Preparation, Characterization and Stability Studies of Multilayer Nano Thin films

M. Geetha Devi[*1], M. Kavya Rao[1], Joefel Jessica Dumaran[1]

MIE department,

[1]Caledonian College of Engineering,

Oman

Abstract — **In this study, the investigation of possible use of multilayer thin films composed of Chitosan and Poly Vinyl Alcohol (PVA) in the pharmaceutical application was studied. Multilayer thin films were fabricated by Layer-by-Layer (L-b-L) adsorption of Chitosan and PVA on glass substrate. Various experiments have been carried out using batch adsorption techniques to study the effect of assembling pH, number of bilayers and polymer concentration on the thickness and surface roughness. The stability studies of the fabricated thin films in plain water of different pH have been studied. The film thickness increased with increase in pH up to 6 and above which there was a decreasing trend. The maximum roughness was observed at pH 5, above which it decreased again. For a given number of layers, the thickness of the multilayer nano thin films increased and the roughness decreased with increase in number of layers. The surface morphology studies using Atomic Force Microscopy (AFM) shows that peaks and valleys are present on the film surface. The fabricated films were subjected to post treatment with different pH water. The layer thickness and surface morphology of the adsorbed polymer chain can be controlled by adjusting the dipping solution pH, which controls the charge density of the adsorbed polymer layer.**

Keywords— Adsorption; Layer-by- Layer; chitosan; Poly Vinyl Alcohol; Surface Roughness; Thin Films; Atomic Force Microscopy.

I. INTRODUCTION

Layer-by-layer (L-b-L) assembly is a unique method for the fabrication of multilayer thin films with nanometer precision. The basis of the method involves alternate adsorption of polycation and polyanion adsorption on to a substrate, resulting in the reversal of the surface charge after deposition of each layer. A novel and versatile layer-by-layer method was initially introduced by Decher and coworkers [1] using polyelectrolytes by sequential adsorption procedure on templates. This approach has been applied to fabricate nano thin films in a variety of applications [2].

Multilayer thin films have been fabricated using Poly Styrene Sulphonate (PSS) and Poly Allyl amine Hydrochloride (PAH) as layer constituents. The thickness and surface roughness of the films are controlled by adding salt to the polyelectrolyte dipping solutions [3, 5]. Main applications of L-b-L films include catalysis, drug delivery, electrochemical sensing and bio sensing etc. The principal driving force is the electrostatic interaction between the polyelectrolytes accompanied by hydrogen bonding, hydrophobic interactions and charge transfer. There is a charge reversal in each adsorption step and this excess charge resides at the surface which favors further adsorption in next

steps [6-8]. The recent research reported on the fabrication of multilayer nano thin films using biodegradable polymers shows the suitability of natural polymers in pharmaceutical applications [9].

The main advantages of L-b-L method are simple in construction, independent of size and shape of substrate, minimum polymer requirement, and ease of fabrication. Other fabrication techniques employed are spin and spray coating of which spin coating requires less amount of polyelectrolyte sample and requires less coating time [10 - 12]. The relative ease in fabrication and control over different varieties of substrate extends its applications into different fields such as catalysis, biosensors, light emitting diodes, selective membranes and drug delivery [13-19].

In the present work, the assembly of multilayer thin films composed of high molecular weight chitosan as a natural polyelectrolye and Poly Vinyl alcohol (PVA) has been reported. The effect of variation of assembling pH, number of bilayers, and polymer concentration on the thickness and surface roughness has been studied. The multilayer thin films were subjected to post treatment with different pH water.

2. EXPERIMENTAL SECTION

2.1 Materials

Chitosan (Mw 650 kDa, degree of deacetylation >75%) and Poly Vinyl Alcohol (Mw 50 kDa), were obtained from Sigma Aldrich, India. Glass plates of dimension 8 cm x 2 cm were employed as template. TiO_2 was used as nano catalyst; HCl and NaOH were obtained from Merck, India. Millipore water (18.2 $M\Omega$ resistivity) was used in all experiments. To ensure the accuracy, reliability and reproducibility of the collected data, all batch experiments were carried out in triplicate and the mean values of three data sets are presented.

2.2. Thin Film preparation

Multilayer thin films were prepared by the L-b-L technique [16] with chitosan as the first layer. Silica templates were etched in 25% NH_3, 30% H_2O_2 and water in the ratio 1:1:5 for 20 minutes to ensure a better attachment of chitosan to the bare silica surface and thoroughly washed with water. The adsorption of polyelectrolytes was performed for 20 minutes followed by three washings in water. Then the next layer is coated with PVA. The experiment is repeated till the desired number of bilayers was adsorbed. The resulting films were dried with a stream of nitrogen and further dried in a vacuum desiccator at room temperature for further characterization.

The Thickness and surface morphology of the prepared films were measured using Ellipsometry and Atomic force microscopy.

2.2.1 AFM imaging

The surface morphology and roughness of thin films were studied by imaging with a MFP-3D AFM (Asylum Research, USA). The imaging was carried out using NCR-20 cantilevers having a resonance frequency of 285 kHz and force constant of 42 N/m (Nanoworld, Switzerland). Minimum of 4 images were recorded from different areas of the sample and the roughness values was obtained. Surface roughness measurements were done on 20 layer films deposited on glass plates with a Dimension of 8 cm x 2 cm.

2.2.1 Ellipsometry

The film thickness was determined using a SE850 spectroscopic ellipsometer (Sentech Instruments, Germany) over a spectral range of 300 to 800 nm at an incidence angle of 70^0. At least 4 measurements were made at different spots and averaged. All measurements were carried out at room temperature.

3. RESULTS AND DISCUSSION

3.1 Effect of variation of assembly pH

The effect of variation of thickness and roughness on polymer solution pH was studied by varying the solution pH. The pH of the chitosan and PVA solutions were systematically varied from 3 to 9 in order to determine how the polymer solution pH influences surface morphology and organization of the film. Figure 1 shows the average incremental thickness and roughness contributed to each multilayer layer with different pH. By simply varying the pH, it is possible to control the layer thickness.

The surface morphology of the films is shown in Figure 2, which displays the average thickness and surface roughness. It is seen that the thickness of the multilayer film increased with increase in pH up to 5, above which it shows a decreasing trend. The difference in thickness is due to change in the surface charge of the adsorbed polymer chains in the pH range studied. The details concerning the adsorption behavior of chitosan/ PVA are shown in Figure 2. The increase in layer thickness, results from the increasing surface charge density of a previously adsorbed polymer chain with increasing pH. At lower pH, the protonation of chitosan leads to an excess of charges which cause a swelling and the dissolution of multilayers. Chitosan pKa value is nearly 6.5, at this point the soluble – insoluble transition occurs. At low pH, the amines are protonated and positively charged and chitosan becomes a more water soluble at low pH. The deprotonation of amino group takes place at high pH, which results in loss of surface charge and becomes neutral.
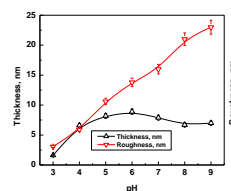

Figure 1. Effect of variation of film thickness and roughness with solution pH in chitosan-PVA multilayer films (conditions: 0.5 mg/ml polymer concentration, 10 layers
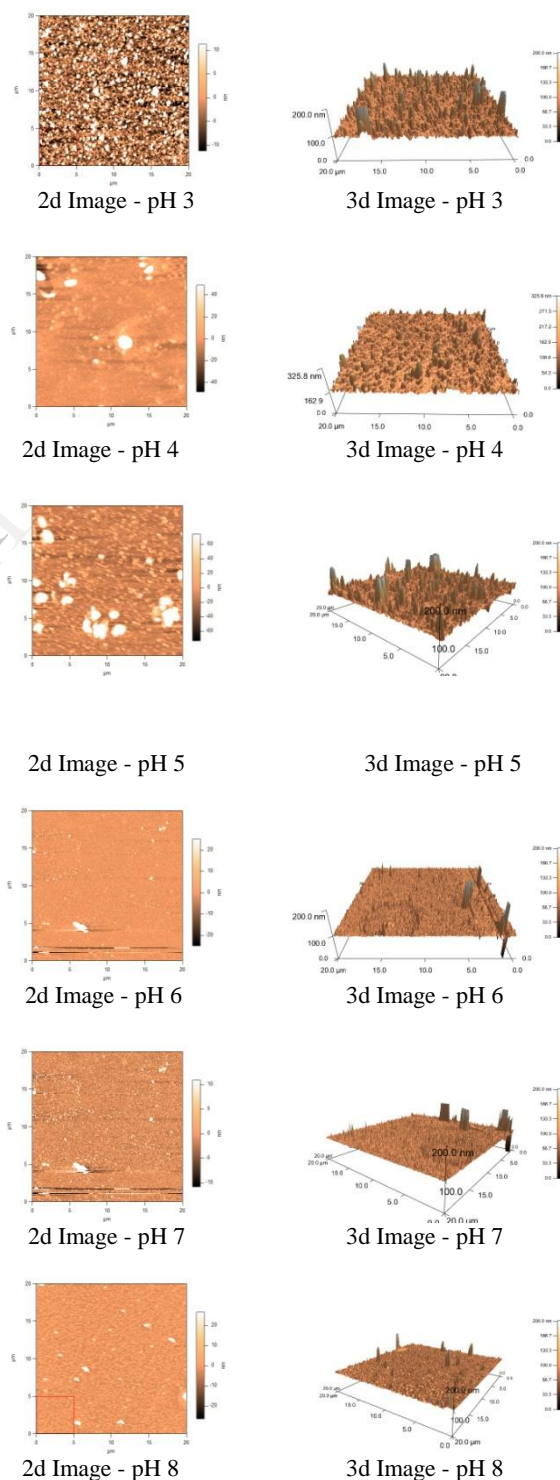

2d Image - pH 3   3d Image - pH 3

2d Image - pH 4   3d Image - pH 4

2d Image - pH 5   3d Image - pH 5

2d Image - pH 6   3d Image - pH 6

2d Image - pH 7   3d Image - pH 7

2d Image - pH 8   3d Image - pH 8

Figure 2. AFM 2d and 3d images of chitosan-PVA films assembled at different pH (polymer concentration = 0.5 mg/ml, number of layers = 10)

3.2. Effect of number of layers

The effect of variation of number of assembling steps with thickness and roughness was studied by varying the number of layers by keeping all other parameters constant (pH 5, polymer concentration 0.5 mg/ml). The AFM images are shown in Figure 4. For the initial bilayers the surface is featureless with grainy surface morphology. The increase in layer number increases the thickness with the presence of peaks and valleys on the surface. Further increase in the layer number, the peaks and valleys disappear and the surface become smooth after the desired thickness has attained. The hole formation results in increase in surface roughness as shown in Figure.4
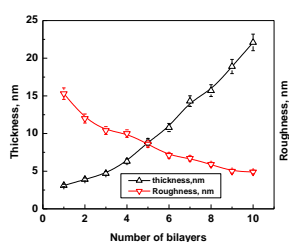

Figure 3. Dependence of the film thickness and roughness on the number of layers in chitosan-dextran sulphate multilayer films (conditions: 0.5 mg/ml polymer concentration and assembly pH 6

1bilayer

2 bilayer

3 bilayer

4 bilayer

5 bilayer

6 bilayer

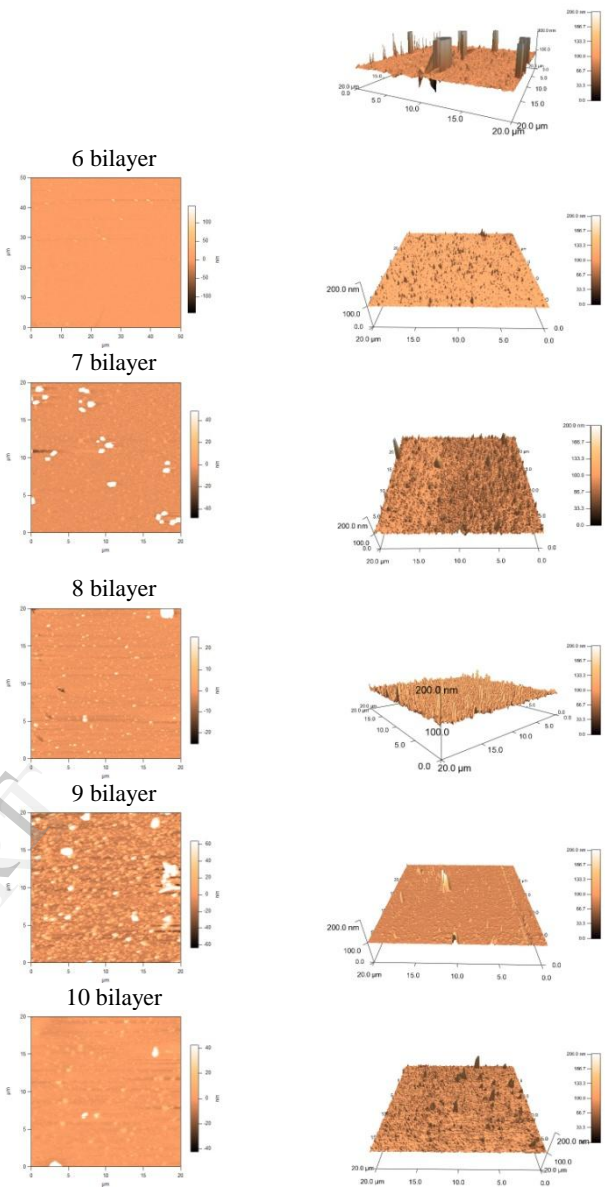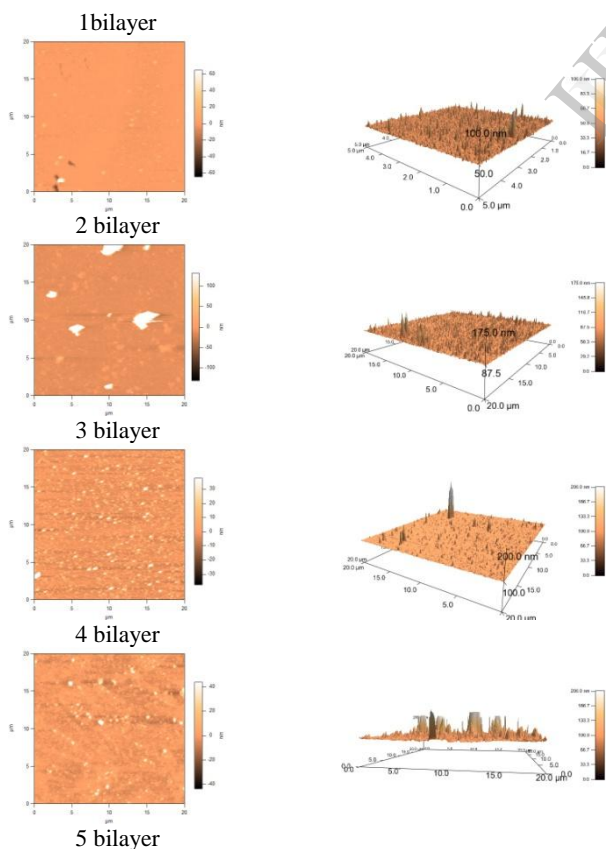7 bilayer

8 bilayer

9 bilayer

10 bilayer

Figure 4. AFM 2d and 3d images of chitosan-PVA films assembled at different number of bilayers from 1 to 10 (polymer concentration = 0.5 mg/ml)

The thickness increased with increase in number of layers up to 10 bilayers where as the surface roughness decreased continuously up to 10 bilayers as shown in Figure 3. The layer growth is in a non linear trend due to the vermiculate structure. Further increase in number of layers will smoothen the surface by widening the peaks by merging and filling the cavities. There is an exponential increase in thickness due to increase in number of layers due to multilayer formation. The roughness of bare slide was 900 pm. After one layer of deposition the roughness was increased to 940 pm shows that the roughness of first layer is almost similar to the bare surface roughness. During the beginning stages of deposition the polyelectrolyte chains are not homogeneously adsorbed on the surface of the template, which had scratches, holes and edges with high charge concentrations. At the second stage, for longer deposition times of nearly 30 minutes the

polyelectrolyte chains are gradually spread out and the surface roughness decreased. The surface morphology of the thin films depend on the experimental conditions such as time of aggregate growth, nature of polyelectrolytes employed and number of deposition layers.

3. 3. *Effect of Polymer Concentration*

The effect of variation of thickness and surface roughness with concentration of polymer was studied by varying the polymer solution concentration from 0.1 mg/ml to 0.5 mg/ml by keeping pH 4 and number of layers 10 constant. The thickness of the thin film increased with increase in polymer concentration, whereas the roughness value decrease with increase in polymer concentration as shown in Figure 5.The AFM images of the variation of polymer concentration are shown in Figure 6 . The chitosan – PVA multilayer thin film thus completely cover the surface of the template after 10 bilayers of deposition. The average layer thickness was measured using ellipsometry.

The film thickness increased with increase in polymer concentration until 0.5 mg/ml. the maximum increase in thickness is due to the electrostatic nature of the L-b-L process.
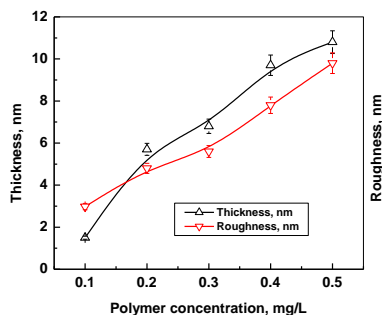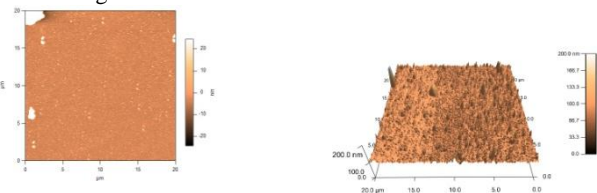

Figure 5. Dependence of the film thickness and roughness on polymer concentration in chitosan-dextran sulphate multilayer films (conditions: assembly pH 6, number of layers = 10)
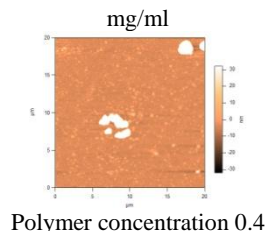
Polymer concentration 0.1 mg/ml

Polymer concentration 0.2 mg/ml

Polymer concentration 0.3

mg/ml

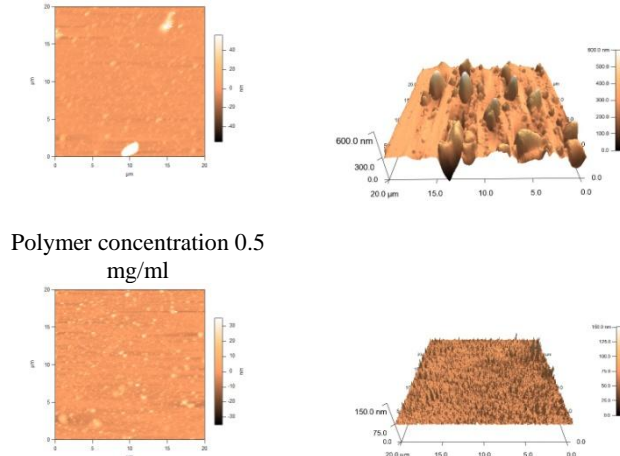Polymer concentration 0.4 mg/ml

Polymer concentration 0.5 mg/ml

Figure 6. AFM 2d and 3d of chitosan-PVA films assembled in different polymer concentrations.

4. POST TREATMENT WITH DIFFERENT pH WATER

Post treatments of the fabricated multilayer thin films were carried out by dipping into different pH water for 24 hours to study the stability of the films. The pH of the dipping solution was prepared by using plain water. The pH was adjusted by 0.1 N NaOH and 0.1 N HCl. With increasing pH the degree of swelling increased and roughness reached to a maximum. The influence of dipping solution pH is essentially a product of the acid-base chemistry of the chitosan – PVA. The overall swelling behavior depends on the internal structure and dissociation behavior of the free functional groups within the film. The morphological characteristics of the film after dipping in different pH water are shown in Figure 11 and the effect of thickness and roughness variation shown in Figure 12.
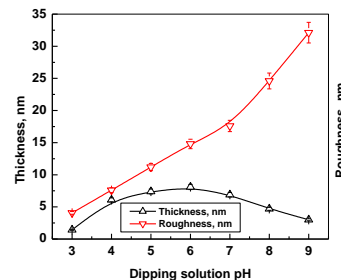

Figure 7. Effect of variation of film thickness and roughness with dipping solution pH in chitosan-PVA multilayer films (conditions: 0.5 mg/ml polymer concentration, 10 layers)
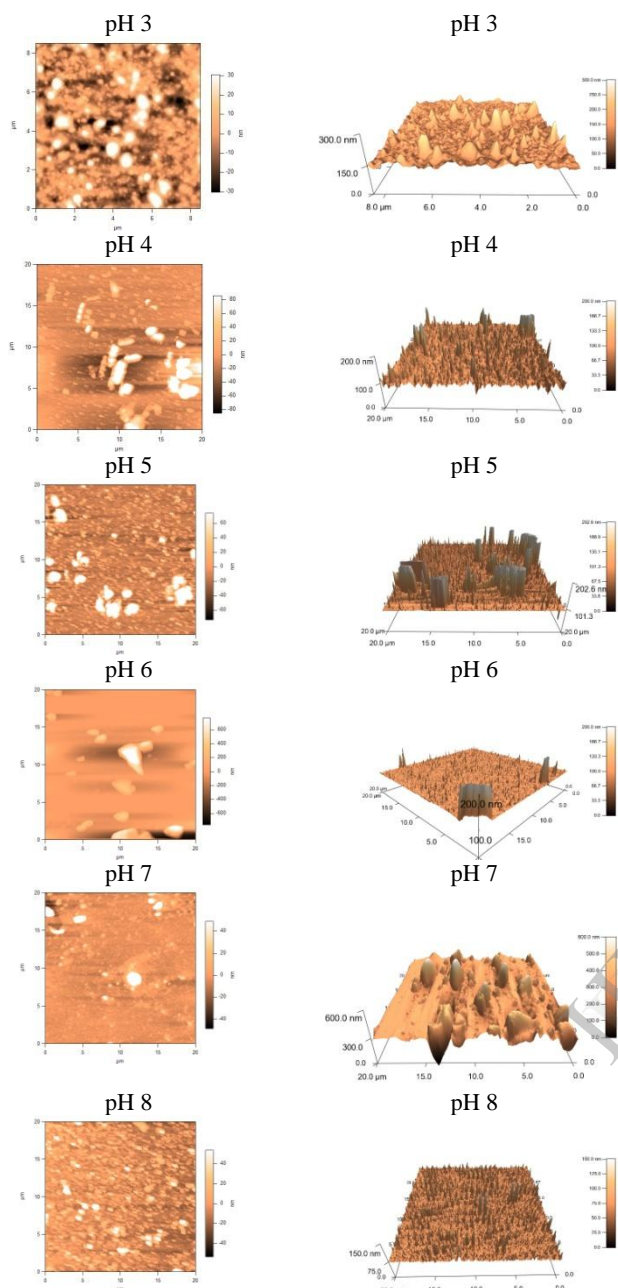
Figure 8. AFM 2d and 3d images of chitosan-dextran sulphate multilayer thin films after treatment with different pH Water.

4. CONCLUSION.

The experimental result demonstrates that polyelectrolyte multilayer thin films of nanometer precision can be fabricated using chitosan and poly vinyl alcohol by layer by layer method. The thickness of the films is tuned by changing the assembling pH, number of layers and polymer concentration. The surface morphology of the film was studied using atomic force microscopy and the thickness measurement using ellipsometry. The surface charge of the film is sensitive to polymer solution pH. The thickness increased with increase in number of layers whereas the roughness decreased with increase in layer number and the trend observed was non linear in both the cases. The fabricated thin films were subjected to post treatment with different pH water and the

result showed different micro structural characteristics with swelling. The result demonstrates that Chitosan – PVA films can be fabricated by Layer-by-Layer technique using glass slide as template. The result also explored the possibility of using chitosan and poly vinyl alcohol for various pharmaceutical applications.

REFERENCES

[1]. B. Philipp, H. Dautzenberg, K.J. Linow, Kotz, and J. Dawydoff, "Polyelectrolyte complexes - recent developments and open problems,"W. *Prog. Polym. Sci. 14*, 91, 1989.

[2]. G. Decher, "Fuzzy Nanoassemblies: Toward Layered Polymeric Multicomposites," *Science,* 277, pp. 1232-1237, 1997.

[3]. F. Caruso, W. Yang, D. Trau, and R. Renneberg, "Multilayer Self-Assembly." Langmuir*, 16*, 8932, 2000.

[4]. A. A. Antipov, A.A. Sukhorukov, D. B. Donath, and H. Mohwald, "Sustained Release Properties of Polyelectrolyte Multilayer Capsules,". J. Phys. Chem. B, 198, pp 2281-2284,2001.

[5]. L. Richert, P. Lavalle, E. Payan, X. Zheng Shu, G. D. Preswich, J. Stoltz, J. F. Schaaf, P. Voegel, and C. Picart, "Layer by Layer Buildup of Polysaccharide Films: Physical Chemistry and Cellular Adhesion Aspects," *Langmuir*. 20 (2) pp. 448-458, 2003.

[6].F. Caruso, H. Kichtenfeld, M. Giersig, and H. Mohwald, "Electrostatic self-assembly of silica nanoparticle-polyelectrolyte multilayers on polystyrene latex particles," *J. Am. Chem. Soc.* 120, p 8523,1998.

[7]. G. Decher and J. B. Schlenoff (eds.), "Multilayer Thin Films-Sequential Assembly of Nanocomposite Materials," Wiley-VCH, Weinheim, Germany , 2002.

[8]. J. D. Hong, K. Lowack, J. Schmitt, and G. Decher, "Layer-by-layer deposited multilayer assemblies of polyelectrolytes and proteins: from ultrathin films to protein arrays," *Progress in Colloid & Polymer Science,* 93, pp. 98-102, 2000.

[9]. M. Geetha Devi, Susmita Dutta, Ashraf Talib Al Hinai, and S. Feroz, "Surface Morphology Study of Chitosan-Dextran Sulphate Multilayer Thin Films," Journal of Chitin and Chitosan Science, Vol. 2, 1–14, 2014.

[10] K. Varahramyan, and Y. Lvov, "Nanomanufacturing by Layer-by-Layer Assembly,". *Journal of Nanoengineering and Nanosystems.* 1, pp. 29-37, 2006.

[11]. J. B. Schlenoff, S. T. Dubas, and T. Farhat, "Sprayed polyelectrolyte multilayers,"*Langmuir* 16, pp 9968 , 2000.

[12]. S. S. Lee, J. D. Hong, C. H. Kim, K. Kim, J. P. Koo, and K. Lee, "Fabrication of highly ordered multilayer films using a spin self assembly," *Macromolecules,* 34, pp 5358, 2001.

[13]. P. A. Chiarelli, M. S. Johal, J. L. Casson, J. B. Roberts, J. M. Robinson, and H.-L. Wang, "Controlled fabrication of polyelectrolyte multilayer thin films using spin assembly," *Adv. Mater.* 13, pp 1167, 2001.

[14].Y. Sun, X. Zhang, C. Sun, B. Wang, and J. Shen, "Fabrication of ultrathin film containing bienzyme of glucose oxidase and glucoamylase

based on electrostatic interaction and its potential application as a maltose sensor," *Chem. Phys.* 197, pp 147 ,1996.

[15]. J. W. Baur, S. Kim, P. B. Balanda, J. R. Reynolds, and M. F. Rubner, "Thin-film light-emitting devices based on sequentially adsorbed multilayers of water-soluble poly(*p*-phenylene)," *Adv. Mater.* 10, pp 1452, 1998.

[16]. J. Levasalmi and T. J. McCarthy, "Poly (4-methyl-1-pentene)-supported polyelectrolyte multilayer films: Preparation and gas permeability,"*Macromolecules* 30, pp 1752, 1997.

[17]. G. B. Sukhorukov, A. A. Antipov, A. Voigt, E. Donath, and H. Mohwald, "pH-controlled macromolecule encapsulation in and release from polyelectrolyte multilayer nanocapsules," Macromol. *Rapid Commun.* 22, pp 44, 2001.

[18]. S. T. Dubas and J. B. Schlenoff, "Polyelectrolyte multilayers containing a weak polyacid: Construction and deconstruction,"*Macromolecules* 34, pp 3736, 2001.

[19]. Z. P. Liang, C. Y. Wang, Q. L. Sun, Z. Tong, "Novel microcapsule fabricated by L-b-L nano self- assembly,". Prog. Chem., 16, pp 485-491, 2004.