STUDY ON CHARACTERIZATION OF CHITOSAN-ZnO FILM

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Abstract

The chitosan, the naturally abundant and renewable polymers, have excellent properties such as biodegradability, bio-compatibility, non-toxicity and absorption. The polymer sample consisting of the purified chitosan powder was firstly prepared by the slow evaporation of aqueous solution. Demineralization and deproteinization processes were done to obtain purified chitosan powder. The molecular vibration spectrum of the purified chitosan powder was recorded by using Fourier Transform Infrared (FTIR) Spectroscopy. Chitosan, zinc acetate and chitosan-ZnO films were deposited onto the glass slide by using the spin-coating method. The crystalline state of chitosan powder, the chitosan-ZnO powder and the film were characterized by X-ray diffraction (XRD) and Scanning electron microscopy (SEM). The lattice microstrain of as-grown chitosan powder was calculated to be about 0.9 and it was consistent with the theoretical value of orthorhombic crystal. The crystallite size was calculated to be about 33.2 nm for the chitosan-ZnO powder. According to the XRD results, the chitosan-ZnO film has smaller crystallite size than the chitosan-ZnO powder and it was about 25.6 nm.

Keywords: Chitosan, demineralization, deproteinization, characterization, spin-coated film

Introduction

Chitin is a long-chain polymer of N-acetylglucosamine and a derivative of glucose. It is a primary component of cell walls in fungi, the exoskeletons of arthropods, such as crustaceans(e.g., crabs, lobsters and shrimps). The structure of chitin is comparable to another polysaccharide-cellulose, forming crystalline nanofibers or whiskers.

Chitosan is a natural biopolymer that can be retrived from alkaline deacetylation of chitin. Chitosan can dissolve in dilute acetic acid at room temperature. Chitosan has a amine group in which the nitrogen atom has lone

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pair electron. This lone pair electron can interact with the cation from the salt to form a polymer which is a criterion that must be fulfilled for polymer electrolytes.

Zinc acetate is the chemical compound with the formula $(O_2CCH_3)_2$ Zn but more commonly refers to the dehydrate $(O_2CCH_3)_2$ $Zn(H_2O)_2$. Both the hydrate and the anhydrous forms are colourless solids that are commonly used in chemical synthesis and as dietary supplements. Zinc acetates are prepared by the action of acetic acid on zinc carbonate or zinc metal.

If the sample is a mixture, XRD data can be analyzed to determine the proportion of the different minerals present. Thin film diffraction methods are used as important process development and control tools, as hard X-rays can penetrate through the epitaxial layers and measure the properties of both the film and the substrate.X-ray powder diffraction is most widely used for the identification of unknown crystalline materials (e.g. minerals, inorganic compounds).

A Scanning Electron Microscope (SEM) is a tool for seeing otherwise invisible worlds of microspace and nanospace. IR spectroscopy utilizes a special light source to pass infrared radiation through the substance being analyzed and then measures how much of the infrared light is absorbed at each frequency. The absorbance bands that appear at various wavelengths indicate the presence of certain types of bonds in the molecular structure of the sample[6]. In this paper, structural, microstructural, vibrational and optical characteristics of the as-prepared chitosan-ZnO powder and film are studied by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Fourier Transform Infrared (FTIR) spectroscopy.

Experimental Procedure

Preparation of Chitosan Powder

Purified chitosan powder was obtained by slow evaporation of aqueous solution. The choice of raw material was chitin shown in Fig 1. Firstly, the raw material of chitin was weighed by digital balance. A purification step was introduced and recommended optimum condition for the two stages of demineralization and deproteinisation.

Demineralization was performed the following steps.

- Weight out the desired quantity of chitin.
- Added the ratio of 2ml of acetic acid to 1g of chitin.
- Left mixing for 1h to allow any minerals present to dissolve.
- Filtered by passing through filter paper.
- Washed with de-ionized water to remove any excess acid and prevent an acid.

Illustration of demineralization processes were demonstrated in Fig 2(a & b).

Deproteinisation process was as follow.

- Added 1M sodium carbonate to mixture solution drop by drop and mixing for 1h at room temperature to dissolve any unwanted proteins by p^H control shown in Fig 3.
- Filtered to remove the sodium carbonate and washed with de-ionized water sample in 50ºC oven to dry.

Final product yield purified chitosan powder. The experimental procedure of chitosan powder was shown in Fig 4.

Preparation of Chitosan-ZnO Powder

Chitosan-ZnO powder was prepared using in precipitation method. The precipitation was prepared using a 2% chitosan solution of degree of deacetylation> 85%. Fig 5 showed the schematic overview of the preparation of chitosan-ZnO powder. The zinc acetate salt was added to a solution of chitosan in acetic acid and was kept for 24h. Then sodium hydroxide solution was added drop wise and kept for 12h. The precipitate formed was filtered, washed several times with water and dried at 100ºC. Chitosan-ZnO obtained was dried and calcined temperature. The chitosan-ZnO powder formed was calcined at 600ºC.

Preparation of Chitosan-ZnO Film

To get the chitosan-ZnO film, the substrate in this experiment was used as glass substrate. Before the deposition, glass substrate was cleaned with standard cleaning process. After the cleaning process chitosan-ZnO powder was dissolved in acetic acid. This mixture was continuously stirred with a magnetic stirrer to be homogeneous for 1 h. The solution was deposited onto glass substrate by spin-coating technique and heat treated at 600°C for 1h. Finally chitosan-ZnO film was successfully formed. The experimental procedure of chitosan-ZnO film was shown in Fig 6.

In this paper, as-prepared chitosan-ZnO powder and film are studied by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Fourier Transform Infrared (FTIR) spectroscopy.

Figure 1: Raw chitin

Figure 2: (a) Chitin + Acetic solution

Figure 2:(b). Filtering process

Figure 3: p^H control process

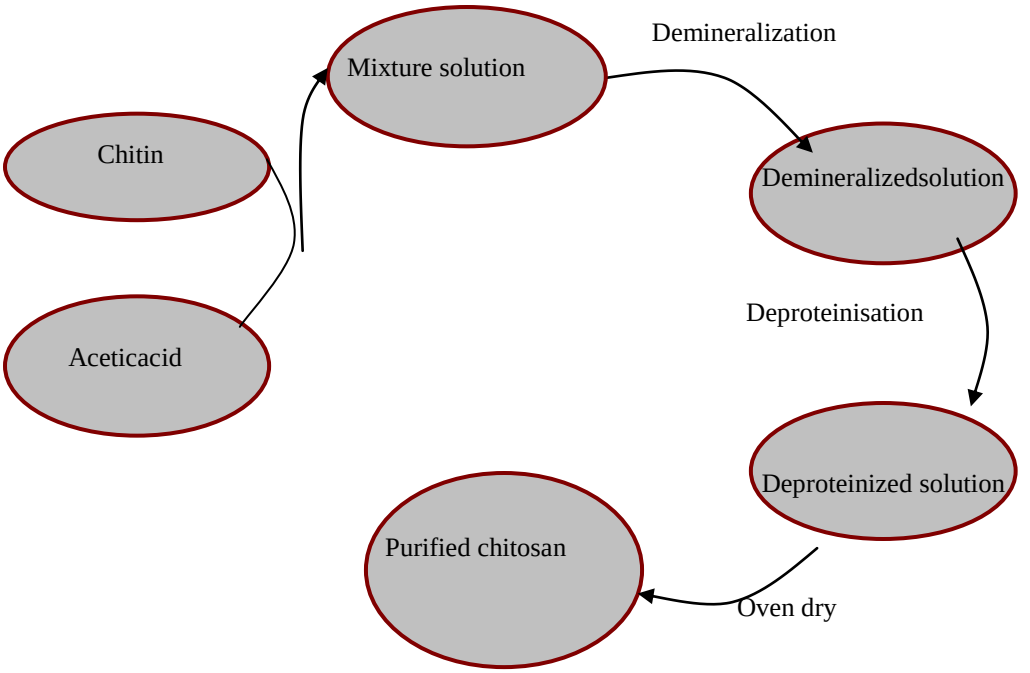

Figure 4: Schematic diagram of experimental procedure

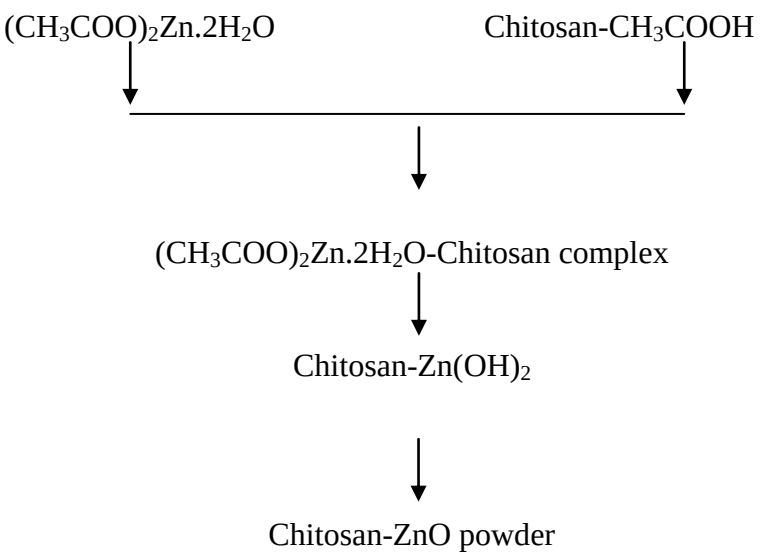

Figure 5: Schematic overview for precipitation of chitosan-ZnO powder.

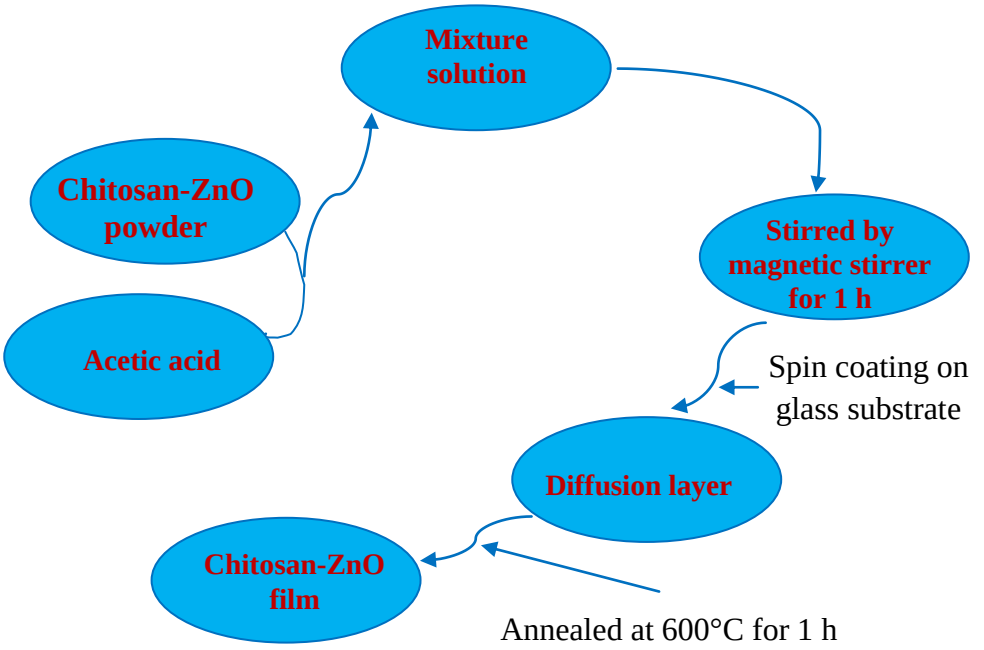

Figure 6: Experimental procedure of the chitosan-ZnO film

Results and Discussion

Structural Characterization of Chitosan Powder

X-ray diffraction, XRD is a non-destructive technique for the qualitative and quantitative analysis of the crystalline materials, in form of powder or solid. The information about the crystallographic properties such as crystallite size and lattice parameters of over all the samples has been obtained from the XRD profiles. The XRD spectrum of chitosan powder, the upper site of the graph was represented the observed peaks and the lower site of the graph was represented the standard peaks. Fig 7 gave the observed XRD spectrum of as grown chitosan. On the spectrum, 20 reflection of observed peaks were scanned within diffraction angle (2θ).

The chitosan powder annealed at 200ºC was shown in Fig 8. From the figure appeared 8 reflections. They were (042), (007), (081), (161), (202),

(033), (0,0,10) and (1,10,1). The corresponding Bragg angles were 20.855º, 27.265º, 27.570º, 31.613º, 32.724º, 37.520º, 39.344º and 41.30º. The XRD profile of chistosan at 300ºC was shown in Fig 9. On the spectrum, 18 reflections were formed between diffraction angle (2θ) of some scanned range (10º to 70º). The (hkl) planes were successfully formed in Fig 7 & 9.

Lattice Parameter Determination

Some crystallographic parameter such as crystallite size and bond length were calculated and collected in Table 1. Comparison of lattice parameters of chitosan powder and lattice parameters of chitosan presented by Mazeau K et al (1994)was shown in Table 2.Concerning with the above Table2 the observed lattice parameters were found to be little different in those of Mazeau K.

Microstructural Properties of Purified Chitosan

A microstructural property of purified chitosan powder was studied by SEM. The magnification of scanning electron image was 2700. Fig 10 showed scanning electron image of purified chitosan powder. In this Fig, it could be clearly seen that polymer like nature of microstructure was uniformly distributed.

Molecular Vibration of Purified Chitosan

Chitins were major constituents of exo-skeleton of crustaceans such as crab, shrimp and lobster. They were biopolymer composed of glucosamine and N-acetylated glucosamine linked by glycosidic bonds. Chitosan has an amine group in which nitrogen atom has a lone pair electron. Molecular vibrational spectrum of purified chitosan powder was shown in Fig 11. Vibrational frequency and mode assignment of chitosan powder was tabulated in Table 3.

XRD Analysis of Chitosan-ZnO Powder and Film

Fig 12 gave the observed XRD spectrum of chitosan-ZnO powder at 600°C. On the spectrum, 9 reflections of observed peaks were scanned within diffraction angle (2θ) of some scanned range(10°to 70°).The chitosan-ZnO

film annealed at 600°C was shown in Fig 13. From the figure, 5 reflections were appeared. The (hkl) planes were successfully formed in Fig 12&13. From the figures that the major reflection between 30° and 40° (2θ value) indicate higher crystalline region in the chitosan-ZnO samples. Also the less intense peaks 47.5°,57°,68° (2θ's) indicate the high crystallinty of chitosan-ZnO samples.

Lattice parameters, lattice distortions and Bond length were given in Table 4. Bond Length (BL) was calculated by the following equation (1)

$$BL = \sqrt{\frac{a^2}{3} + (\frac{1}{2} - u)^2 c^2} \quad (1)$$

Where u = position parameters = $\frac{a^2}{3c^2}$ +0.25

The crystallite size was calculated by Debye Scherer formula in equation (2)

$$G = \frac{\beta \times \lambda(\text{Å})}{\text{FWHM(deg)} \times \cos\theta_B} \quad (2)$$

Where β = Scherer constant ≈ 0.899

G = Crystallite size

λ_{CuK_α} = wavelength of CuK_α= 1.54056 Å

FWHM = Full Width at Half Maximum

θ_B = Bragg angle

Table 5 showed crystallite size of chitosan-ZnO powder and film at 600°C. The full width at half maximum of an (hkl) peak at (θ value) and crystallite size of all the chitosan-ZnO samples show that chitosan-ZnO film has smaller crystallite size compared to the chitosan-ZnO powder. It is also seen that chitosan-ZnO film shows lower particle size but higher FWHM value.

Table 6 showed crystallite size and FWHM value of chitosan-ZnO powder presented by Sousa V C et al (1998). Concerning with the Table 5 & 6

the observed crystallite size were found to be little difference in those of Sousa V C.

SEM Analysis of Chitosan-ZnO Powder and Film

A microstructural property of chitosan-ZnO powder and film at 600°C were studied by SEM. The magnification of scanning electron image was 2700. Fig14(a-b) showed scanning electron image of chitosan-ZnO powder and film. Grain growth patterns were observed all samples. The grain size were (0.35μm) and (1.31 μm) respectively. From the Fig 14(a), it is clear that the chitosan-ZnO powder is formed uniform and honey comb like shape. It is also found that the photograph of chitosan-ZnO powder is formed crystalline as its shape is changed from the cauli flower structure of chitosan-ZnO film was shown in Fig 14(b).

Table 1: Crystallite size and bond length of chitosan powder

Condition	**G (nm)**	**BL(Å)**
as-grown	5.797	7.06
200 °C	2.183	3.16
300 °C	2.173	3.14

Table 2: Comparison of lattice parameters of chitosan powderand Mazeau Kchitosanpowder (1994)

Lattice parameters				
Condition	**a (nm)**	**b (nm)**	**c (nm)**	**c/a**
as-grown	1.190	0.901	1.095	0.92
200 °C	0.384	2.716	1.092	2.84
300 °C	0.392	2.702	1.084	2.75
Mazeau K - chitosan	0.807	0.844	1.032	1.27

Table 3: Vibrational mode assignment of purified chitosan powder

No	Wave No(cm^{-1})	Vibrational Mode Assignment
1	538.1	C-H Stretching
2	621.0	C-H Stretching
3	700.1	C-C Bending
4	779.2	C-H Bending
5	862.1	C-H Bending
6	906.5	O-H Bending
7	1035.7	C-O-C Symmetric Stretching
8	1072.3	C-O Bending
9	1155.3	C-O Bending
10	1257.5	C-O-C Asymmetric Stretching
11	1375.2	CH Stretching for CH_3
12	1419.5	CH Stretching for CH_3 and CH_2
13	1483.2	CH Stretching for CH_3 and CH_2
14	1585.4	NH_2 Bending
15	1656.7	NH_2 Bending
16	3401.2	NH_2 Group Stretching

Table 4: Lattice parameters, lattice distortion and bond length.

Sample	Lattice Parameter (Å)		$\frac{c}{a}$	BL(Å)
	a-axis	c-axis		
Powder (600°C)	3.2229	5.1796	1.606	1.962
Film (600°C)	3.2095	5.1569	1.610	1.9551

Table 5: Crystallite size and FWHM value of chitosan-ZnO powder and film

Sample	Crystallite size (nm)	d spacing (101)	FWHM (deg)
Powder (600°C)	33.2	2.4571	0.252
Film (600°C)	25.6	2.4467	0.326

Table 6: Crystallite size and FWHM value of chitosan-ZnO powder presented bySousa V C(1998)

Sample	Crystallite size (nm)	FWHM (deg)
Powder (550°C)	33.59	0.25982

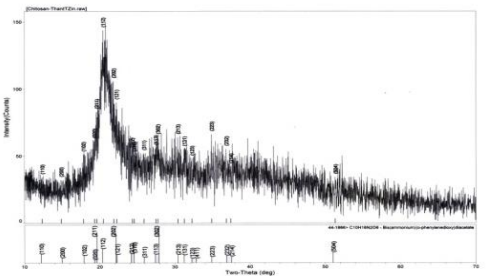

Figure 7: XRD profile of as-grown chitosan powder

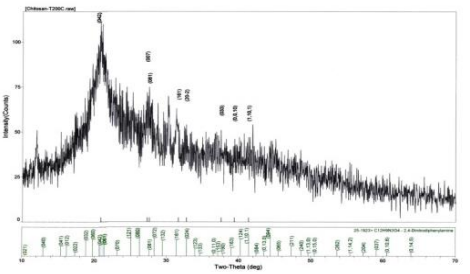

Figure 8: XRD profile of chitosan powder at 200ºC

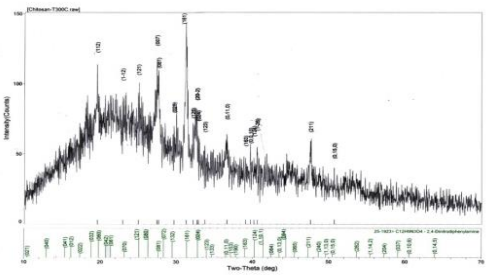

Figure 9: XRD profile of chitosan powder at 300ºC

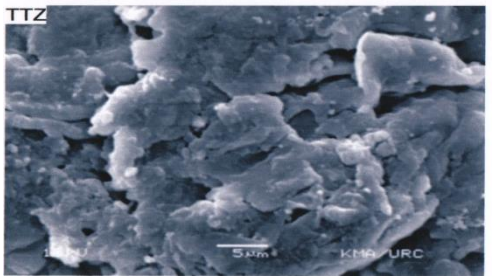

Figure10: Scanning Electron Image of purified chitosan powder

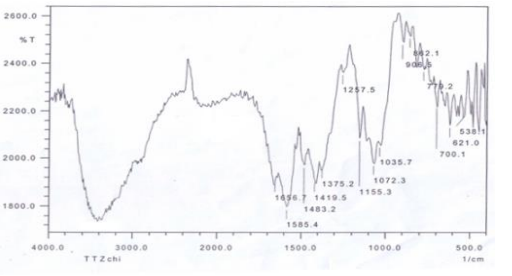

Figure 11: IR transmission spectrum for purified chitosan powder

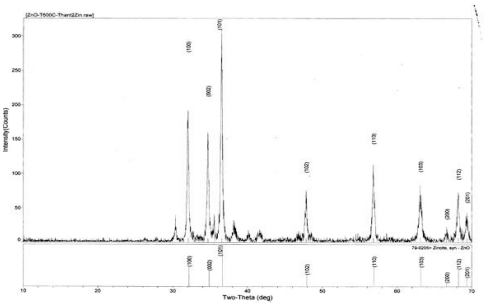

Figure 12: XRD spectrum of chitosan-ZnO powder at 600°C

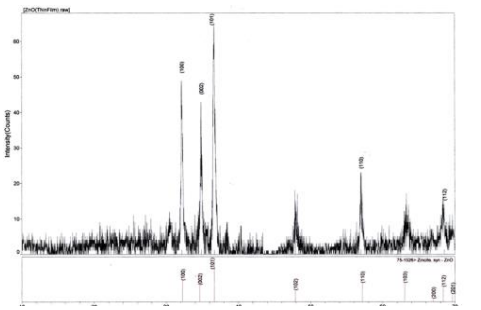

Figure 13: XRD spectrum of chitosan-ZnO film at 600°C

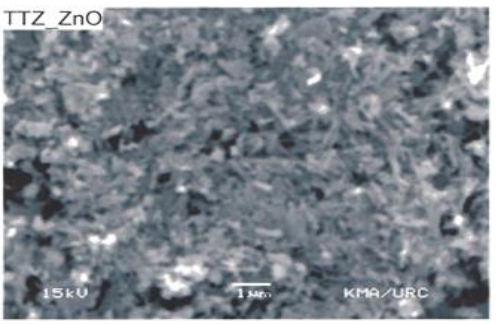

Figure 14: (a). SEM image of chitosan-ZnO powder at 600°C

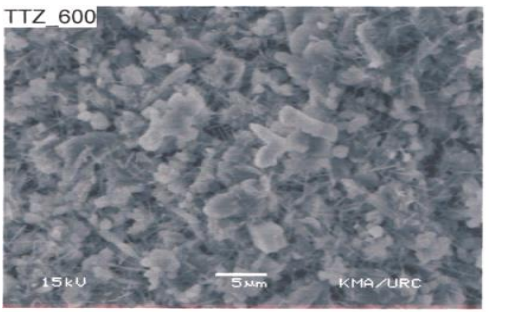

Figure 14: (b).SEM image of chitosan-ZnO film at 600°C

Conclusion

According to the XRD results, it was obvious that all chitosan powders were clearly formal with orthorhombic symmetry. The as-grown chitosan was also appeared and gave the low temperature condition. The lattice microstrain of as-grown powder was calculated to be about 0.9 and consistent with the theorectical value of orthorhombic crystal. Mazerau K et al (1994) reported that the c/a value was 1.27. Concerning with that report, the as-grown powder was better than Mazeau K et al (1994) (chitosan at 180ºC).

From SEM image, polymer like nature of microstructure was uniformly distributed on purified chitosan powder. Our measurement of FTIR spectrum was good agreement with reported values. IR transmission spectrum has characteristics of alcohol, N-H containing amine.

Characterization and crystalline state of ZnO powder and film with chitosan medium have been successfully implemented. According to the XRD results, it was obvious that, chitosan-ZnO film has smaller crystallite size than that of chitosan-ZnO powder. The chitosan-ZnO powder and film were also appeared and gave the temperature at 600°C. The crystallite size was calculated to be about 33.2 nm for chitosan-ZnO powder and corresponding FWHM was 0.252 deg. Sousa V C et al (1998)reported that the crystallite size was 33.59 nm and corresponding FWHM was 0.259 deg. Concerning with this report, the observed chitosan-ZnO powder was smaller than Sousa V C et al (1998) (chitosan-ZnO at 550°C) in crystallite size. Micro grain of chitosan-ZnO powder and film were uniformly distributed and high dense.

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References

Ardel G et al (1996) Solid State Ionics 85

Barnes P R F et al (2002) Journal of Microscopy205 (2) 118

Danilatos G D (1988) "Foundations of environmental scanning electron microscopy". Advances in Electronics and Electron Physics 71 109

Ogawa K et al (2004) J Biological Macromolecules 34 1

Suryanarayana C & Grant Norton M (1998)“ X-ray Diffraction”(New York :Plenum)

Tiwari A et al (2007) Express Polymer Letters 1 (5) 308