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Effect of Milling Time on the Microstructure and Dielectric Properties of Chitosan Nanopowder

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ABSTRACT

The effect of milling time on the microstructure of chitosan nanopowder had been investigated. This study fabricated chitosan nanopowder via ball milling at different milling time. The milling time used were 0, 60, 180 and 360 minutes, indicated by CHO, CH60, CH180 and CH360, respectively. From the SEM results, the milling time not only resulted in the homogenous dispersion but also the reduction of particle clustering and the reduction of distances between the particles. The optimal grain and crystallite size of CH180 is 8.5 nm and 20.1 nm, respectively. The chitosan nanopowder showed that the milling time does affect the crystallite size. The average crystallite size of chitosan nanopowder is 20 nm. The dielectric constant and loss values decrease with the frequency and increase with the milling time. Thus, the effect of milling time on microstructures and dielectric properties of chitosan nanopowder could increase the internal structure of the granules and applied to synthesis the solid electrolyte.

Keywords: Milling Time, Microstructure, Chitosan, Nanopowder.

1. INTRODUCTION

Nowadays, solid polymer electrolytes are important in creating materials for energy storage devices such as batteries that require the best performance in terms of thin, small size, conductivity, and flexibility. The materials are expected to replace the conventional organic sol-gel electrolyte in the future due to its dimensional stability, processability, electrochemical stability, safety, and long-life. Additionally, environmentally friendly is also an important factor in the usage of materials. One of the materials is chitosan.

Chitosan $[C_6H_{11}NO_4]_n$ is particularly susceptible to the formation of additional compounds. Chitosan was chosen because it is one of the promising and mostly used organic biopolymers which has properties such as non-toxic, biocompatible, biodegradable, biofunction, hydrophilic, and environmentally friendly characteristics. Chitosan consists of amine and hydroxyl [1,2]. Development of chitosan nanoparticles widely attracts more interest because of nano-sized particle and large surface area to physical modifications, including radiation, electrical

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treatment and mechanical milling [3]. Mechanical milling treatment is needed in order to decrease the particle size and to increase the surface area of the materials [4,5].

Ball milling is a common mechanical process to produce superfine powders (nano-sized particles) such as starch, cellulose, and chitosan [6,7]. The chitosan nanopowder is widely used for further research. The mechanical milling method is one of the milling methods for reducing particle size that affect the physicochemical properties and structure of chitosan and influence its performance [8]. According to the literature, preparation and characterization of chitosan nanopowder and its properties using ball milling produced particles sizes in micrometres that were successfully synthesized using the ball milling [9,10]. The chitosan properties can be synthesized to study the effects of biocompatibility and biodegradable [11,12]. The influence of polygonum minus by ball milling can reduce the particle size [13]. The preparation of nano-sized chitosan using ball milling treatment with a variety of milling time have been investigated and indicated that the average grain size is 15.1 nm [14]. Dielectric properties indicated that ion conduction mechanism between electrode and electrolyte are very important for electrochemical devices [15-17].

However, there were few researches of as-prepared chitosan by ball milling with various milling time. The synthesis of chitosan nanopowder using ball milling may offer a new possibility for the chitosan nanopowder applications because the process is very simple, low cost and yield high surface area. Despite using the ball milling to prepare the chitosan nanopowder is still done with several challenges, such as the large average size range of the as-prepared chitosan, this study would get different results beyond the theme. Here, the writer intends to analyse some efforts for the development of as-prepared chitosan that were applied by the mechanical treatment in order to get smaller particles, to reduce grain size and surface modification of chitosan through ball milling.

This study focused on the effect of milling time on microstructure and dielectric properties of chitosan nanopowder. This work begins with preparation of the chitosan nanopowder by ball milling with different milling time. The grain size, crystallite size and dielectric properties of the chitosan nanopowders are also discussed.

2. EXPERIMENTAL

The prepared chitosan (CH0) was purchased from Biotech Surindo (Cirebon, Indonesia) with a deacetylation degree (DD) about 85%. The CH0 was processed to produce nano-sized chitosan CH60, CH180 and CH360, with the milling time of 60, 180 and 360 minutes, respectively.

A high-energy milling machine 8000M SPEX CertipPrep Mixer/Mill was used. The jars and the milling medium were made of stainless steel. The diameter of the small ball is 0.5 mm. The time for grinding operations were 60, 180 and 360 minutes and rotated at the constant speed 1500 rpm and its rotational direction is on every 1 hour and off for 30 min, for every experiment continuously. The milling process was done by means of a planetary ball milling with some parameters with respect to size reduction. After milling, the dried samples were ground for 10 minutes and then characterized.

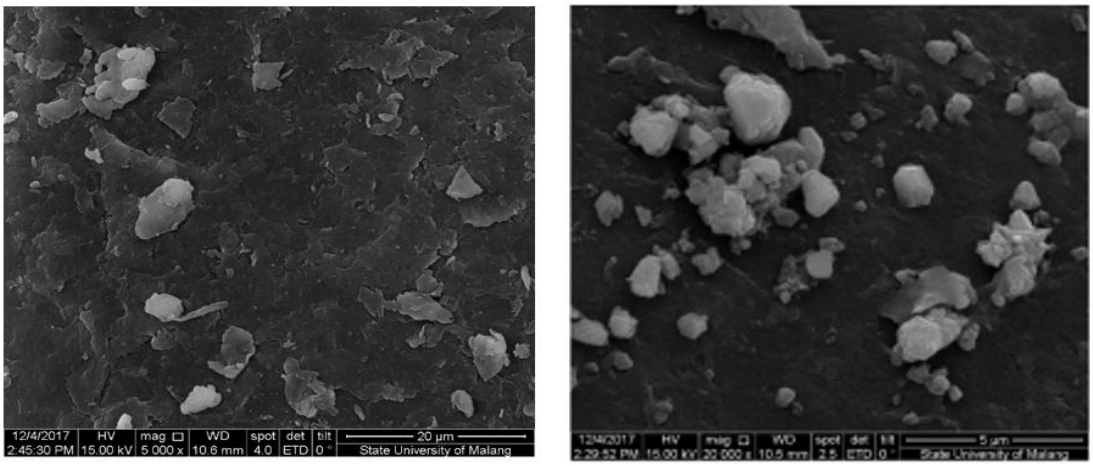
Microstructures characterization of CH0, CH60, CH180 and CH360 were studied using a scanning electron microscope (SEM) type JEOL, JSM-6510LA. A transmission electron microscopy (TEM) type JEOL, JEM-1400 was used to take the CH360 image. The image of the CH0, CH60, CH180 and CH360 were analysed by Image J and origin 10 to determine the grain size and its dispersity.

Crystal structure of CH0, CH60, CH180 and CH360 were performed using X-ray Diffraction (XRD) type Rigaku D/max 2500 V diffractometer (Rigaku, Japan) with the Cu-Kα radiation with λ = 1.54060 Å, 40 kV, 30 mA, divergence slit/scattering slit, and 0.3 mm receiving one.

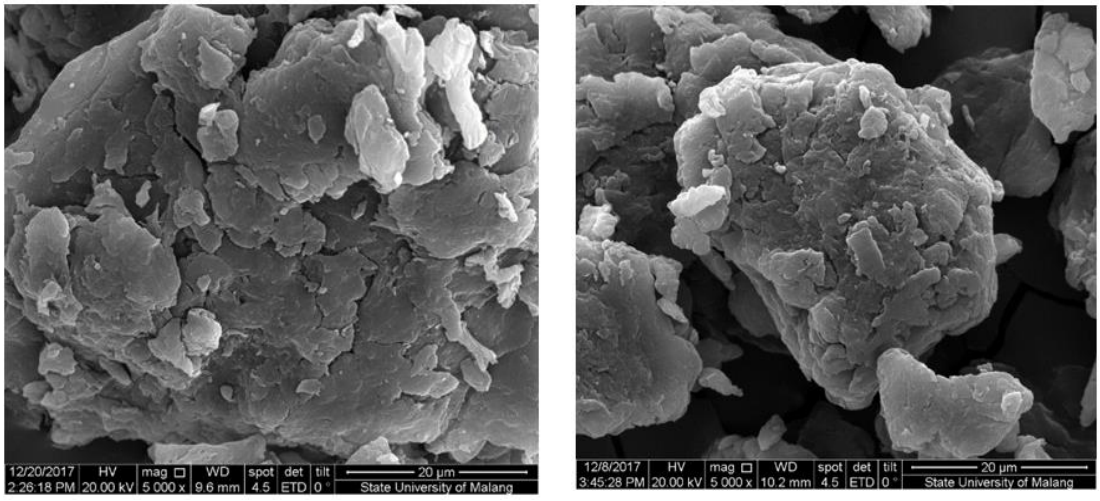
The dielectric properties of CH0, CH60, CH180 and CH360 were pelletized into 15 mm diameter spherical forms using 15 Mpa uniaxial pressures. Impedance spectra were collected at an applied of 1 V and frequency range of 42 Hz – 5 MHz using HIOKI LCR HiTESTER 3532-50.

3. RESULTS AND DISCUSSION

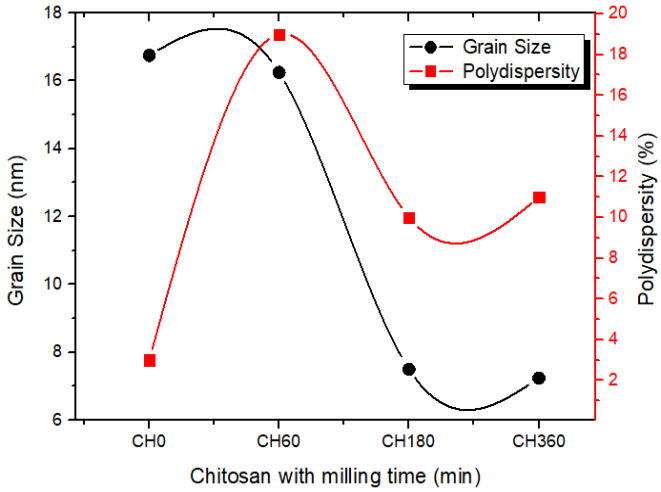
A few changes in the specific area were observed after milling. The SEM images confirm that the change of structure, grain size and agglomeration of CH0, CH60, CH180 and CH360, as shown in Figure 1. The grain size of the CH0, CH60, CH180 and CH360 have irregular particle shape. The grain size of the chitosan nanopowder decreased by the longer of milling time. The smaller diameter of the granules on the surface of chitosan nanopowder caused the particles to be highly agglomerated in the CH180. The surface area of chitosan with various milling time was observed where it significantly decrease and increase which caused by the friction between the ball and the jar made of aluminium that produce heat.



(a) (b)



(c) (d)



(e)

Figure 1. SEM images of (a) CH0, (b) CH60, (c) CH180, (d) CH360, (e) grain size and polydispersity.

Figure 1 (a) depicts the CH0 microstructures. The CH0 image indicates a homogeneous and smooth distribution of particles. There is no agglomeration formed on the CH0 surface structure. The SEM image confirms that in the CHO, the size of the aggregates is about 16.8 nm and dispersity of particles is 2.9%. There has been no agglomeration among molecules. Figure 1 (b) shows that grain size and dispersity of the CH60 are 16.3 nm and 19.1%, respectively. Figure 1 (c) shows the grain size and dispersity of the CH180 are 8.5 nm and 20%. Then, Figure 1 (d) depicts the grain size and dispersity index of CH360 were 7.2 nm and 11.2%.

In brief, Figure 1 (b), (c) and (d) confirmed that there is noticeable change in the shape and size of grains. Some gaps or cavities also could be observed which indicate that ball milling can be used to produce fine particles. Here, the structure and size of the grains decrease otherwise the agglomeration increase. After milling for 60 minutes, the volume of the refinement chitosan increases to a great amount of aggregate and the particles of chitosan shape become flat. On the other hands, it suggests that there is a significant change in the internal structure of the chitosan granules. The small particles should be bonded to each other resulting in agglomeration and more cavities on the surface.

The smaller aggregates of CH360 was observed in TEM as shown in Figure 2. The grain size and dispersity of CH360 are 15.1 nm and 11%. Inside the particles, a dark contrast appeared for the crystallites size that is in diffraction position. The CH360 are round and agglomerated. The CH360 are irregular in shape and obscure.

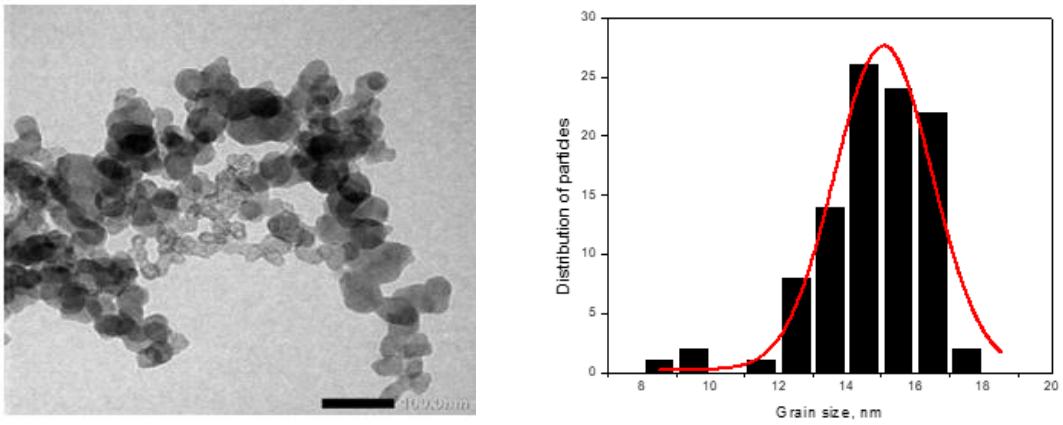


Figure 2. TEM images of CH360.

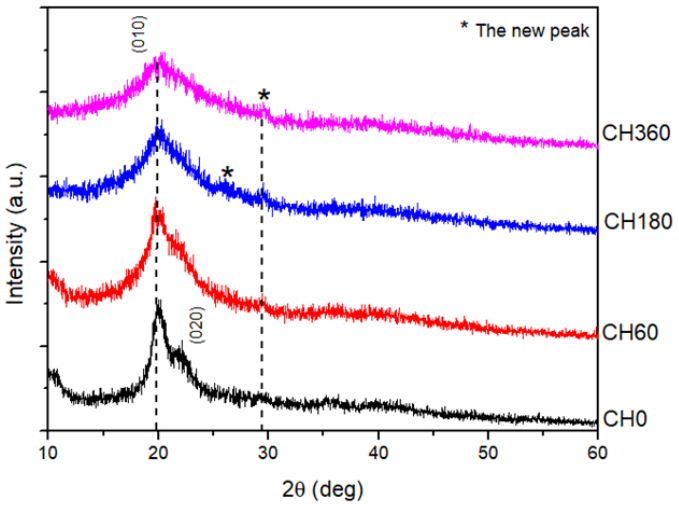


Figure 3. XRD patterns of CH0, CH60, CH180 and CH360.

Figure 3 shows the XRD patterns for CH0, CH60, CH180 and CH360. The XRD phases of the CH0, CH60, CH180 and CH360 were identified with the standard Joint Committee on Powder Diffraction Standards (JCPDS Card No. 39-1894). Figure 3 shows that the two peaks of CH0 (2θ = 21° and 11°) were assigned to (001), (100) and (101) crystallographic planes, respectively. The crystallite size and crystalline degrees are 20.8 nm and 49%. Polydispersity index is 44%. The peaks of CH60 were at about 21° and 11°. The crystallite size and crystalline degrees are 20.1 nm and 36%. Polydispersity index is 36%. The XRD pattern of CH180 and CH360 showed the peaks at 20° and 11°. The crystallite size and crystalline degree of CH180 and CH360 are 20.1 nm. Polydispersity index is 17%. The milling process decreased crystallite size and crystallite degrees but significantly increased the polydispersity index. The crystallite size and grain size of CH0, CH60, CH180, and CH360 are shown in Figure 4.

Figure 4 depicts the crystallite size and grain size of CH0, CH60, CH180 and CH360. The crystallite size decrease while the grain size increase as a function of milling time. The results indicate that the particles are highly agglomerated and relatively dispersed. The particle are highly agglomerated and relatively dispersed because, during the milling process, some

parameters can influence the material particle size distribution and balls are typically larger and heavier. They can reduce the empty spaces and heat between the milling elements hence increasing the friction between the balls and the particles.

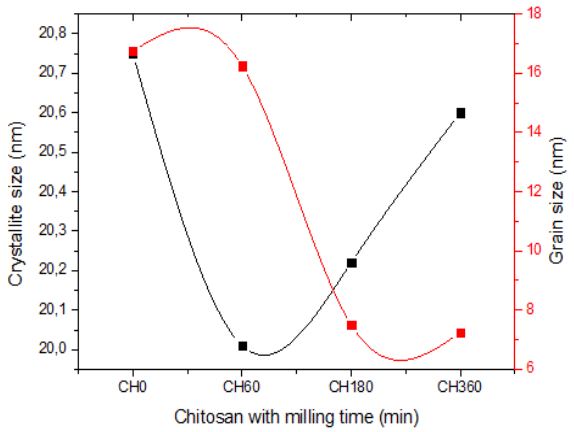
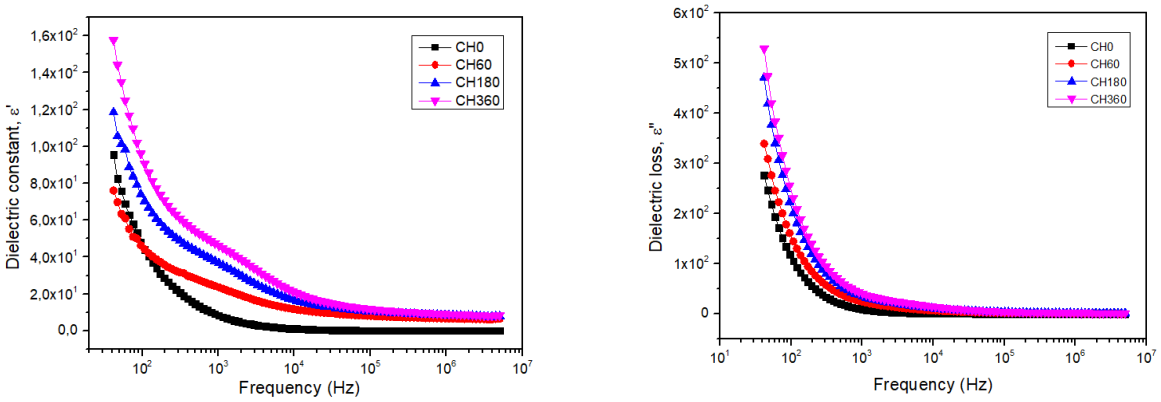


Figure 4. Milling time-dependent the crystallite size and the grain size of CH0, CH60, CH180 and CH360.

The real part of the complex permittivity is the dielectric constant (ε') and the imaginary part is the dielectric loss (ε''). Variation of the dielectric constant and dielectric loss as a function of frequency at various milling time for chitosan can be seen in Figure 5(a) and 5(b). Figure 5(a) and 5(b) show the real and imaginary plot of permittivity for CH0, CH60, CH180 and CH360, respectively. The electromagnetic absorption of a material depends on the dielectric properties that related to the complex permittivity (ε' and ε'') and permeability (μ). The frequency dependent dielectric constant indicates that the dispersion increases continuously at higher frequency.



(a) (b)

Figure 5. Frequency-dependent plot of permittivity for CH0, CH60, CH180 and CH360, (a) dielectric constant, (b) dielectric loss at RT.

The complex dielectric constant and dielectric loss can be calculated by the equation:

$$\varepsilon' = \frac{Z_r}{\omega Co\left(Z_r^2 + Z_i^2\right)} \quad (1)$$

$$\varepsilon'' = \frac{Z_i}{\omega Co\left(Z_r^2 + Z_i^2\right)} \quad (2)$$

where $C_o = \varepsilon_o \frac{A}{t}$ (ε_o is permittivity of free space), A is the surface area, t is the thickness of pellet, ω = 2π f (f is frequency), Z_i is the imaginary part of the complex permittivity, Z_r is the real part of the complex permittivity, ε' is the real part of dielectric constant, and ε'' is the imaginary part of the dielectric loss.

In both parts of permittivity, a very strong dispersion was observed in the low-frequency region. The dielectric constant and dielectric loss for all the samples show a relatively high value at low-frequency range and it decreases with increasing frequency. For the dielectric material, this effect is due to the contribution of charge polarization at the electrode-electrolytes interfaces for the dielectric constant and the dispersion is due to the migration of ions in the material for the dielectric loss. The dielectric constant decreased with increase in frequency. The dielectric constant indicates the storage of energy in the system and the dielectric loss confirm the dissipation of energy in the system. This is due to the reversal of the electric field periodically and rapidly, respectively and to the limitation of ion vibrations. Further, increase in milling time reduce the dielectric constant thereby preventing the polarization. The low values of dielectric constant might be attributed to chitosan nanoparticles that introduce more defects.

4. CONCLUSIONS

In this study, the effect of milling time on microstructure and dielectric properties of chitosan nanopowder have been conducted. Synthesis of the chitosan nanopowders with various milling time has been done using ball milling treatment. The SEM images, the CHO, CH60, CH180 and CH360 of grain size are 16.8 nm, 16.3 nm, 8.5 nm and 7.2 nm, respectively. The SEM images showed that chitosan nanopowder was highly compacted and agglomerated. The XRD patterns showed the crystallite size is about 20.1 nm. From the SEM image and XRD pattern, it showed that chitosan nanopowder is easily agglomerated to produce cavities between granules and the size of the granules. The dielectric constant and the dielectric loss for all the samples show a relatively high value at low frequency and it decreases with increasing frequency. The dielectric constant values for the higher frequency showed that the increase of the milling time may be revealed to one of the sources of ion conduction. It can be concluded that the effect of milling time can decrease the crystallite size and the grain size of chitosan nanopowder. With increased the milling time, the high values of dielectric constant confirmed the high-frequency applications.

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