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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. The chitosan nanopowder was fabricated using ball milling with the various time. Those 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 grain size and crystallite size optimium of CH180 were in 8.5 nm and 20.1 nm. The chitosan nanopowders showed that the milling time contributed on the crytallite size. The average crytallite size of chitosan nanopowder were 20 nm. The dielectric constant and loss values decreased with the frequency and increased 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

Nowdays, solid polymer electrolytes are important in creating materials for energy storage devices that require the best performance with thin, size, conductivity and flexibility, such as batteries and others. This is expected to replace the conventional organic sol-gel electrolyte the future due to its dimensional stability, processability, electrochemical stability, safety and longlife. In other hands, environmental friendly is also important issue 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 additioan compounds. Chitosan was choosen because one of the most promising and used an orgarnic biopolymers which has maninly the properties such as non-toxic, biocompatible, biodegradable, biofunction, hydrophilic and enviranmental 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 treatment and mechanical milling [3]. To decrease the particle size and to increase the surface area of materials, mechanical miling treatment is needed [4,5].

Ball milling is a common mechanical process to produce surperfine powders. It is used to get the 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 milling method for reducing particle size, some physicochemical properties and structure of chitosan will change and influence its performance [8]. According to the literature, preparation and characterization of chitosan nanopowder and its properties using ball milling obtained a great part of particles had sizes in micrometers are successfully synthesized using the ball milling [9,10]. The chitosan properties can be synthesized to study the effects of biocompatibility and biodegrable [11,12]. The influence of plygonum minus by ball milling can be reduced 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 of grain size is 15.1 nm [14]. Dielectric properties showed that ion conduction mechanism between electrode and electrolyte are very important for electrochemical devices [15-17].

However, there were few research of as-prepared chitosan by ball milling with various milling time. The synthesis of chitosan nanopowder using ball milling may offer new possibility for the chitosan nanopowder applications because of the process is very simple, low cost and highly surface area that is high yield. Although, in fact, using of 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, in this study would get different results beyond the theme. Here, the writer intends to analysis some efforts for the development of as-prepared chitosan that were applied by the mechanical treatment to get smaller particles, to reduce grain size and surface modification of chitosan through ball milling.

This study will focus on the effect of milling time on microstructure and dielectric properties of chitosan nanopowder. This work is started by 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 as well.

2. EXPERIMENTAL

The prepared chitosan (CH0) was purchased from Biotech Surindo (Cirebon, Indonesia) with a deacetylation degree (DD) about 85%. The CH0 was conducted to the processed to be 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 here was used. The jars and the milling medium were made of stainless steel. The diameter of 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 every on 1 h and off 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.

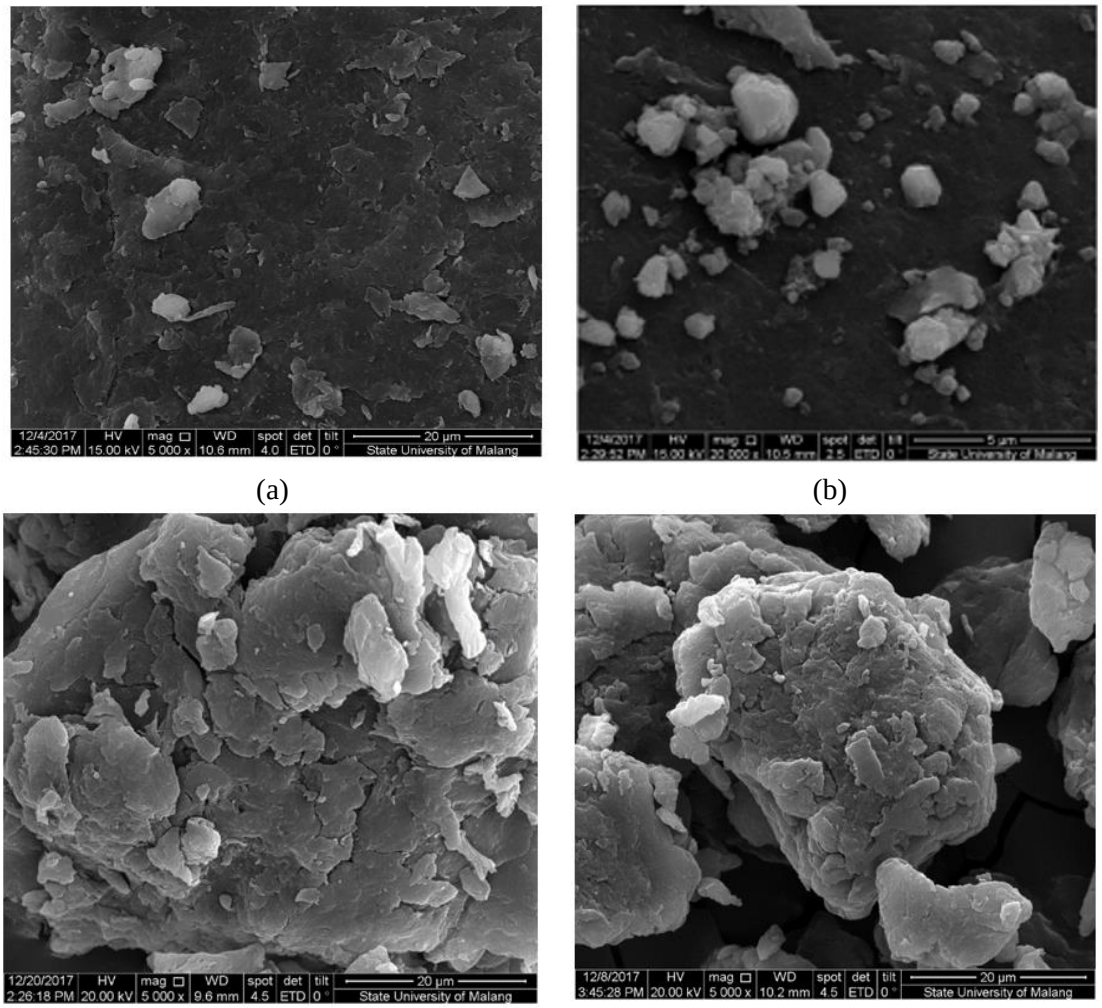
Microstructures characterization of CH0, CH60, CH180 and CH360 were studied by a scanning electron microscope (SEM) type JEOL, JSM-6510LA. A transmission electron microscopy (TEM) type JEOL, JEM-1400 was taken to the CH360 image. The image of the CH0, CH60, CH180 and CH360 were analyzed by image J and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

Crystal structure of CH0, CH60, CH180 and CH360 were performed using X-ray Diffraction (XRD) tyoe Rigaku D/max 2500 V diffractometer (Rigaku, Japan) with the Cu-Kα radiation with $\lambda = 1.54060$ 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 are 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 are irregular particle shape. The grain size of chitosan nanopowder decreased by the longer of milling time. It showed the smaller diameter of the granules on the surface of chitosan nanopowder. the particles are highly aggolomerated in the CH180 and the surface area of chitosan with variaous milling time are observed significantly the decrease and increase are caused by friction between the ball and the jar made of aluminum to produce heat.



(e)

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

Figure 1 (a) depicts the CH0 microstuctures. The CH0 image indicate that a homogeneous and smooth distribution of particles. There is no agglomeration formed on the CH0 surface structure. SEM image confirms that in the CHO, the size of the aggregates about 16.8 nm and dispersity of particles was 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% and 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, from Figure 1, there are (b), (c) and (d) confirm there is noticeable changed in shape and size of grains. Some gaps or cavities could be observed as well which show that ball milling can be used to produce fine particles. Here, the structure and size of the grains decrease and otherwise the agglomeration increase. After milling for 60 minutes, the volume of the refinement chitosan increase to get a great amount of aggregate and the particles of chitosan shape become flat. In 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 were in 15.1 nm and 11%. Inside the particles, a dark contrast apperared for the crystallites size that are in diffraction position. The CH360 are round and agglomeration. The CH360 are irregular shape and obsucure.

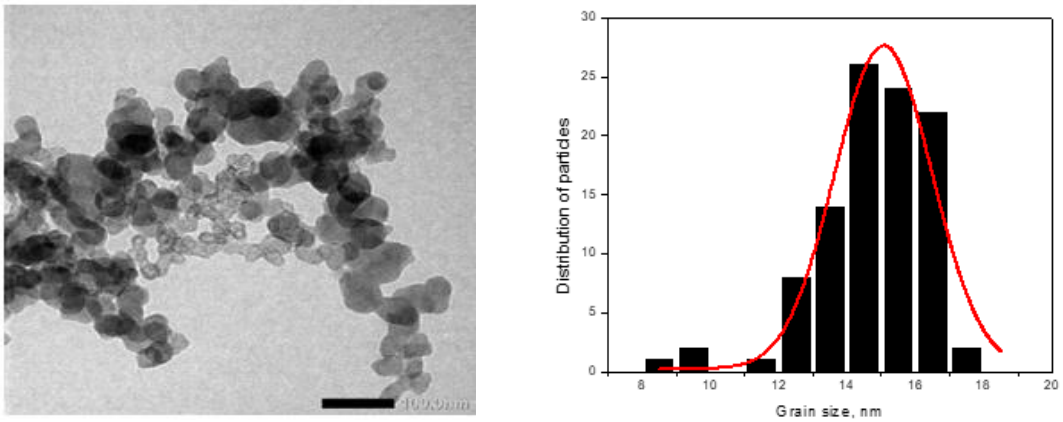


Figure 2. TEM images of CH360

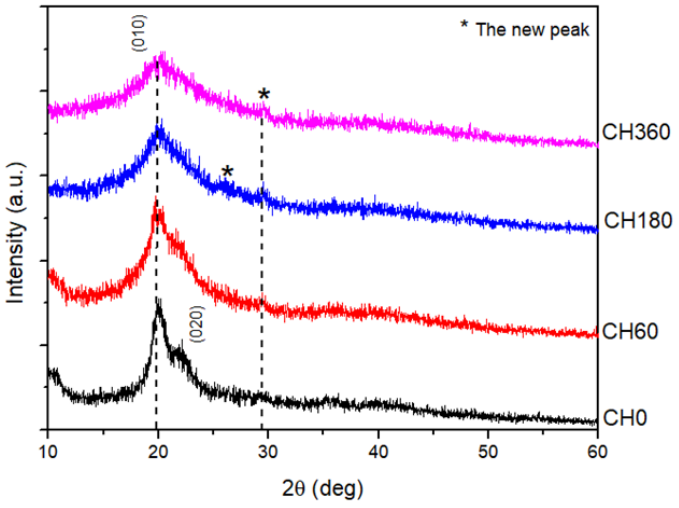


Figure 3. XRD patterns of CH0, CH60, CH180 and CH360

Figure 3 shows the XRD patterns for CH0, CH60, CH180 and CH360. The XRD phases of the CH0, CH60, CH180 and CH360 were indetified with the standard Joint Committee on Powder Diffraction Standards (JCPDS Card No. 39-1894). In the Figure 3 shows that the two peaks of CH0 ($2\theta = 21^0$ and 11^0) were assigned to (001), (100) and (101) crytallographyc planes, respectively. The crystallite size and crystalline degree were 20.8 nm and 49%. Polidispersity index is 44%. The peaks of CH60 were at about 21^0 and 11^0. The crystallite size and crystalline degree were 20.1 nm and 36%. Polydispersity index was 36%. The XRD pattern of CH180 and CH360 showed the peaks at 20^0 and 11^0. The crystallite size and crystalline degree of CH180 and CH360 were 20.1 nm. Polydispersity Index was 17%. The milling process decreased crytallite size and crytallite degree, but significantly increased the polydispersity Index. The crystallite size and grain size of CH0, CH60, CH180, and CH360, respectively as shown in Figure 4.

Figure 4 depicts crytallite size and grain size of CH0, CH60, CH180 and CH360. The crystallite size decrease while the grain size indecrease as a function of milling time. The results indicate the particles are highly agglomerated and relatively dispersed. The particle were highly agglomerated and relatively dispersed because in the milling process was done, 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 increasing the friction between the balls and the particles.

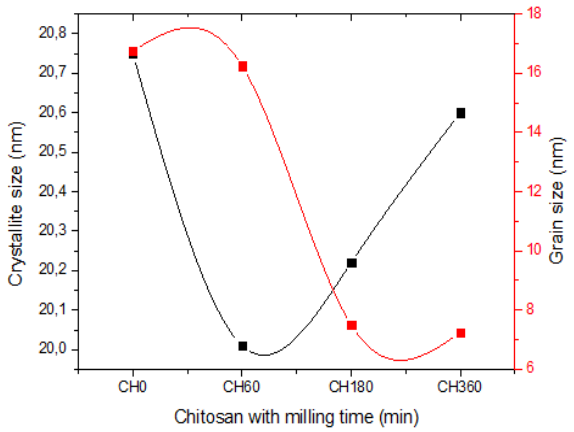
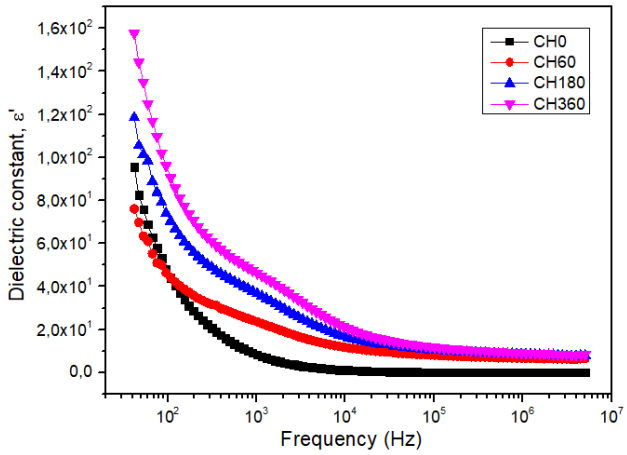
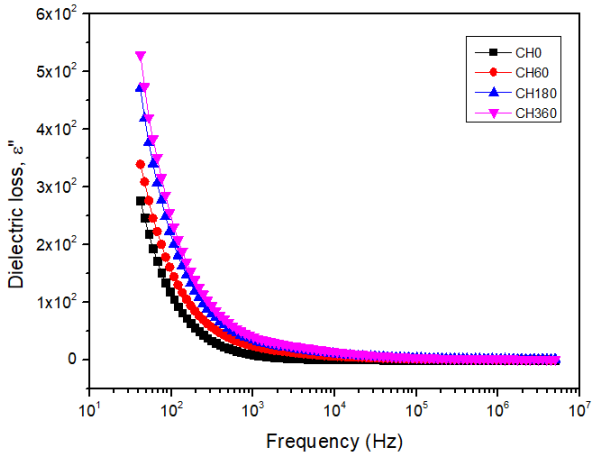


Figure 4. Milling time dependent the crystallite size and the grain size of CH0, CH60, CH180 aand CH360

The real part of 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 (b). Figure 5 (a) and (b) show the real and imaginary plot of permitivity for CH0, CH60, CH180 and CH360, respectively. The electromagnetic absorption of a material depends on the dielectric properties which are related to the complex permittivity (ε' and ε'') and permeability (μ). The frequency dependence dielectric constant indicates a continuous increase the dispersion at higher frequency.



(a)



(b)

Figure 5. Frequency-dependent plot of permittivit 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, t are the surface area and thickness of pellet, $\omega = 2\pi f$ (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 costant and ε'' is the imaginary part is the dielectric loss.

In both parts of permittivity, a very strong dispersion is 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 indicate 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, increasing in milling time reduces 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

Based upon 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 have 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 were highly compacted and aggomerated. 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 so as 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 decrease with increasing frequency. The dielectric constant values for the higher frequency showed that the increase of the milling time may be revelead 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 constat confirmed the high frequency applications.

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