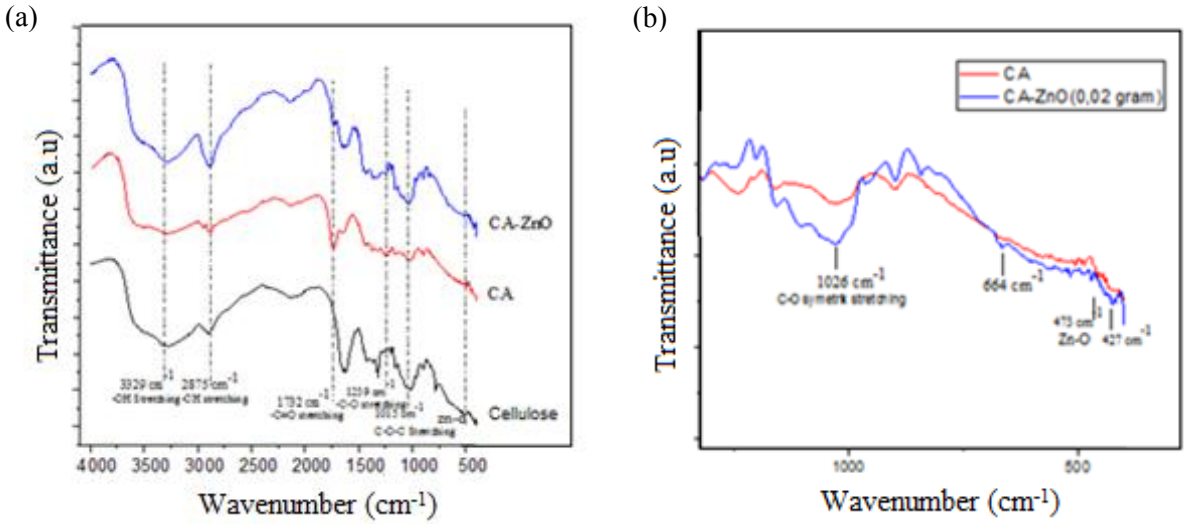


Figure 1. IR Spectrum on (a) Cellulose, CA, and CA-ZnO/ITOFilm,and (b) magnification scale 400 – 1000 cm^{-1} wave number in the CA and CA-ZnO film

3.2. XRD analysis

Based on Figure 2, the diffraction of the mass variety of ZnO which is added to nano CA indicates the constructed composite of nano CA-ZnO. It was shown on the new peak of nanoCA-ZnO/ITO film when ZnO was added. It is called composite since there are peaks that showed 2 phases. These phases are nano CA as matrix and ZnO as a dopant. The crystallinity of nano CA-ZnO/ITO film was obtained using the following equation (1).

$$Crystallinity = \frac{Crystalline\ Area}{Crystalline\ Area + Amorphous\ Area} x\ 100\ \% \quad (1)$$

It is shown in Table 1 that the Addition of ZnO has increased the crystallinity of ZnO and has decreased the crystallinity of CA which can also be seen in Figure 2.

Table 1. The Crystallinity of Nano CA-ZnO/ITOas a function of ZnO.

ZnO Mass (gram)	Crystallinity (%)	
	CA	ZnO
0	65.32	-
0.02	59.92	44.02
0.04	55.48	47.11
0.06	49.65	48.68
0.08	40.91	49.57

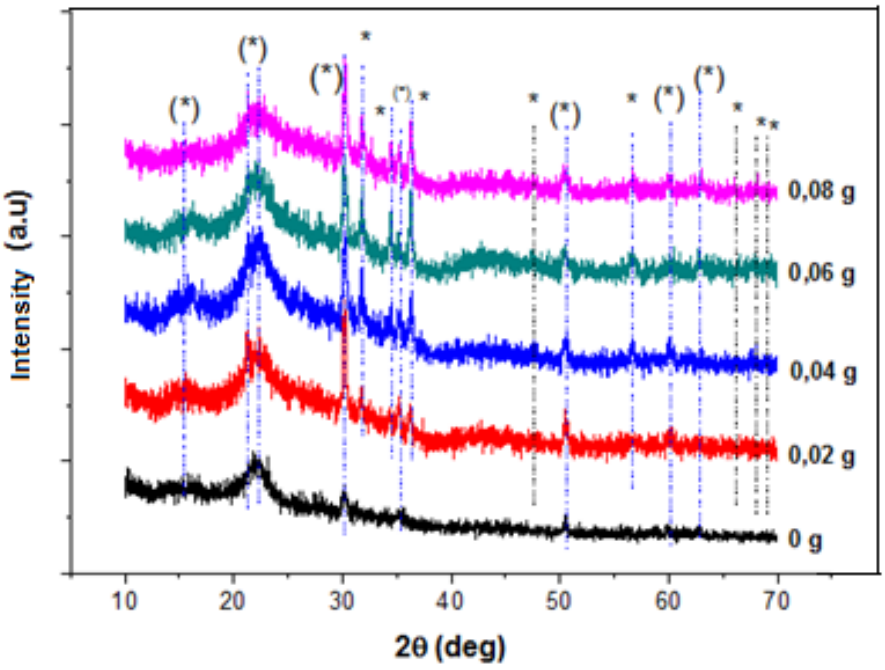


Figure 2. Diffraction Pattern of NanoCA-ZnO/ITO Composite Film for various ZnO which are 0; 0.02; 0.04; 0.06 and 0.08 grams. The symbol of (*) and * are designated respectively for CA and ZnO.

The crystal sizes of CA and ZnO on the Nano-CA-ZnO/ITO film were shown in Table 2. The crystal size was obtained by using equation 2. The crystal sizes of CA and ZnO are about 4,5 – 5.7 nm and 16.5 – 59 nm, respectively.

$$D = \frac{k\lambda}{\beta \cos\theta} \tag{2}$$

In formula 2, D is the crystal size, *k* is the crystal shape factor, λ is the wavelength of Cu (1.54056 Å), B is the FWHM (rad), and θ is the diffraction angle (^{0}).

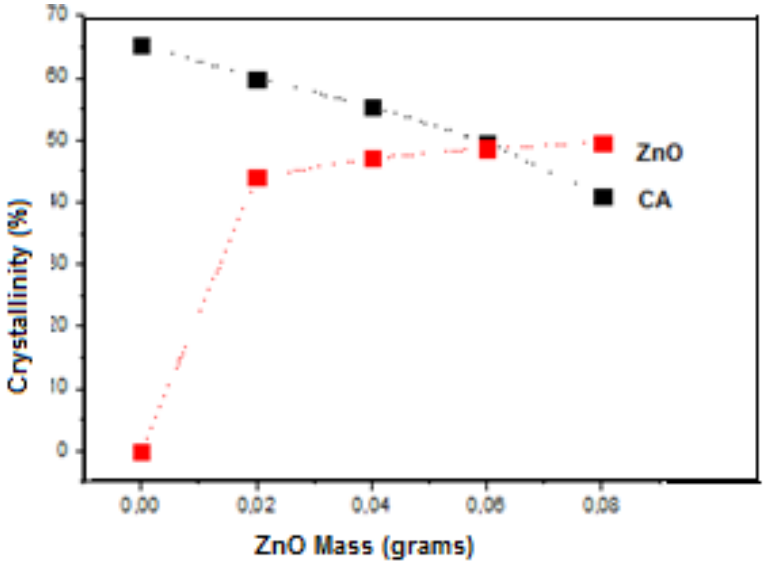


Figure 3. The Crystallinity of CA and ZnO at various Mass of ZnO of CA-ZnO/ITO Films.

Table 2. The crystalsize of CA and ZnO based on the addition of ZnO mass in the Nano CA-ZnO/ITO Films

ZnO (grams)	crystalsize (nm)	
	CA	ZnO
0	5.4	-
0.02	5.7	59.0
0.04	5.6	29.2
0.06	5.6	16.5
0.08	4.5	26.0

Table 3. Porous on the Morphology of Nano CA-ZnO Film

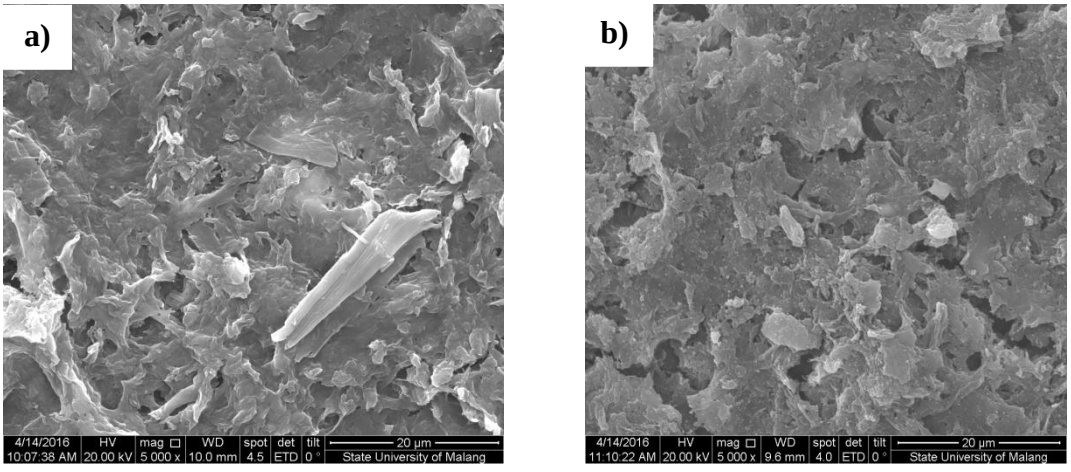
ZnO (grams)	porous (μm)
0	1.149
0.02	1.385
0.04	0.807
0.06	1.278
0.08	0.718

3.3. The Morphology of Nano CA-ZnO/ITO Film

The images of SEM show that nano CA-ZnO/ITO is the porous film. The porosity is related to the density of nano CA-ZnO film which can decrease or increase as shown in Figure4 (b,d) and Figure4 (c,e), respectively. The porosity of nano CA-ZnO/ITO can be found in Table 3.The porosity has been calculated using equation 3. In Figure4, ZnO spreads on the surface of nano CA-ZnO films. It shows in Figure 4f by the elemental mapping of nano CA-ZnO/ITO film

$$porous = \frac{\sum A_{porous}}{A_{total}} \tag{3}$$

where A is area of SEM result of film.



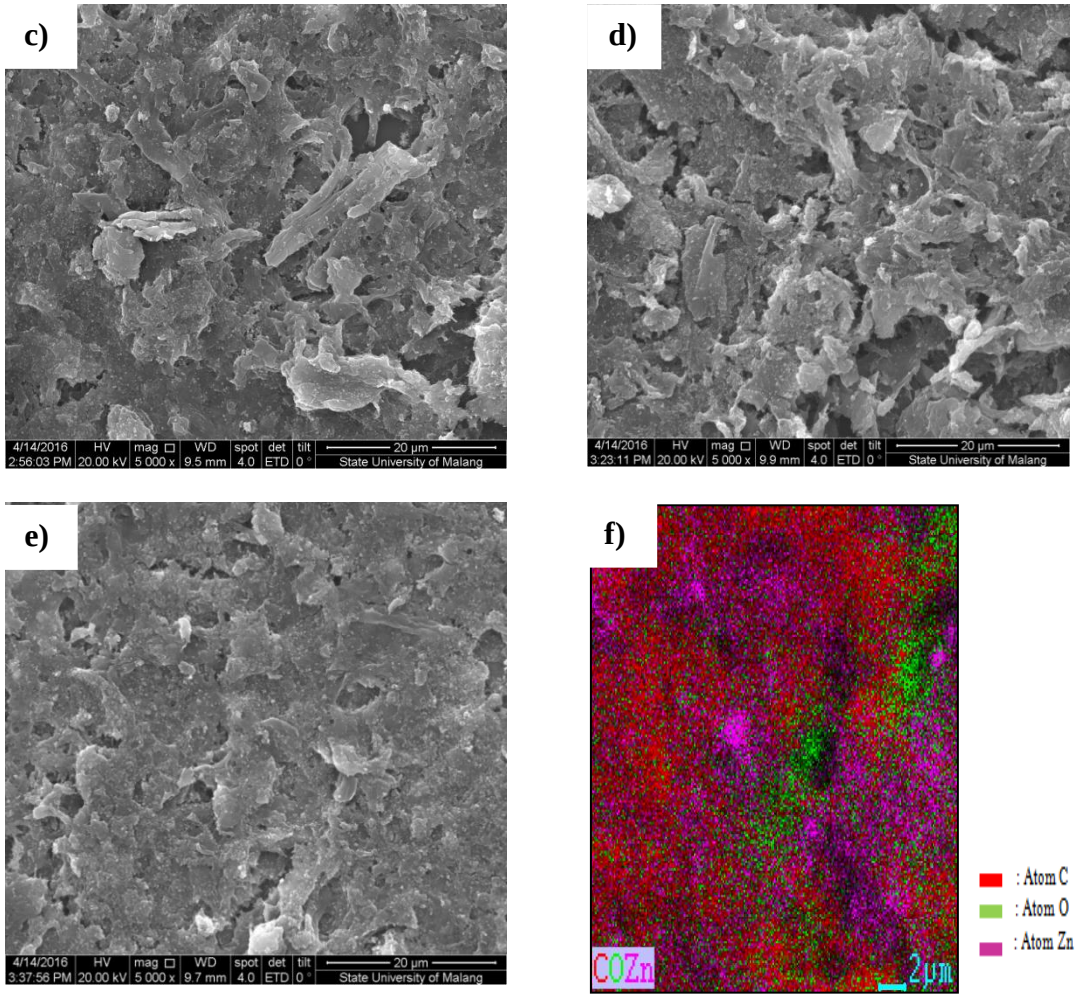


Figure 4. The Morphology of (a) CA; (b) CA-ZnO(0,02); (c) CA-ZnO(0,04); (d) CA-ZnO(0,06) and (e) CA-ZnO(0,08) and (f) the Elemental Mapping of nano CA-ZnO/ITO Film

3.4. Dielectric constant of nano CA-ZnO/ITO film

The addition of ZnO results in decreasing crystallinity of Nano CA-ZnO film as indicated in Figure 3. The decreased of crystallinity of CA significantly increase the dielectric constant of CA as shown in Figure 5. It is the result of its molecules being more polarized under the influence of the external field. The dielectric constant was calculated using Equation 4

$$\varepsilon_r = \frac{C.d}{\varepsilon_0.A} \qquad (4)$$

where ε_r and ε_0 are relative dielectric constant and permittivity ≈8.854 x 10^{-12} C^2/N m^2. A is the area measured of the sample. C is capacitance and d is the distance between plate but in this case d is the thickness of the sample. The thickness is shown by the cross section of nano CA-ZnO/ITO film which was inspected by SEM.

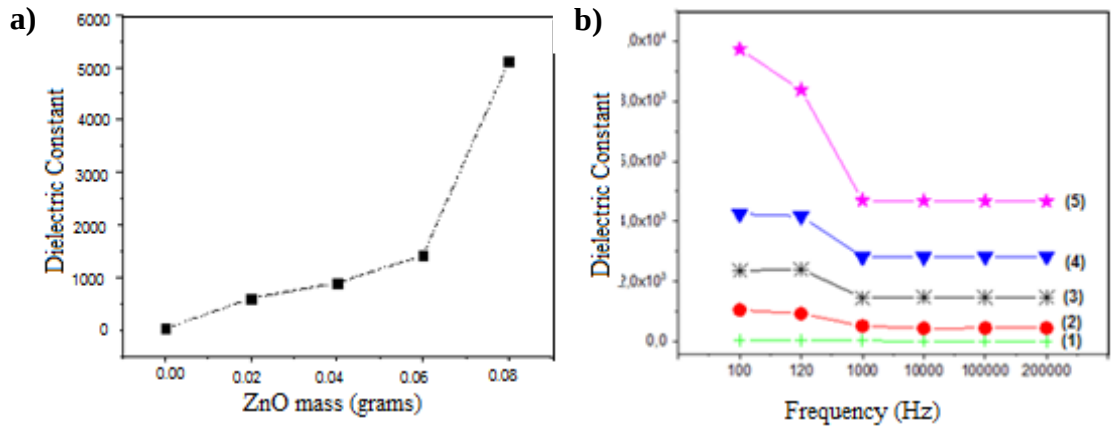


Figure 5. The dielectric constant of (a) The Nano CA-ZnO/ITO by The Mass Variety ZnO and By The Frequency of CA-ZnO (1) undoped nano CA film, (2) 0.02, (3) 0.04,(4)0.06, and (5) 0.08 of ZnO doped.

Figure5 (b) reveals that the frequency had influenced the dielectric of Nano CA-ZnO/ITO film. It investigated the polarization mechanism which was conducted. The dielectric decrease was followed by the increase of the frequency. Increasing frequency reduce the dielectric constant from ZnO, as well as the CA as a composite. The dielectric constant of ZnO and CA are mainly originated from ionic and weak dipole polarization mechanisms. The rise of electric field frequency may also produce vacancy before the full polarization occurs, which can reduce the dielectric constant [24].

4. Conclusion

The cellulose has been extracted from the water hyacinth which has 67,72% purity. ZnO-embedded nano CA film has been successfully prepared through the use of spin coating methods. From the analysis of FTIR spectra, it could be concluded that the nano CA-ZnO film is the composite film, which is also supported by XRD analyses. The grain size of CA and ZnO were 4.5 – 5.7 nm and 16.5 – 59.0 nm, respectively. The morphology of nano CA-ZnO/ITO film by analyzing SEM is categorized asporous film. Furthermore, inducing ZnO doped onto CA film inreasesits dielectric constant, while frequency tend to reduce its dielectric constant.

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