CHAPTER III

EXPERIMENTAL

3.1 Raw materials

3.1.1 Poly (allylamine hydrochloride) (MW = 70,000, PAH, Aldrich) was used as a polycation to fabricate PET film

3.1.2 Poly (acrylic acid) (35 wt% in H_2O, MW = 100,000, PAA, Aldrich) was used as a polyaninon to fabricate PET film

3.1.3 Hydrochloric acid (35.0-37.0 wt%, cica-reagent, MW = 36.5, HCl, KANTO CHEMICAL CO., INC) was used for the creation of surface roughness.

3.1.4 Zinc oxide (95.0% purity, MW = 81.39, Particle size 0.02μm, ZnO, Wako Pure Chemical Industries, Ltd.) was used for preparation of suspension of ZnO in PAA.

3.1.5 Zinc acetate dihydrate (99.0% purity, cica-reagent, MW = 219.51, Zn $(CH_3COO)_2 \cdot 2H_2O$, KANTO CHEMICAL CO., INC) was used as a starting material in sol-gel method.

3.1.6 Absolute ethanol (99.99% purity, MW = 46.07, CH_3CH_2OH, Merck) was used as a solvent for preparation of sol-gel ZnO and using for cleaning glass substrates.

3.17 Acetone (MW=58.08, $(CH_3)_2CO$, KANTO CHEMICAL CO., INC) was used for cleaning glass substrates.

3.1.8 Acetic acid (99.7% purity, cica-reagent, MW = 60.05, CH_3COOH, KANTO CHEMICAL CO., INC) was used as a stabilizer for preparation of sol-gel ZnO method.

3.1.9 Zinc nitrate hexahydrate (99.0% purity, MW = 297.49, $Zn(NO_3)_2 \cdot 6H_2O$) was used as a material for precipitation method.

3.1.10 Ammonia water (25%, 25.0-27.9% purity, NH_3 = 17.03, Wako Pure Chemical Industries, Ltd.) was used for preparation of ammonium hydroxide as a solvent for precipitation ZnO method.

3.2 Experimental procedures

Deposition of polyelectrolyte (PET) film on glass substrate

Prior to PET film formation, all glass substrates (2.5cm×3.0cm×0.1cm) were ultrasonically cleaned in deionized water (DI-water), ethanol and acetone, respectively.

Fabrication of the PET film was prepared by using a dip coater and LbL technique which was modified from procedures of Nimittrakoolchai and Supothina [3].

3.2.1 The PET film was assembled by dipping the cleaned substrate in 0.02 M PAH aqueous solutions as a polycation with withdrawal speed (WS) 3.0 cm/min for 15 min.

3.2.2 Next layer was coated with polyanion solution as 0.02 M PAA using dip coating technique with WS 3.0 cm/min about 15 min. The polycation monolayer assembles with that of polyanion is called a bilayer coating film.

3.2.3 The same process was repeated by changing the concentration of PAH and PAA, withdrawal speed (WS) and the number of polyelectrolyte layers following to the conditions as shown in Table 3.1-3.3.

In this section, the experiment was investigate the optimal condition to prepare the sufficient PET film for coating ZnO which was selected as it gave the transparency, thickness and surface roughness of the samples. And then, the suitable PET film was coated ZnO by using different methods.

Part A: **Investigation effect of polymer concentration, withdrawal speed, and number of dipping cycle on the transparency and film thickness of the preparation of PET film**

Table 3.1 **Parameters for preparation of the 1st layer of PET film to study effect of polymer concentration**

Conditions	PAH and PAA concentration (M)	Number of coating bilayer	Properties
1	0.02	1	Transparency and Thickness
2	0.20	1	Transparency and Thickness
3	0.50	1	Transparency and Thickness
4	1.00	1	Transparency and Thickness
5	2.00	1	Transparency and Thickness

Table 3.2 **Parameters for preparation of the bilayer PET film to study effect of withdrawal speed at the suitable concentration as as result from experiment in Table 3.1**

Conditions	PAH and PAA concentration (M)	Withdrawal speed (WS) (cm/min)	Number of coating bilayer	Properties
1	X_1	3	1	Transparency and Thickness
		6		
		9		
2	X_2	3	1	Transparency and Thickness
		6		
		9		

Whereas, both of X_1 and X_2 were the suitable concentrations for fabrication the bilayer PET film as the result in part A. The appropriate concentrations were considered with transparency and thickness of the PET film.

Table 3.3 **Parameters for controlling surface roughness and thickness of PET film to study effect of the number of dipping on desired surface roughness and thickness of PET film**

Condition	PAH and PAA Concentration (M)	Number of coating bilayer	Properties
1	X	1	Thickness, Grain size and Roughness
		2	
		3	

Where X was the appropriate concentration for preparation polyelectrolyte film and gave higher thickness and smooth surface as a result from experimental in Table 3.2.

3.3 Analytical instruments used

3.3.1 The viscosity of polymer solutions for fabrication polyelectrolyte was measured by Rheometer (Rheostress 600; Haake)

3.3.2 The transmittance spectra of the PET films were analyzed by UV-Vis spectrophotometer (UV-VIS-NIR; UV3150; SHIMADZU).

3.3.3 The film thickness and surface roughness of PET films were measured by confocal laser scanning microscope (CLSM; LEXT 3D MEASURING LASER MICROSCOPE CLS-4000; OLYMPUS).

3.3.4 The grain size and surface roughness of PET films was observed by atomic force microscopy (AFM; Veeco, Scanning Probe Microscopy Controller).

Part B: Investigation an appropriate methodology for deposition ZnO on photoinduced hydrophilic properties of ZnO incorporated with PET film

PET film was deposited ZnO by using 3 methods to examine the method that exhibit the best hydrophilic property after UV irradiation at the certain time. The methods were suspension of ZnO in the polymer, sol-gel ZnO and precipitation method.

Method 1: Preparation of ZnO on the PET film with precipitation method using a dip coater which was modified from technique of Wang [10]

The PET film on glass substrate was respectively dipped in freshly prepared Zn $(NO_3)_2$ solution and NH_4OH solution (0.01 M) for 15 min which the schematic diagram of the formation of the ZnO nanocrystals was shown in Figure 3.1. This process was repeated every 20 min. Then, the modified film was dried at 180°C for 2 h. The procedure resulted in the fabrication of the multilayer films containing ZnO nanoparticles. There were various numbers of precipitation reaction cycles.

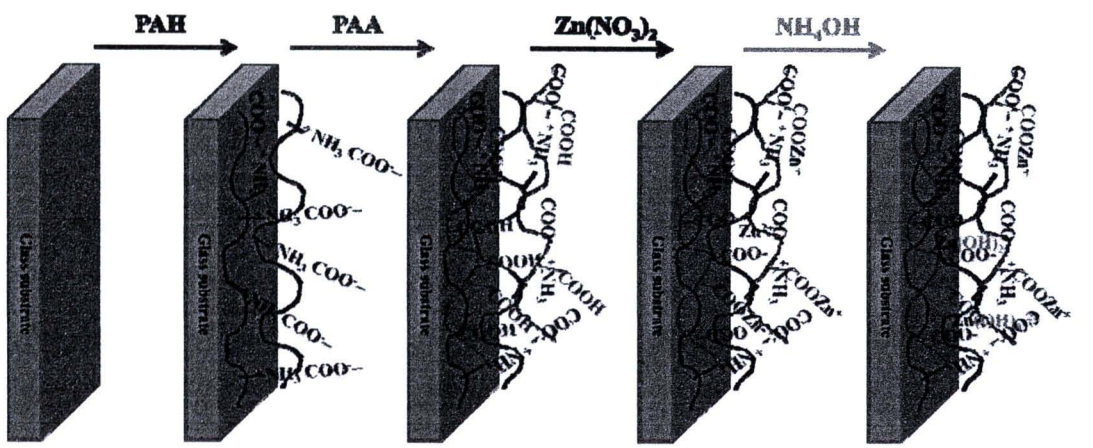

Figure 3.1 Schematic diagram of formation of ZnO nanocrystals.

Method 2: Preparation of ZnO on the PET film by suspension of ZnO in polymer method using a dip coater which was modified from procedures of Nimittrakoolchai and Supothina [3].

The PET film was modified surface roughness to create and open porosity or roughness on the surface. The sample was treated by a two-step chemical etching using HCl solutions having pH of 2.3 and 1.1, respectively for various immersion times (15, 30, 60 and 90 min). Then, ZnO nanoparticle having particle size of 20 nm were deposited on the dried PET film by dipping it into a suspension of ZnO in polymer as PAH or PAA. The ZnO suspensions were prepared by ultrasonically mixing ZnO in PAH or PAA with different content of ZnO in between 0.1-0.2 wt%. Finally, the ZnO incorporated with PET film was dried at 180°C for 2 h.

Method 3: Preparation of ZnO on the PET film by sol-gel ZnO method using a dip coater which was modified from technique of Numpud [35]

The step for deposition sol-gel ZnO on PET film was shown in Figure 3.2 which was prepared by dissolving zinc acetate in 50 mL ethanol at room temperature. The concentration of zinc acetate was studied at 0.1 M as the optimal condition in the Numpud research for preparing sol-gel ZnO. The solution was dried at 60 °C with magnetic stirring at 300 rpm for 30 min. Deionizied water and acetic acid were respectively added to the mixture solution. The acetic acid was used for adjusted pH of solution and stabilizer. The pH of solution was varied from 1 to 5 by adding acetic acid in between heat and stir until a transparent and homogeneous solution was obtained. After that, the PET films were immersed in the sol-gel solution with withdrawal speed 3 cm/min for 30 sec. The coated substrates were calcined at 500°C for 1 h with heating rate 1 °C/ min.

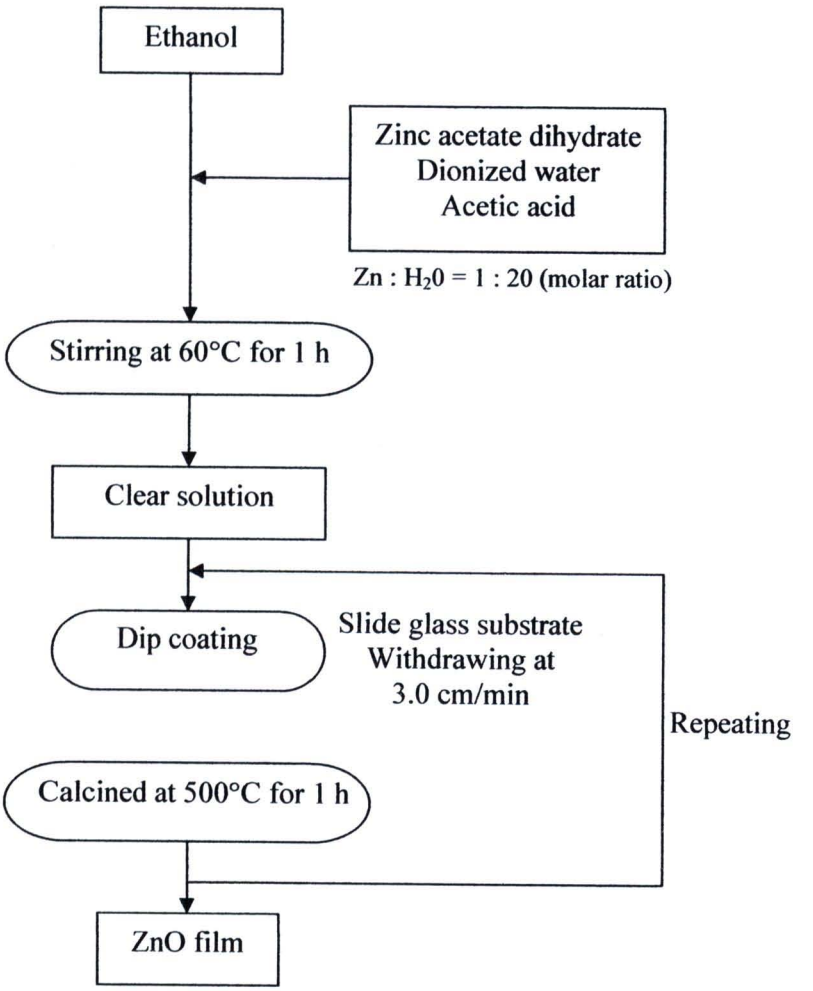

Figure 3.2 Preparation of sol-gel ZnO.

3.4 Characterization methods used

3.4.2 The viscosity of polymer solutions for fabrication polyelectrolyte was measured by Rheometer (Rheostress 600; Haake).

3.4.3 The optical transmittance spectra of the ZnO incorporated with PET films was analyzed by UV-Vis spectrophotometer (UV-VIS-NIR; UV3150; SHIMADZU) in the wavelength of 300-800 nm.

3.4.4 The film thickness and surface roughness of the ZnO incorporated with PET films were measured by confocal laser scanning microscope (CLSM; LEXT 3D MEASURING LASER MICROSCOPE CLS-4000; OLYMPUS).

3.4.5 The grain size of ZnO incorporated with PET films was observed by atomic force microscopy (AFM; Veeco, Scanning Probe Microscopy Controller).

3.4.6 The morphology and grain size of ZnO incorporated with PET films was obtained with field emission scanning electron microscope (FE-SEM; JSM5410V; JEOL).

3.4.7 The reaction between polycation with polyanion and polymer with ZnO on the films by analyzing the chemical bonding and molecular structures were investigated by Fourier transform infrared spectroscopy (FTIR; FT/IR6200 JASCO).

3.4.8 The elemental analysis of the ZnO incorporated with PET films was analyzed by energy dispersive X-ray spectrometer (EDX; EDX-600HS; SHIMADZU).

3.4.9 The hydrophilic property of ZnO incorporated with PET films was measured by water contact angle measurement.