PREPARATION OF ZINC OXIDE NANOPARTICLE

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Abstract

Zinc Oxide nanoparticle was prepared by the mixing of ammonium hydroxide and zinc nitrate hexahydrate with hydrothermal process. The studied parameters were the concentrations of ammonia and zinc nitrate hexahydrate (0.1, 0.5, and 1.0 mol/l), treatment temperatures (75, 95,100,105, and 125 °C), dispersion media (Ethylene glycol, and polyvinyl alcohol), volume of dispersion media (30, 50, and 100 ml.), and treatment method (oven, and ultrasonic). The expected zinc oxide nanoparticle was characterized by XRD and SEM. The best condition for preparing ZnO nanoparticles can be obtained by 0.1 mol/l of starting materials in 100 ml ethylene glycol at 75°C. The ZnO nanoparticles were applied to P(MMA-co-HEMA) and cast on transparent PET film. The polymer film with ZnO nanoparticle can absorb UV light.

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SYMBOLS AND ABBREVIATION

EG	Ethylene glycol
PVA	Polyvinyl alcohol
MMA	Methyl methacrylate
PMMA	Poly (methyl methacrylate)
HEMA	2-Hydroxyethyl methacrylate
PHEMA	Poly (2- hydroxylethyl methacrylate)
BPO	Benzoyl peroxide
DMT	N, N-Dimethyl-4-toluidine
XRD	X-ray diffraction
XRF	X-ray fluorescence
SEM	Scanning electron microscope
UV-Vis	Ultraviolet-Visible Spectrometer

Chapter 1
Introduction

1.1 Introduction

Nowadays, there has been growing interest in nanotechnology, which applied to use in the convergence of information and communication technology, life sciences, and biotechnology. Due to nanotechnology will usher in the Industrial Revolution of the 21st century as a platform technology with potential to revolutionize a broad range of industries. Nanomaterials are materials that have one or more dimensions less than 100 nm. Some of the major industries using or planning to use nanotechnology manufactures.

In previous time, zinc oxide (ZnO) is mainly used as the base constituent of various paints. From year to year during the last decade zinc oxide vary large increase in develop and applied to more goods. ZnO is one of the most important oxide materials for such wide ranging industrial applications, such as varistors, transparent conductors, UV-protection films, chemical sensors, and etc. ZnO nanoparticles have also been extensively studied because of their size-dependent electronic and optical properties.

In this study, zinc oxide was synthesized by hydrothermal treatment at low temperature by varying conditions i.e. the concentration of starting material, reaction temperature, dispersion media, volume of dispersion media and treatment systems. ZnO nanoparticle was then applied to copolymer of P(MMA-co-HEMA). The chemical and physical characteristics of zinc oxide and composite film were investigated by XRD, XRF, SEM, and UV-VIS.

1.2 Objective

1.2.1. To investigate the suitable condition for synthesis of ZnO nanoparticle

1.2.2. To prepare ZnO nanoparticles/poly(methymethacrylate)-co- poly (2-hydroxyethyl methacrylate) composite

1.3 Scope of Study

1.3.1. Preparation of ZnO nanoparticles by low-temperature heat using various conditions, as follows:

- Varying concentrations of NH_4OH and $Zn(NO_3)_2 \cdot 6H_2O$, i.e. 0.1, 0.5, and 1.0 mol/l
- Varying treatment temperature, i.e. 75, 95, 100, 105, and 125 °C
- Varying dispersion media, i.e. Ethylene glycol, and Polyvinyl alcohol
- Varying volume of dispersion media, i.e. 30, 50 and 100 ml
- Varying treatment systems, i.e. oven and ultrasonic

1.3.2. Characterization of ZnO nanoparticles by using XRD and SEM

1.3.3. Preliminary study on the preparation of ZnO nanoparticles/ P(MMA-co-HEMA) composites

1.4. Expected results

1.4.1. To obtain the most suitable condition for preparation ZnO nanoparticles

1.4.2. To obtain ZnO nanoparticles/ P(MMA-co-HEMA) composite film

Chapter 2

Theory and Literature Review

2.1 Nanoparticle [1]

Nanoparticle (or nanopowder or nanocluster or nanocrystal) is a microscopic particle with at least one dimension less than 100 nm. Nanoparticle research is currently an area of intense scientific research, due to a wide variety of potential applications in biomedical, optical, and electronic fields.

2.1.1. Classification [2]

Generally there are different approaches for a classification of nanoparticle.

- Classification by dimension
  - 3 dimension: Paritcles, quantumdot, hollow spheres, and etc.
  - 2 dimension: Tubes, fibers, wires, platelets, and etc.
  - 1 dimension: Films, coatings, multilayer, and etc.
- Classification by Phase composition
  - Single-phase solids: Crystalline, amorphous particles and layers, and etc.
  - Multi-phase solids: Matrix composites, coated particles, and etc.
  - Multi-phase systems: Colloids, aerogels, ferrofluids, and etc.
- Classification by manufacturing process
  - Gas phase reaction: Flame synthesis, condensation, CVD, and etc.
  - Liquid phase reaction: Sol-gel, precipitation, hydrothermal processing, and etc.
  - Mechanical Procedure: Ball milling, plastic deformation, and etc.

2.1.2 Characterization [1, 3]

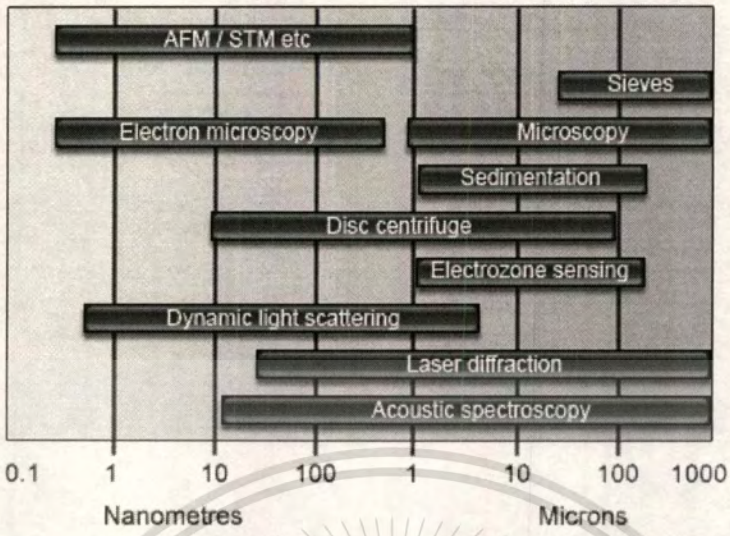


Figure 2.1 Techniques for measuring the size of nanoparticles

Nanoparticle characterization is necessary to establish understanding and control of nanoparticle synthesis and applications. Characterization is done by using a variety of different techniques, mainly drawn from materials science. Common techniques are electron microscopy [TEM, SEM], atomic force microscopy [AFM], dynamic light scattering [DLS], x-ray photoelectron spectroscopy [XPS], powder x-ray diffractometry [XRD], and Fourier transform infrared spectroscopy [FTIR].

2.1.3 Applications [4]

Analytics

Improve sensor properties and instruments for analysis, nanoanalysis using nano-chemical sensors.

Optics

Ultra high precision processing of optical components, lithography for producing ever smaller electronic components, optical components with function surfaces (spheres) for data projectors, cameras, spectacle lenses, and scanners.

Material sciences

Ultrafine nanolayers, nanocrystals, nanostructures for microelectronic components, fuel cells, scratch-proof surfaces, water and dirt repellent surfaces; antireflective properties, photoactive radiation.

Biotechnology and medicine

Use of nanoparticles in the fight against tumours, nanostructured and functionalised surfaces and membranes, improved diagnosis and more targeted use of active agents; neuro-active implants.

2.2 Zinc Oxide [1, 5]

Zinc oxide is a chemical compound with the formula ZnO. It is nearly insoluble in water but soluble in acids and alkalis. It occurs as white hexagonal crystals or a white powder commonly known as zinc white.

Figure 2.2 Zinc oxide structure

In the nature,zinc oxide was called "zincite". Zincite is a rare locality mineral. Its color is orange-yellow to deep red or brown. The structure of zincite consists of tetrahedrons of ZnO_4. The tetrahedrons in zincite all are oriented in one direction and produce the hexagonal symmetry.

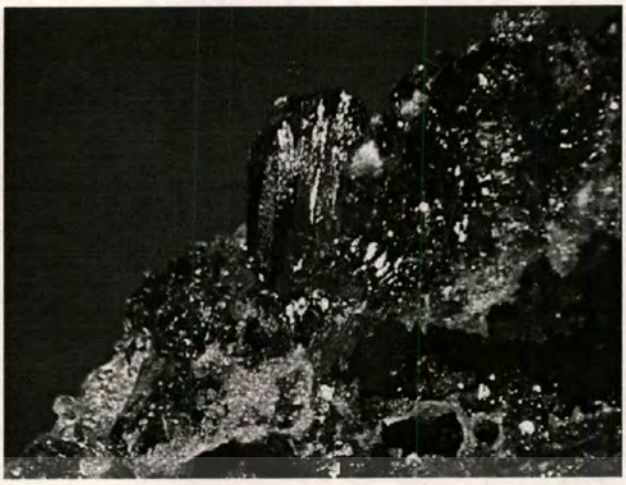


Figure 2.3 Mineral Zincite

2.2.1 Production method [1]

The production of zinc oxide has 2 main processes.

1. Indirect process (French process)

Metallic zinc is melted in a graphite crucible and vaporized above 907 °C. Zinc vapor instantaneously reacts with the oxygen in the air to give ZnO, accompanied by a drop in its temperature and bright luminescence. ZnO particles are transported into a cooling duct and collected in a bag house.

A typical French process, ZnO normally consists of agglomerated ZnO particles with an average size of 0.1 micron to a few microns. By tonnage, most of the world's ZnO is manufactured via French process and major applications involve industries related to rubber, varistors, suncreens, paints, healthcare, and poultry nutrients. Recent developments involve acicular nanostructures (rods, wires, tripods, tetrapods, plates) synthesized using a modified French process known as catalyst-free combust-oxidized mesh (CFCOM) process. Acicular nanostructures usually have micron-length nanorods with nanometric diameters (below 100 nm).

2. Direct process (American process)

In this process, zinc ores or roasted sulfide concentrates are mixed with coal. In a reduction furnace, ore is reduced to metallic zinc and the vaporized zinc is allowed to react with oxygen to form ZnO.

2.2.2 Application of zinc oxide [1, 6]

Rubber

ZnO increases the number of the many optical, physical and chemical properties. It is the most effective activator to speed up the rate of cure with the new accelerators.

Heavy-duty pneumatic tires carry high loadings of ZnO for heat conductivity as well as reinforcement since heat-buildup is critical at their higher operating speeds compared with their solid-rubber counterparts.

Plastics

Zinc compounds can provide a variety of properties in the plastics field. Heat resistance and mechanical strength are imparted to acrylic composites by ZnO.

ZnO contributes to the formation and cure of epoxide resin. Addition of ZnO to epoxy resins cured with aliphatic polyamines imparts higher tensile strength and water resistance. ZnO imparts fire-resistant properties to nylon fibers and moldings. ZnO is also useful in the preparation of nylon polymers and in increasing their resistance. The formation of polyesters in the presence of ZnO imparts higher viscosity and other improvements. ZnO reacts with unsaturated polyesters to form higher viscosity and a thixotropic body. The dyeability of polyester fibers is improved by ZnO. ZnO mixtures stabilize polyethylene against aging and ultraviolet radiation. ZnO increases the transparency of poly (chlorofluoroethylene) molding resin. Polyolefin's are improved in color, tensile strength, and vulcanization properties by addition of ZnO. Thermal stabilization of PVC is effected by ZnO. Antistatic, fungistatic and emulsion stability are additional properties imparted to vinyl polymers by ZnO. Applications in development for ZnO-stabilized polypropylene and high-density polyethylene include safety helmets, stadium seating, insulation, pallets, bags, fiber and filament, agricultural and recreational equipment.

Ceramics

The properties imparted by ZnO to some of the newer applications are as electronic glass, low-melting glass for metal-to-glass seals, thermistors for use as lighting arresters and devitrified glasses of low thermal expansion. ZnO imparts a unique combination of properties when used in glass. ZnO reduces the coefficient of thermal expansion, imparts high brilliance and luster and high stability against deformation under stress. As a replacement flux for the more soluble constituents, it provides a viscosity curve of lower slope. The specific heat is decreased and the conductivity increased by the substitution of ZnO for BaO and PbO.

Cosmetics

The optical and biochemical properties of ZnO and its derivatives impart special features to a variety of cosmetic preparations for care of the hair and skin. In powders and creams it protects the skin by absorbing the ultraviolet sunburn rays; in burn ointments it aids healing. Simple salts of zinc provide astringent and skin-conditioning properties to creams, while more complex salts furnish fungistatic properties which contribute to the effectiveness of deodorants, soaps, and antidandruff preparations.

Paints

ZnO in organic coatings provides a broad spectrum of properties: optical, chemical, biochemical and physical. Over the past century the paint industry, in its constant development of improved products, has utilized various aspects of those properties to high degree. Manufacturers discovered that they could produce coatings of brushing consistency and good suspension properties by incorporation of ZnO into their pastes. Painters noted that they furnished better hiding power, whiteness, cleaner tints, tint retention, and durability as well as nondarkening in the presence of sulfur fumes. French-process ZnO has been proved superior to American-process type in fungus resistance and less sulfide staining.

Medical applications

ZnO lozenges are a popular over-the-counter cold remedy, but numerous studies have failed to demonstrate any significant effect.[1] ZnO in a mixture with about 0.5% iron(III) oxide (Fe_2O_3) is called calamine and is used in calamine lotion. There are also two minerals, zincite and hemimorphite, which have been called calamine historically. When mixed with eugenol, ZnO eugenol forms which has restorative and prosthodontic applications in dentistry.

Zinc peroxide, ZnO_2 .½ H_2O, is a white to yellow powder that is used in antiseptic ointments. And other application of ZnO such as biochemical activity,dielectric strength, heat stabilization, light stabilization,foods and food-packaging materials etc.

2.2.3. Application of ZnO nanoparticle [7]

Zinc oxide nanomaterials are presented in emphasis this time:

Compared with ordinary ZnO (particle size ≥ 100 nm), on the basis of two kinds of property from nanomaterial (surface effect, small size effect, macroscopical quanta tunnel effect) and ZnO (virulence, unflavour, achromaticity), the ZnO nanoparticles has the following characteristic and predominance:

1. Sunscreen and anti-bacteria in cosmetics

ZnO nanoparticles have excellent screen effect to UV-A and UV-B; under the condition of irradiation of sunlight, water and air, the ZnO nanoparticles has the effect of killing most bacteria by chemical reaction.

2. Deodorant, antimicrobial, anti-ultraviolet in textile

3. Self- cleaning in ceramics

When ZnO nanoparticles is added into ceramics, sinter temperature can be down by 200-400, glabrous degree will be heightened, production procedure will be decreased, energy consumption will be reduced, in the meanwhile the ceramics has antimicrobial and deodorant function.

4. Excellent synthetical performance in rubber

ZnO nanoparticles is a kind of important material for high-speed and wearble rubber products, it also can help rubber have the excellence of anti-aging, anti-attrition sparkle, expanding the use life, decreasing the dosage by 30-70%

5. Anti-aging in paint, coating, plastic.

6. Other application: Gas sensor, image track record material, piezoelectricity material, fluorescenter, capacitor etc.

2.3 Poly(2-hydroxyethyl methacrylate) (PHEMA)

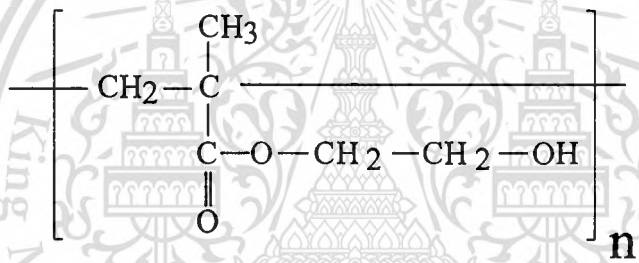


Figure 2.4 PHEMA structure

Poly(2-hydroxyethyl methacrylate) (PHEMA) is a hydrosoluble monomer, which can polymerize at low temperatures (from -20°C to +10 ° C). It can be used to prepare various hydrogels, to immobilize proteins or cells. Boiling point of PHEMA is 205 °C. It is widely used in light curing polymer system and high performance coatings for lasting high gloss against cratching, solvents and weathering. It is used in paint resins and emulsions, binders for textiles and paper. It is used as an adhesion promoter for metal coatings. [12, 14]

2.4 Poly(methyl methacrylate) (PMMA)

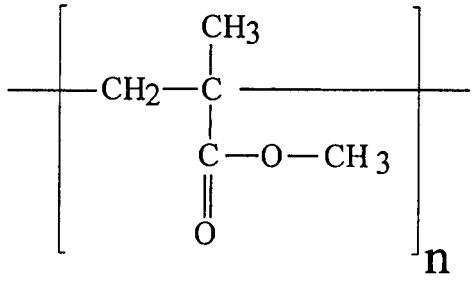


Figure 2.5 PMMA structure

Poly(methyl methacrylate)(PMMA) or poly(methyl 2-methylpropanoate) is the synthetic polymer of methyl methacrylate. This thermoplastic, transparent and is commonly called acrylic glass or simply acrylic. The material was developed in 1928 in various laboratories and was brought to market in 1933 by Rohm and Hass Company. It is widely used in Lenses, light covers, glazing (particularly in aircraft), light pipes, meter covers, bathroom fittings, outdoor signs, skylights, baths, and toys. Acrylic film is laminated over ABS sheet to provide UV protection. [13]

2.5. Literature review

Naofumi Uekawa, Shunsuke Iahii, Takashi Kojima, Kazuyuki Kakegawa, concerned in obtained Zinc Oxide (ZnO) nanoparitcles by heating $Zn(OH)_2$ in a diol solution. When ethylene glycol, 1,3-propanediol and 1,4-butanediol were used for the heat treatment of $Zn(OH)_2$ by heating at more than 308 K. It was found ZnO nanoparticles with an average diameter less than 20 nm were obtained by heating $Zn(OH)_2$ in a diol solution at more than 308K. In particular, when ethylene glycol was used for the heat treatment, the stable sols with the dispersion of the ZnO nanoparticles were obtained. Furthermore, when the heating temperature was 308 K, the spherical secondary particles consisting of ZnO primary nanoparticles were obtained. The porosity of the spherical secondary particles can be controlled by the diol solution used for the heat treatment of $Zn(OH)_2$. The mesoporous spherical aggregated morphology was characteristic of and has valuable morphology for nanostructured materials. [15]

C. Hariharan [2006], concerned in the photodegradation of organic contaminants using the fluorescence emission characteristics of ZnO nanoparticles (ZnO-nano) in aqueous solutions. This is accomplished by preparing nanocrystalline ZnO; the presence of organic contaminants in water is readily detected from the quenching of fluorescence observed from ZnO semiconductor films. Photolysis of ZnO thin films immersed into an aqueous system containing organic contaminants results in the degradation of the contaminants. It was found that the suitability of ZnO nanoparticles (both as suspension and thin films) was prepared using a non-aqueous route and different experimental conditions have been used to tailor the performance of ZnO-nano as a photocatalyst. This study confirms that use of ZnO nanoparticles as a catalytic system is comparable to and sometimes even better than the conventional photocatalyst of choice-TiO_2-Degussa. [16]

Changle Wu, Xueliand Qiao, Jianguo Chen, Hongshui Wand, Fatang Tan, Shitoa Li.[2006], concerned in the nanocrystalline ZnO particles were prepared by a novel aqueous route from zinc nitrate hexahydrate without any requirement of calcinations step at high temperature. It was found that successfully fabricated ZnO nanoparticles using a simple chemical approach. This method produced a large quantity of ZnO nanocrystals (yield is about 90%) at relatively high purity and very low cost. The morphology of ZnO nanoparticles seems to change from rod-like to short prism-like with increasing reaction temperature. Moreover the ZnO nanoparticles have a very strong photoluminescence band at ultraviolet wavelength range. The nanoparticles might have many potential applications in luminescent, electrical devices. A possible formation mechanism has also been proposed. [17]

Ruoyu Hong, Tingting Pan, Jianzhong Qian, Hongzhong Li [2006], concerned in the prepared ZnO precursor by direct precipitation from zinc acetate and ammonium carbonate. ZnO nanoparticles were synthesized by calcinations of the precursor at 450° C for 3 h and the calcinations after the heterogeneous azeotropic distillation of the precursor, respectively. The systhesized ZnO nanoparticles were characterized by FT-Ir. XRD and TEM. It is concluded that the heterogeneous azeotropic distillation of the precursor effectively reduced the formation of hard agglomerates. The surface modification of synthesized ZnO Nanoparticles was conducted by capping with oleic acid, and the existence of organic layer can be confirmed by the Ft-Ir spectra. The lipophilic degree of surface modified ZnO nanoparticles was measured. The ZnO nanoparticle surface was also modified by SiO_2 coating. [18]

Chapter 3

Experimental

3.1. Materials

3.1.1. Ammonium hydroxide (NH_4OH) 30% v/v ,CARLO ERBA, Analytical grade

3.1.2. Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), CARLO ERBA, Analytical grade

3.1.3. Ethylene glycol (C_2H_6OH), CARLO ERBA, Analytical grade

3.1.4. Poly(vinyl alcohol)

3.1.5. Ethanol (C_2H_5OH), CARLO ERBA, Analytical grade

3.1.6. 2-Hydroxy ethyl methacrylate monomer (HEMA)

3.1.7. Methyl methacrylate monomer (MMA) ($C_5H_8O_2$, Molecular weight = 100.12 Density = 0.963 g/ml), Aldrich, Analytical grade

3.1.8. Benzoyl peroxide (BPO) , CARLO ERBA, Analytical grade

3.1.9. N, N-Dimethyl-4-toluidine (DMT)

3.1.10. Sodium hydroxide (NaOH) , LAB scan, Analytical grade

3.1.11. Toluene (C_7H_8), LAB scan, Analytical grade

3.1.12. Anhydrous sodiumsulphate (Na_2SO_4), CARLO ERBA, Analytical grade

3.1.13. Sodium chloride (NaCl), CARLO ERBA, Analytical grade

3.2. Apparatus

3.2.1. Beaker

3.2.2. Graduate Cylinder

3.2.3. Stir rod

3.2.4. Hot plate

3.2.5. Closed- glass vessel

3.2.6. Watch glass

3.2.7. Volumetric flask

3.2.8. Erlenmeyer flask

3.2.9. Dropper

3.2.10. Spoon

3.2.11. Test tube

3.2.12. Separatory funnel

3.2.13. Mortar and pestle

3.2.14. Transparent PET film

3.2.15. Balance, TC-254, Denver Instrument

3.2.16. Centrifuge machine, Centaur 2, Sanyo

3.2.17. X-ray diffractometer (XRD), Bruker AG, D8 Advance

3.2.18. X-ray fluorescence spectroscometer (XRF), SRS 3400, Bruker AG

3.2.19. Scanning Electron microscope (SEM),LEO ,LEO 1455 VP

3.2.20. Ultrasonic, Cole-Parmer, 8892

3.2.21. UV/Visible/Near infrared spectrometer (UV/VIS/NIR), He λ ions α (Double beam), UV/Visible Thermo Electron Corporation

3.3 *Preparation of the ZnO nanoparticles*

3.3.1 An aqueous solution of 0.1 mol/l NH_4OH was mixed with 0.1 mol/l of $Zn(NO_3)\cdot 6H_2O$ for 1 hr.

3.3.2 The precipitate was separated by centrifugation at 3000 rpm for 5 min.

3.3.3 The $Zn(OH)_2$ precipitate was dispersed as sol in 100 ml of ethylene glycol

3.3.4 Solution mixture was heated at 75°C for 24 hr. in closed glass vessels

3.3.5 100 ml of 0.2 mol/l of NH_4OH was added into the treated sol

3.3.6 The solid particles were separated from sol by centrifugation at 3000 rpm for 5 min.

3.3.7 The treated particles were dried at 75°C in an oven

3.3.8 The reactions were repeated by using various conditions, i.e.,

- *Varying concentration of $Zn(NO_3)_2\cdot 6H_2O$ and NH_4OH*

Table 3.1 Varying the concentration of $Zn(NO_3)_2\cdot 6H_2O$ and NH_4OH

No.	Concentration of $Zn(NO_3)_2.6H_2O$ and NH_3 (mol/l)	Reaction Temperature(°C)	Disperse Media	Volume of dispersion media (ml)
1	0.1	75	EG	100
2	0.5	75	EG	100
3	1.0	75	EG	100
4	0.1	75	PVA	30
5	0.5	75	PVA	30
6	1.0	75	PVA	30

- *Varying the reaction temperature*

Table 3.2 Varying the reaction temperature

No.	Concentration of $Zn(NO_3)_2.6H_2O$ and NH_3 (mol/l)	Reaction Temperature(°C)	Disperse Media	Volume of dispersion media (ml)
1	0.1	75	EG	100
2	0.1	95	EG	100
3	0.1	105	EG	100
4	0.1	125	EG	100
5	1.0	75	EG	100
6	1.0	95	EG	100
7	1.0	105	EG	100

- *Varying the dispersion media*

Table 3.3 Varying the dispersion media

No.	Concentration of $Zn(NO_3)_2.6H_2O$ and NH_3 (mol/l)	Reaction Temperature(°C)	Disperse Media	Volume of dispersion media (ml)
1	0.1	75	EG	30
2	0.1	75	PVA	30

- *Varying treatments in oven and ultrasonic*

Table 3.4 Varying treatments in oven and ultrasonic

No.	Concentration of $Zn(NO_3)_2.6H_2O$ and NH_3 (mol/l)	Reaction Temperature(°C)	Disperse Media	Volume of dispersion media (ml)	Treatment in
1	0.1	75	EG	50	Oven 24 hr.
3	0.1	Room Temperature	EG	50	Ultrasonic 2 hr.

- Varying the volume of dispersion media

Table 3.5 Varying the volume of dispersion media

No.	Concentration of $Zn(NO_3)_2.6H_2O$ and NH_3 (mol/l)	Reaction Temperature(°C)	Disperse Media	Volume of dispersion media (ml)
1	0.1	75	EG	100
2	0.1	75	EG	50
3	0.1	75	EG	30
4	0.5	75	EG	100
5	0.5	75	EG	50
6	1.0	75	EG	100
7	1.0	75	EG	50

3.4. Characterization of ZnO nanoparticles

3.4.1. X-ray Diffractometer (XRD)

X-ray diffraction (XRD) pattern was recorded using Cu Kα radiation (Cu Kα = 154 nm) at a voltage of 30 kV., and a current of 30 mA. The scanning started from 20 ° to 60 ° and step size was 0.04 ° with scanning speed of 1 second per step.

3.4.2. Scanning electron microscope (SEM)

The sample was mounted on the sample holder and then sputtered with gold. The microstructure of the sample surfaces was investigated by SEM.

3.5 Extraction inhibitor from Methymethacylate Monomer (MMA)

1. 10 ml of MMA and 10% NaOH solution were mixed well in separatory funnel
2. The mixture was left until complete separation into 2 phases
3. The NaOH phase was removed (bottom phase)
4. Another 10 ml of 10% NaOH solution was added into separatory funnel and 1^{st}-3^{rd} step was repeated
5. Deinhibitor – MMA was washed with distilled water for several times until litmus paper had no change from red to blue
6. 10 ml of saturated NaCl solution was added and extracted the lower phase for twice times
7. Anhydrous sodium sulfate was added into MMA phase to remove water
8. The solid phase of anhydrous sodium sulfate was separated by gravity filtration and the liquid phase (fresh MMA) was collected and kept in the refrigerator

3.6 Preparation of ZnO nanoparticles/P(MMA-co-HEMA) composite film

3.6.1 Ingredient of polymer film

The composite film was prepared by the mixtures of two phases i.e., solid phase and liquid phase. The ingredients were as follows;

- Liquid phase
    1. Methy methacrylate monomer (MMA) (inhibitor –free)
    2. N,N- dimethy-4-toludiene (DMT)
    3. 2-Hydroxy ethyl methacrylate monomer (HEMA)
- Solid phase
    1. ZnO nanoparticles
    2. Benzoyl peroxide (BPO) (1% mole of monomer)

3.6.2 Preparation of film

1. Weight the starting materials as shown in Table 3.6

Table 3.6 Ingredient of film

Formula	Ingredient MMA:HEMA	MMA (g)	BPO (3% mol)	HEMA (g)	ZnO (g)	DMT (drop)
1	5:5	2.5	0.3211	2.5	-	10
2	6:4	3	0.3295	2	-	10
3	7:3	3.5	0.3379	1.5	-	10
4	8:2	4	0.3462	1	-	10
5	5:5	2.5	0.3211	2.5	0.025	10
6	6:4	3	0.3295	2	0.025	10
7	7:3	3.5	0.3379	1.5	0.025	10
8	8:2	4	0.3462	1	0.025	10

2. ZnO nanoparticles were dispersed in HEMA in ultrasonic for 30 min.
3. 3 mol % of BPO was dissolved in MMA
4. The solutions from step 2 and 3 were mixed by using magnetic stirrer
5. The mixture was casted on transparent PET film and then heat at 85 °C in oven for 3 hr.
6. Characterize the ZnO/P(MMA-co-HEMA) film by XRD, XRF, and SEM
7. Ultraviolet – Visible spectrometer (UV-Vis, Thermo electron) Scan range is 190-1100 for investigate absorbance and transmittance

3.7. Characterization of ZnO nanoparticles/P(MMA-co-HEMA) film

1. X-ray fluorescence (XRF)

The samples (0.5 g.) were mixed with boric acid (4.5 g.), ground by bench mill (A 1, Rocklabs) for 1 mins. and then compress to pellet by uniaxial pressing. The chemical composition of the samples was determined by XRF. The XRF method is widely used to measure the elemental composition of materials. Since this method is fast and non-destructive to the sample. XRF is an elemental analysis technique with unique capabilities including highly accurate determinations for major elements and a board elemental survey of the sample composition without standard.

2. X-ray diffraction (XRD)

X-ray diffraction (XRD) pattern was recorded using Cu Kα radiation (Cu Kα= 154 nm) at a voltage of 30kV and a current of 30 mA. The scanning start 20 degree to 60 degree and step size is 0.04 degree by 1 second per step.

3. Scanning electron microscope (SEM)

The sample was mounted on the sample holder and then sputtered with gold. The microstructure of the sample surfaces was investigated by SEM.

Chapter 4

Results and Discussion

4.1 Preparation of ZnO nanoparticles

ZnO nanoparticles were synthesized from $Zn(NO_3)\cdot 6H_2O$ and NH_4OH using various conditions, i.e.

- Concentration of starting materials: 0.1, 0.5, and 1.0 m/l
- Hydrothermal treatment conditions:
  - Temperature: 75, 95, 105, 125 °C
  - Dispersion media: EG and PVA
  - Volume of dispersion media: 30, 50, and 100 ml
  - Treatment method: Sonication and oven

The synthesized ZnO nanoparticles were characterized by XRD and SEM. The effects of preparation conditions were investigated as follows:

A. Effect of concentration of starting materials

- EG Media

Figure 4.1 (a) shows the XRD patterns of varying concentration of starting materials while the temperature, volume of dispersion media, and type of dispersion media were fixed as 75° C, 100 ml and EG, respectively.

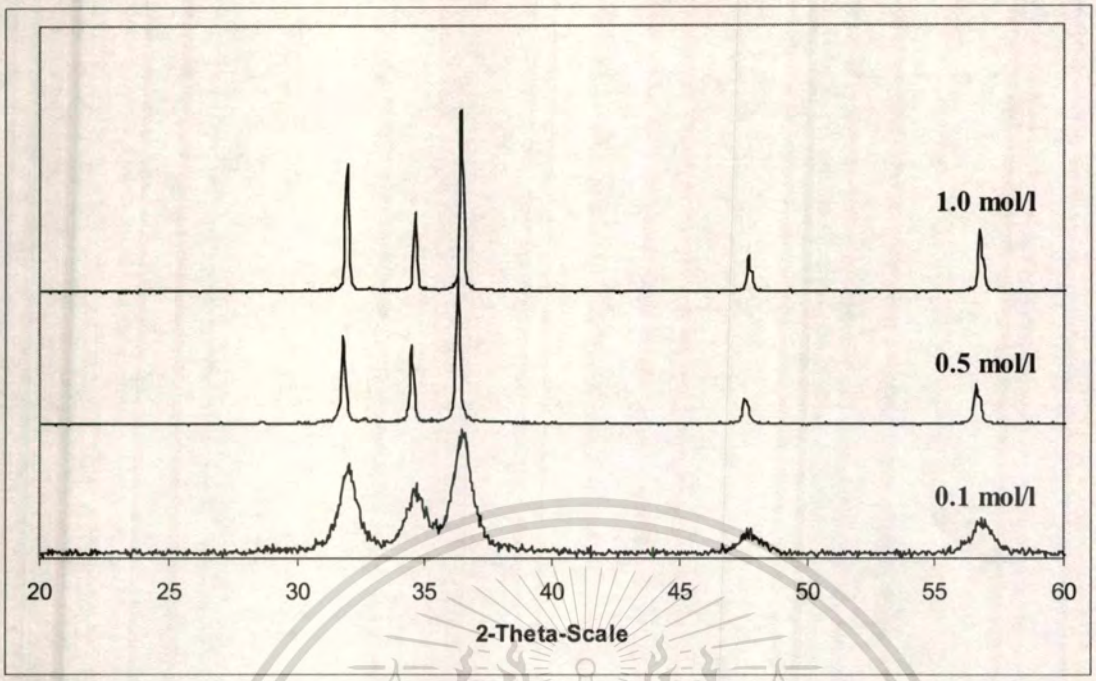
The XRD patterns of all conditions showed the peaks at around 2θ = 31.8°, 34.5°, 36.4°, 47.7°, 56.8°, corresponding to ZnO. The broad crystalline peaks with low peak resolution were obtained when the starting concentration was 0.1mol/l, indicating the agglomerated nanocrystallite size of ZnO. The sharp and good resolution peaks were obtained when using higher concentrations of starting materials. This result suggested that the ZnO synthesized from 0.1 mol/l starting materials had smaller particle size than those from 0.5 and 1.0 mol/l starting concentrations.

Figure 4.1 (b) shows the SEM images of the ZnO nanoparticles synthesized from various concentrations of starting materials. It was clearly illustrated that ZnO particles obtained from the concentration of 0.1 mol/l was agglomerated sphere particles. The higher concentration of starting materials, the larger ZnO particles were obtained. In addition, the ZnO morphology would be changed to rod-type when the concentration of starting materials was increased to 1.0 mol/l

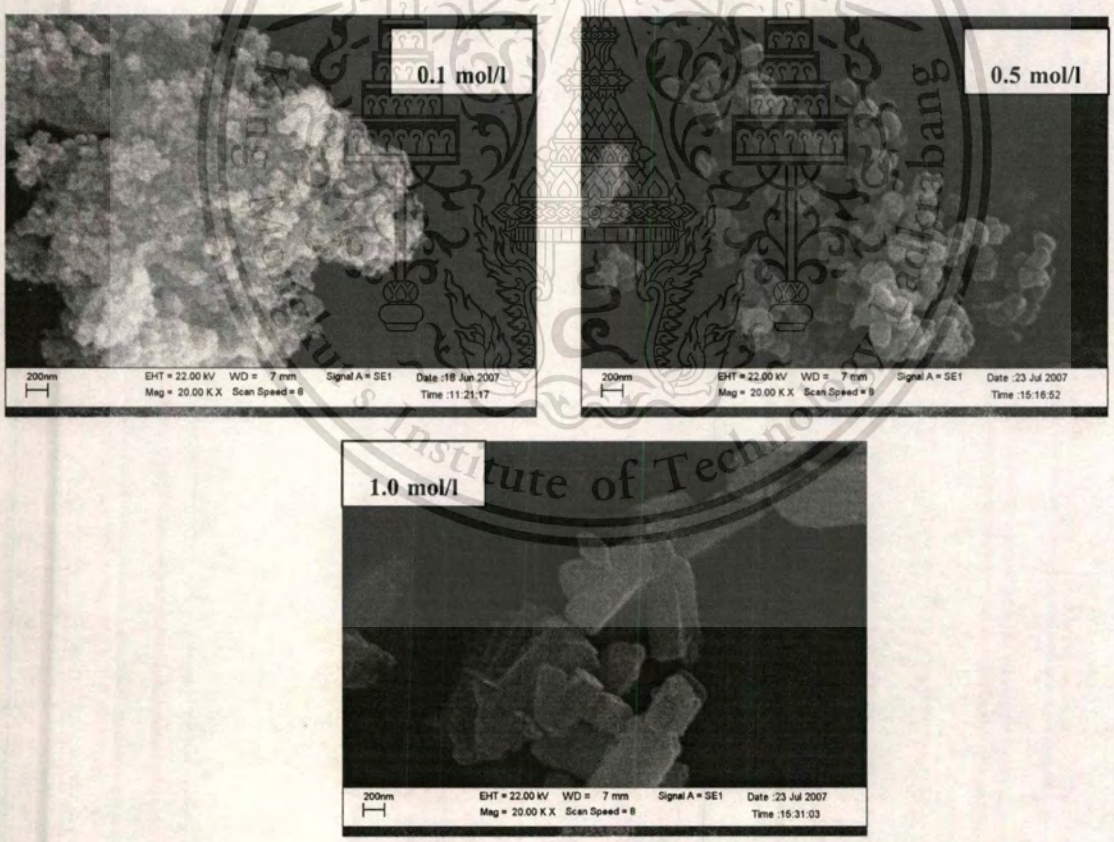
- PVA Media

Figure 4.2 showed the XRD patterns and SEM micrographs of ZnO synthesized from various concentrations of starting materials and then treated in some of PVA solution at 75°C. All crystalline peaks in the XRD patterns can be assigned to ZnO. The sharp and good resolution peaks were obtained in all conditions.

From the SEM micrographs, the rod-type ZnO particles were obtained in all conditions when using PVA media.

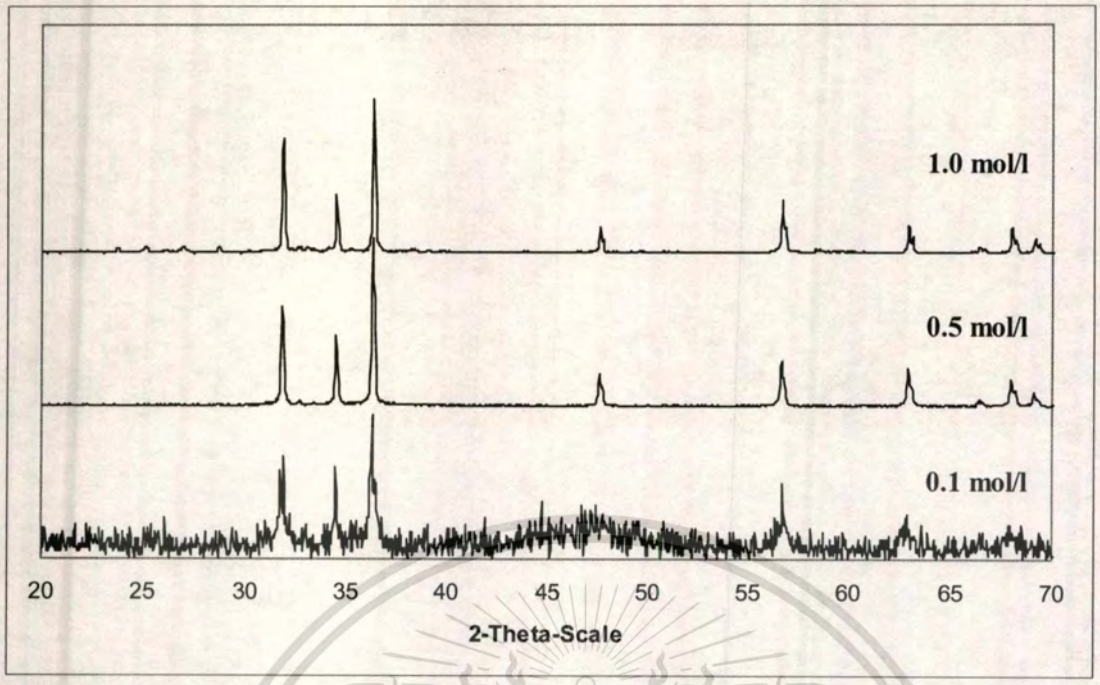


(a)

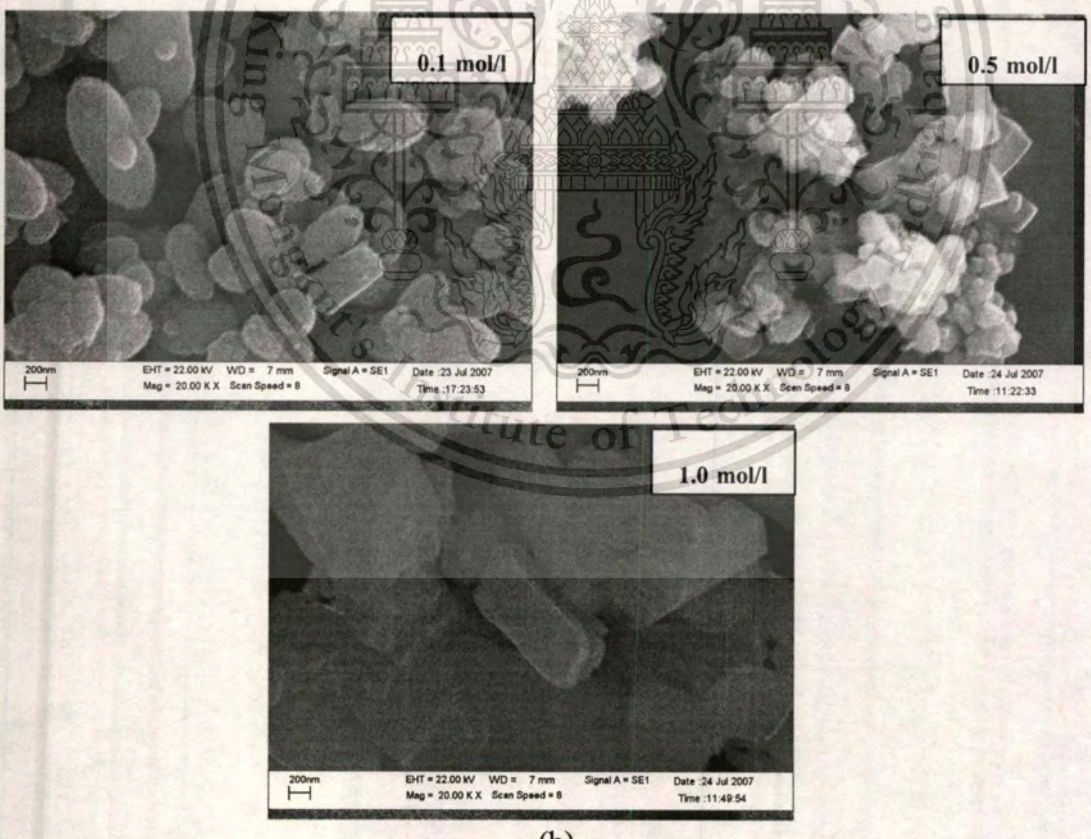


(b)

Figure 4.1 (a) XRD patterns and (b) SEM micrographs of the ZnO nanoparticles at varying concentration of starting materials in EG



(a)



(b)

Figure 4.2 (a) XRD patterns and (b) SEM micrographs of ZnO nanoparticles at varying concentration of starting materials in PVA

B. Effect of hydrothermal treatment temperature

- 0.1 mol/l of starting materials

Figure 4.3 shows the XRD patterns and SEM micrographs of ZnO particles synthesized from 0.1 mol/l starting materials and hydrothermal treated in 100 ml of EG at various temperatures.

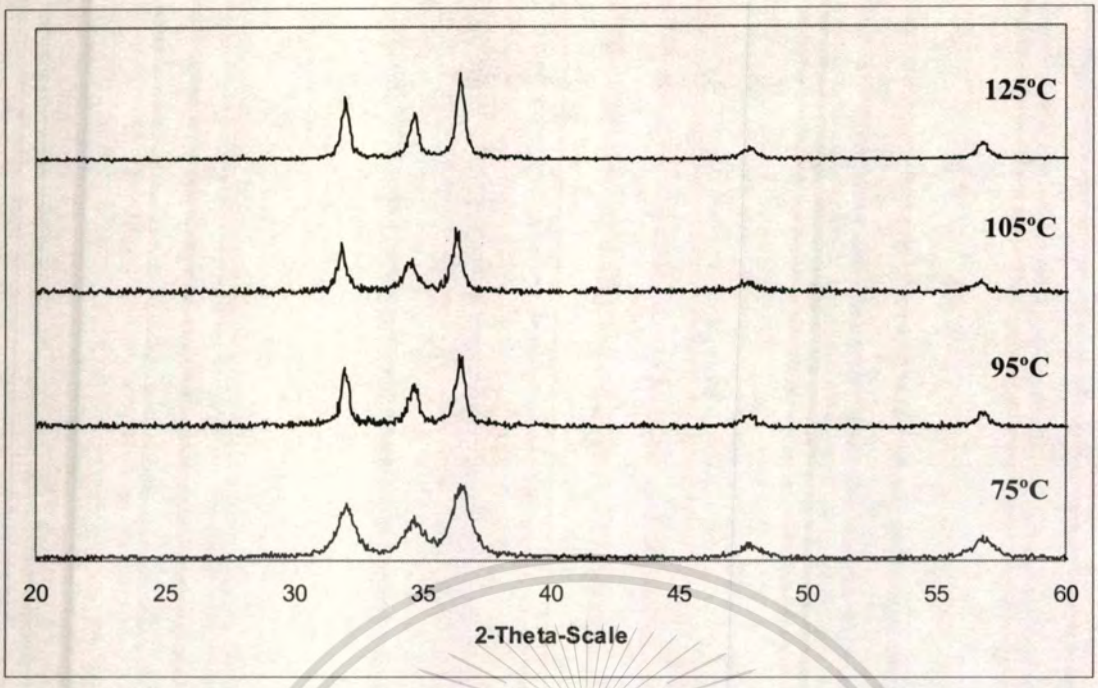
The higher the treatment temperature, the sharper peak and better peak resolution were obtained, indicating the larger particle size of ZnO.

In figure 4.3(b), the agglomeration of nano ZnO particles was obtained in all conditions. The size of agglomerates increased with increasing of treatment temperature.

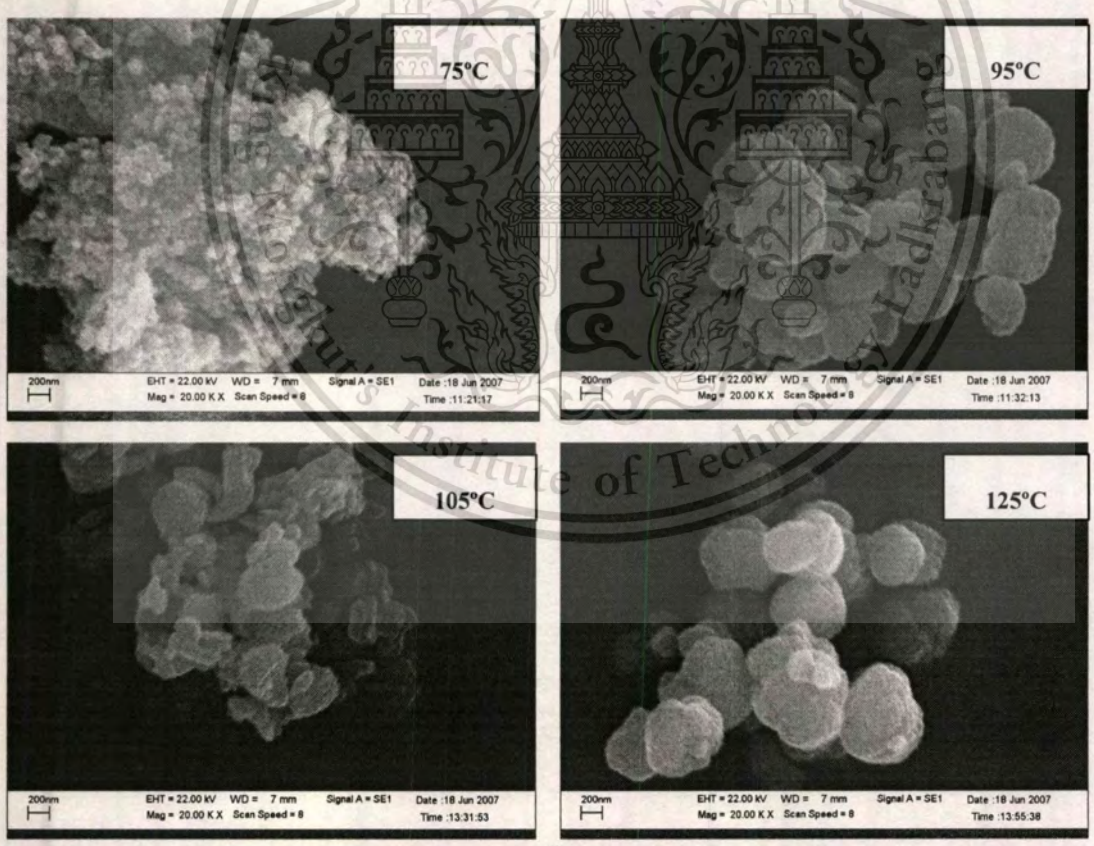
- 1.0 mol/l of starting material

Figure 4.4 shows the XRD patterns and SEM micrographs of ZnO particles synthesized from 1.0 mol/l starting materials and hydrothermal treated in 100 ml of EG at various temperatures.

All treatment temperatures show the sharp peaks of ZnO. The ZnO nanorods were observed in the SEM micrographs of all conditions. The higher the treatment temperature, the larger rods were obtained.

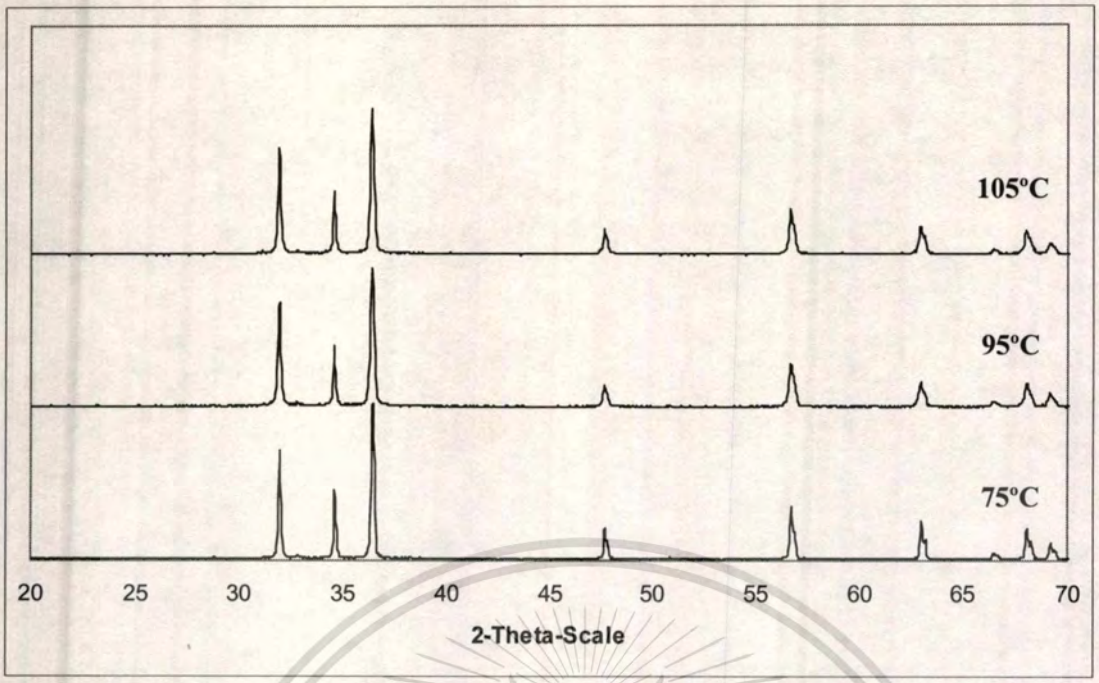


(a)

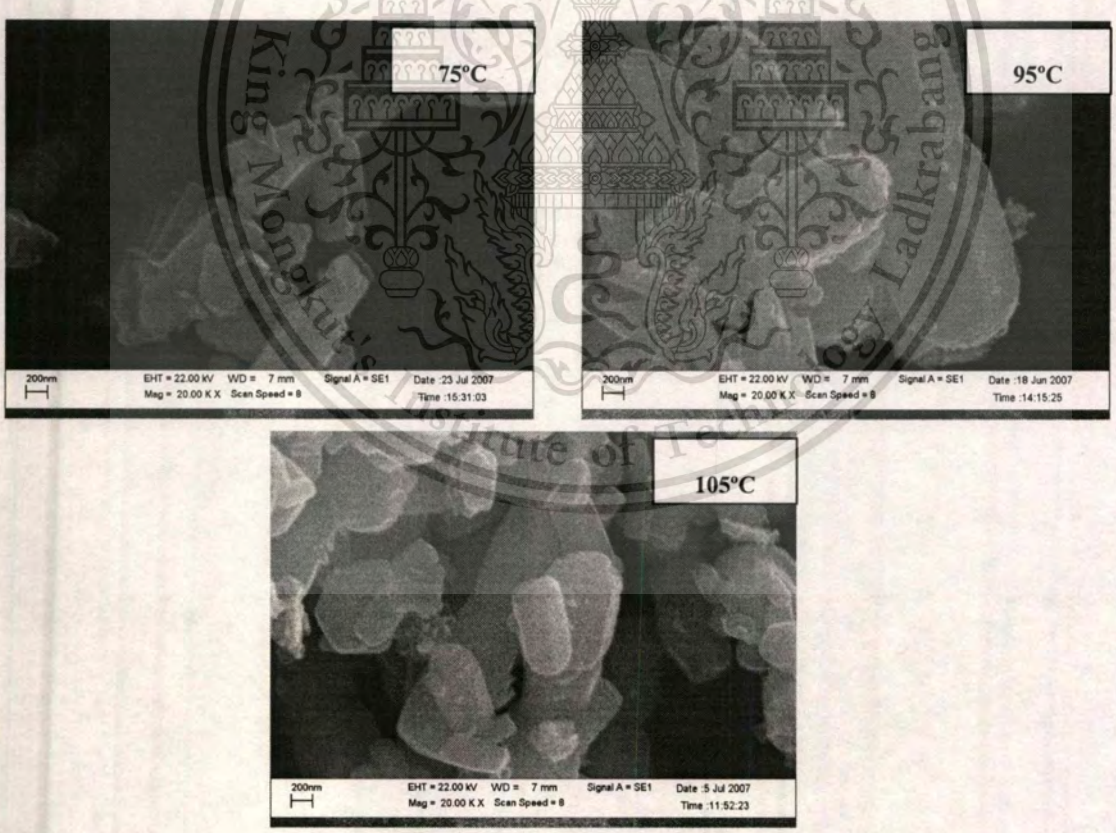


(b)

Figure 4.3 (a) XRD patterns and (b) SEM micrographs of ZnO nanoparticles at varying temperature of 0.1 mol/l starting materials



(a)



(b)

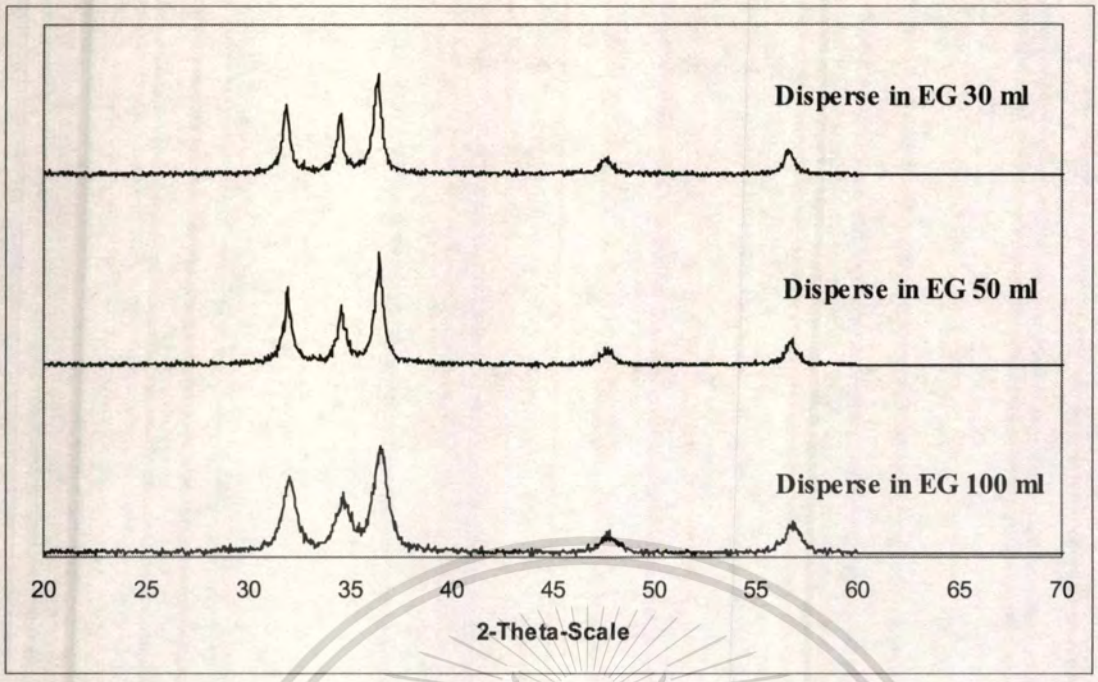
Figure 4.4 (a) XRD patterns and (b) SEM micrographs of ZnO nanoparticles at varying temperature of 1.0 mol/l starting materials

C. Effect of the volume of dispersion media

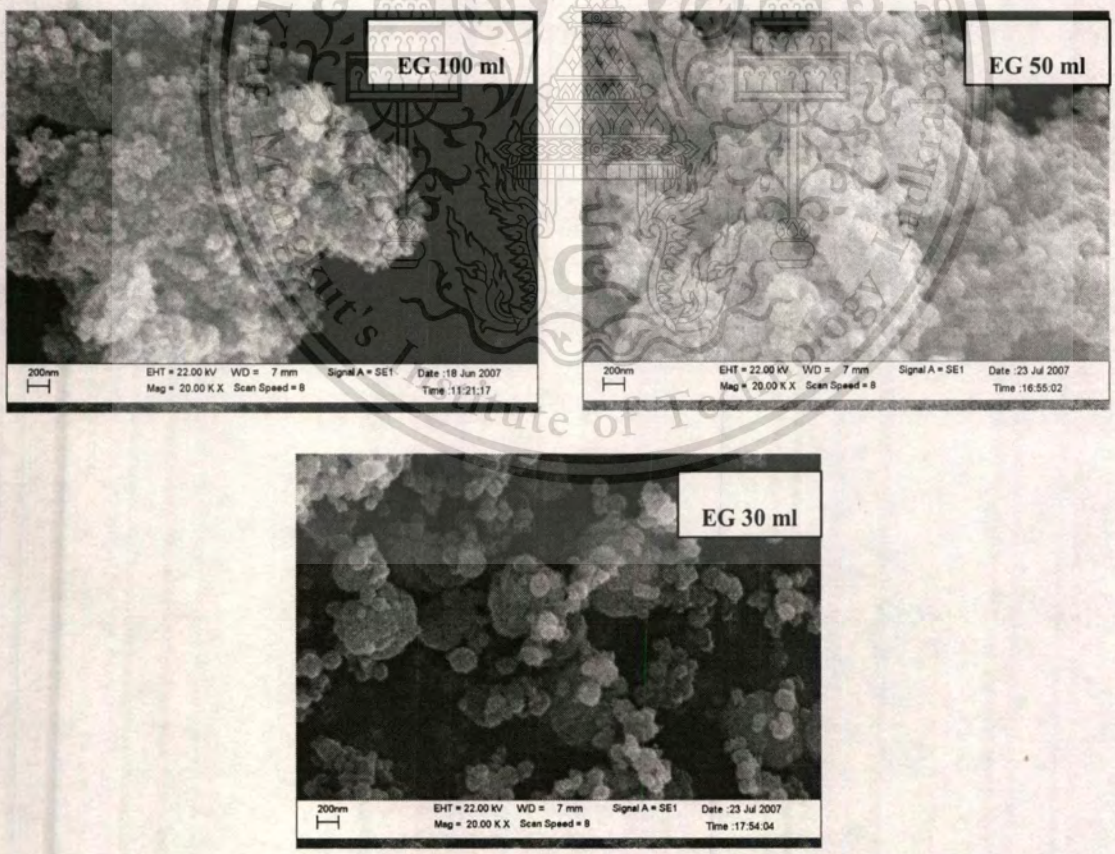
Figure 4.5 shows the XRD patterns and SEM micrographs of ZnO particles synthesized from 0.1 mol/l starting materials and hydrothermal treated as 75°C in EG at various volumes of dispersion media.

From the XRD patterns, the higher volume of dispersion media, the broader crystalline ZnO peaks and the lower peak resolution were obtained.

In figure 4.5(b), the agglomeration of nano ZnO particles was obtained in all conditions. The size of agglomerates decreased with increasing of volume of dispersion media.



(a)



(b)

Figure 4.5 (a) XRD patterns and (b) SEM micrographs of ZnO nanoparticles at varying volume of dispersion media of 0.1 mol/l starting materials

D. Effect of treatments in oven and ultrasonic

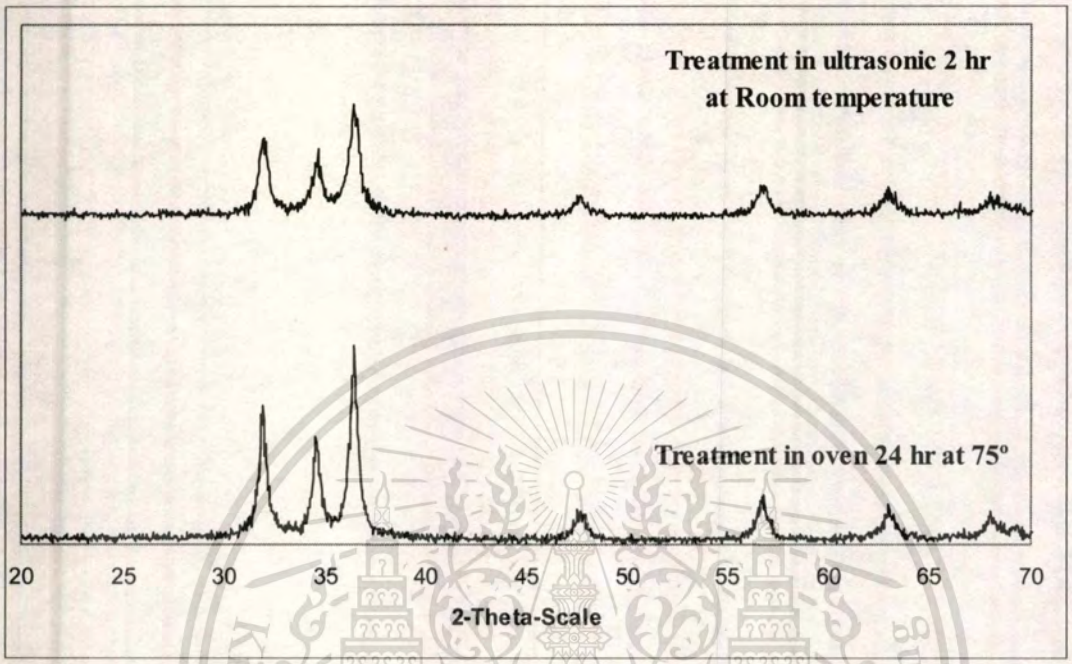
Figure 4.6 shows the XRD patterns and SEM micrographs of ZnO particles treated in 100 ml of EG at 75°C in an oven for 24 hr. and at room temperature in ultrasonic for 2 hr. Both conditions show the broad ZnO peaks with low peak resolution, indicating the formation of ZnO nanoparticles.

The agglomeration of ZnO nanoparticles was observed in the SEM micrographs of both treatment conditions, corroborating with the XRD patterns. These results indicated that the ultrasonic treatment could generate the ZnO nanoparticles although the treatment was performed at room temperature for 2 hr., it was the merit of this method. Ultrasound was considered to breaks up the solid reactants from the energy released from the bubbles created by cavitation collapsing through them. This gave the solid reactant a last surface area to the reaction to proceed over, increasing the reaction rate and ability to form ZnO nanoparticles. This phenomenon is the merit of the ultrasonic treatment.

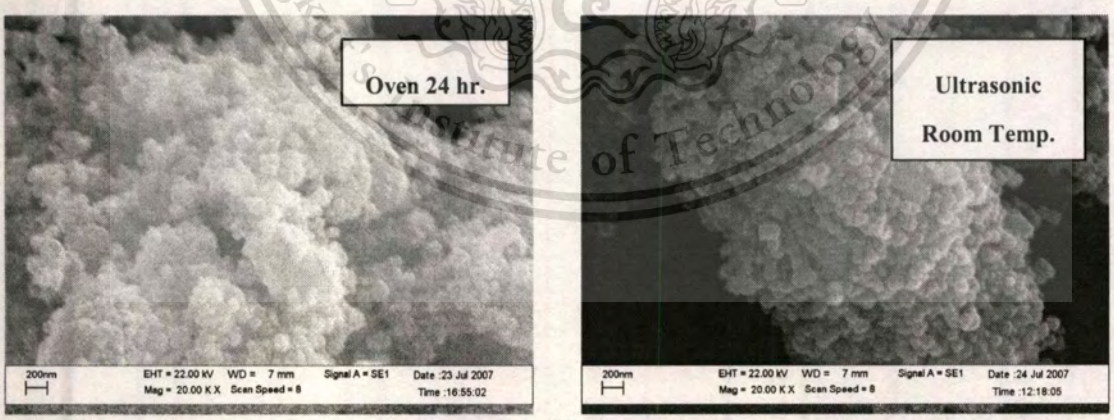
From the previous results and discussion, it can be concluded the effects of treatment conditions on the formation of ZnO nanoparticles as follows:

- When the concentration of starting materials increased and volume of dispersion media decreased, the particle size of ZnO increased. It was because the higher the density of reactant species, the higher chances of crystal growth, but the lower chances of nucleation were obtained.
- Since an increase of treatment temperature increased the chances of collision of reactant species, then the particle size of ZnO increased.
- In case of EG dispersion media, the clusters of ZnO nanoparticles were obtained when the concentration of starting materials was 0.1 mol/l. While, the ZnO nanorod were obtained when the higher concentration of starting materials were used.
- In case of PVA dispersion medias, the larger ZnO nanorods were obtained. It was because the positions of hydroxyl group on PVA were fixed on their molecule. So, hydroxyl group will close to each others, even though PVA concentration in the system is less. Therefore the reaction from above reason will occur together, make higher probability in agglomerate.

- The sonication technique could generate ZnO nanoparticles at low treatment temperature and short aging time.



(a)



(b)

Figure 4.6 (a) XRD patterns and (b) SEM micrographs of varying treatment method

4.2 Preparation of ZnO nanoparticle/P(MMA-co-HEMA) composite film

The composition of HEMA, MMA monomers, ZnO nanoparticle, and BPO were mixed and polymerized during casting to film. The amber color, polymer film was characterized by SEM, XRD, and XRF and tested by UV-Vis spectrophotometer.

The morphology of all films from SEM (Fig. 4.7 (a) and (b)) could not indicate the position of ZnO nanoparticle. It might be suggested in two ways. Firstly, ZnO was dispersed in the polymer film in the level of nanoscale, therefore, SEM technique could not detect. Secondly, small amount of ZnO nanoparticles was added in the film with poorly dispersion. Thus, the specimen used for SEM might not such a good specimen resulting in the disappearance of ZnO nanoparticles in the SEM images.

(a) MMA:HEMA 7:3 (b) MMA:HEMA 7:3 with ZnO

Figure 4.7 SEM morphology of polymer film

Figure 4.8 shows the XRD pattern of polymer film. The pattern shows only the amorphous phase of polymer matrix without the crystalline peaks of ZnO. It was because the content of ZnO was quite low, so that the ZnO signal was concealed with the polymer signal. It was, however, the presence of ZnO in the polymer films was comfirmed by the XRF. The ZnO was detectable in all polymer films, insisting the presence of ZnO in polymer films.

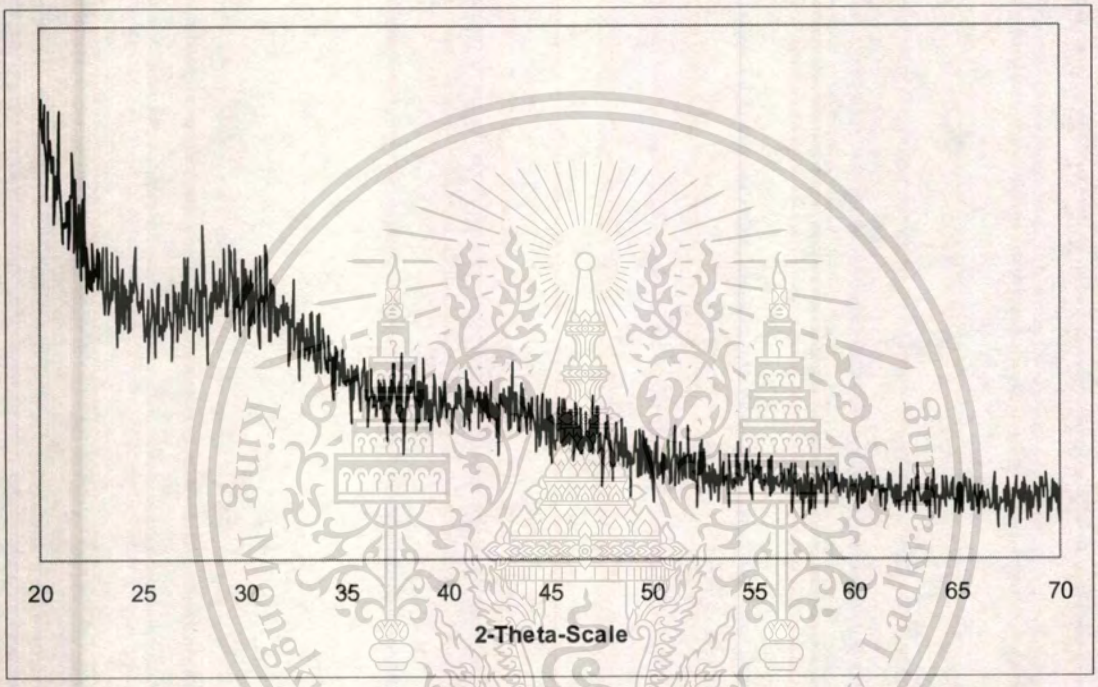


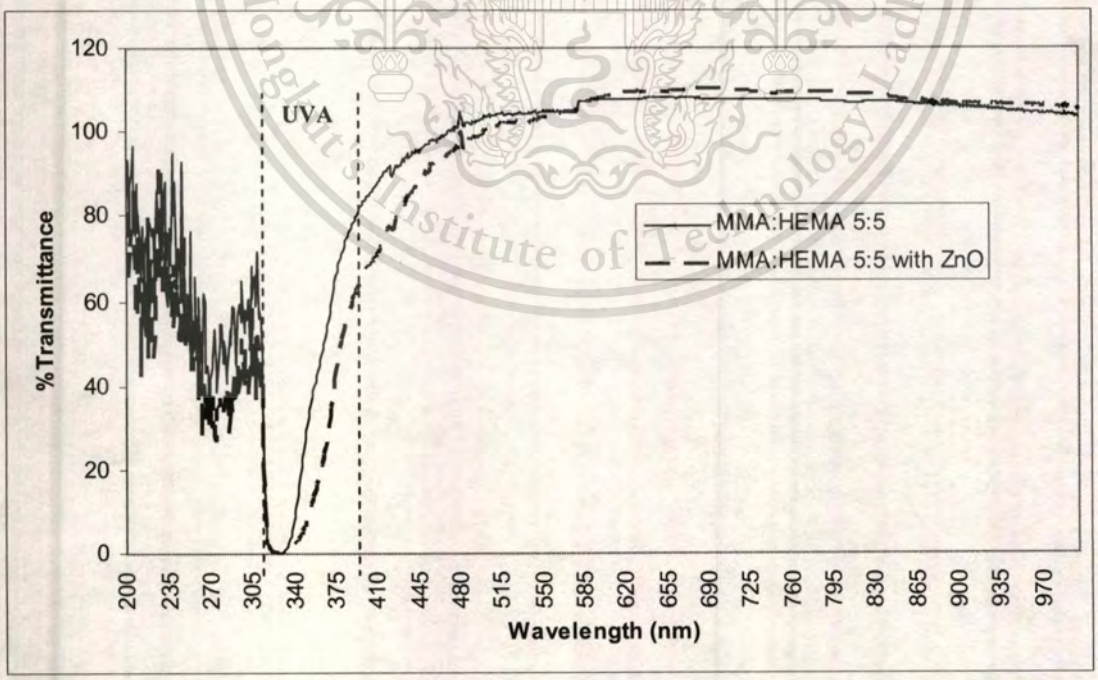
Figure 4.8 The XRD pattern of the polymer film

4.2.1 Ultraviolet-Visible Spectrometer (UV-Vis)

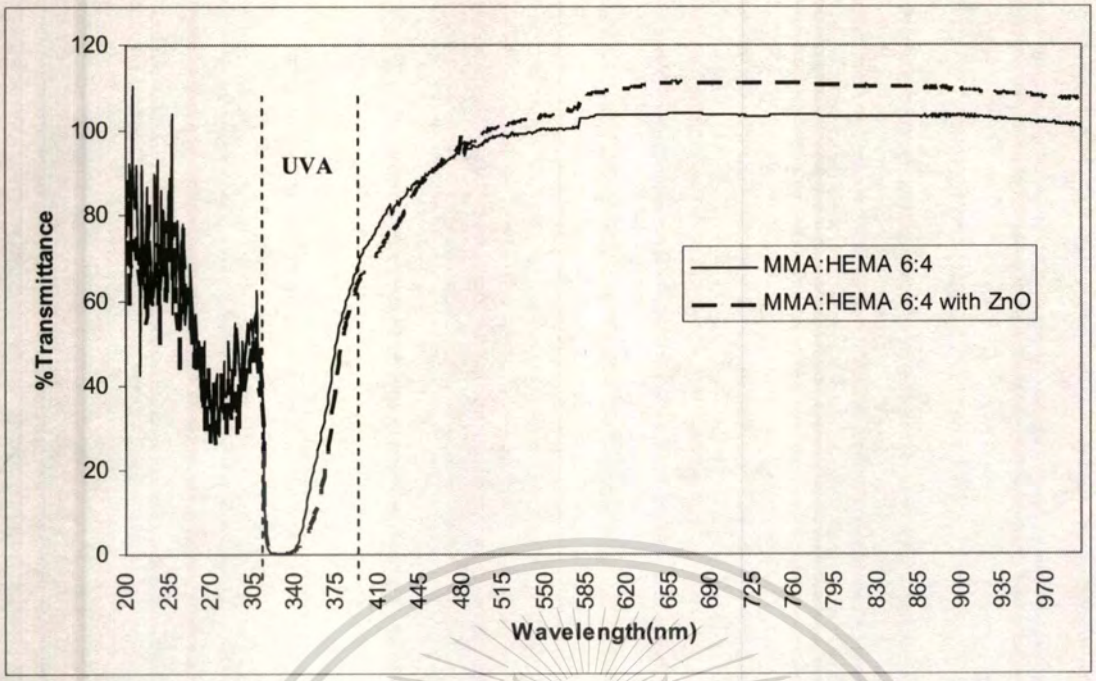
The wavelength of ultraviolet A (UVA) is in the range of 400 nm to 315 nm and of ultraviolet B (UVB) is in the range 315 nm to 280 nm. From figure 4.9 (a)-(c), at same wavelength, the polymer film with ZnO nanoparticle gave less transmittance than that of the polymer film without ZnO nanoparticle at the range of UVA. On the other hand, at the range of visible, the polymer film with ZnO nanoparticle gave the similar transmittance to that of the polymer film without ZnO nanoparticle.

From figure 4.9 (a)-(c), the polymer film with ZnO nanoparticle gave more UVA absorbance than that of the polymer film without ZnO nanoparticle.

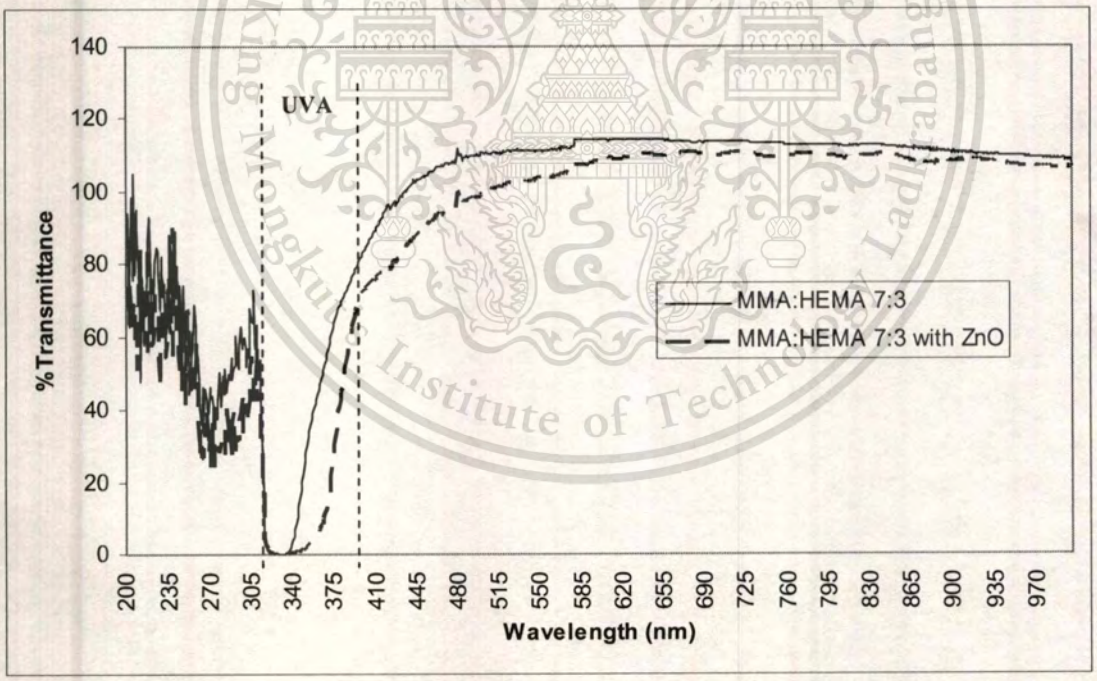
The UV transmittance of the polymer film containing ZnO nanoparticles was lower than that of the pure polymer film. On the other hand, the transmittance of visible light through the polymer film containing ZnO nanopartricles was slightly higher than the pure polymer films. These results were because the UV-visible absorption measurement was performed by scanning from UV to visible region. When the UV was exposed to the polymer film containing ZnO nanoparticles, the ZnO would absorb UV and then excite to higher energy state. After that, the luminescence of excited ZnO would occur in the visible region [19].



(a) Transmittance spectrum of MMA:HEMA 5:5

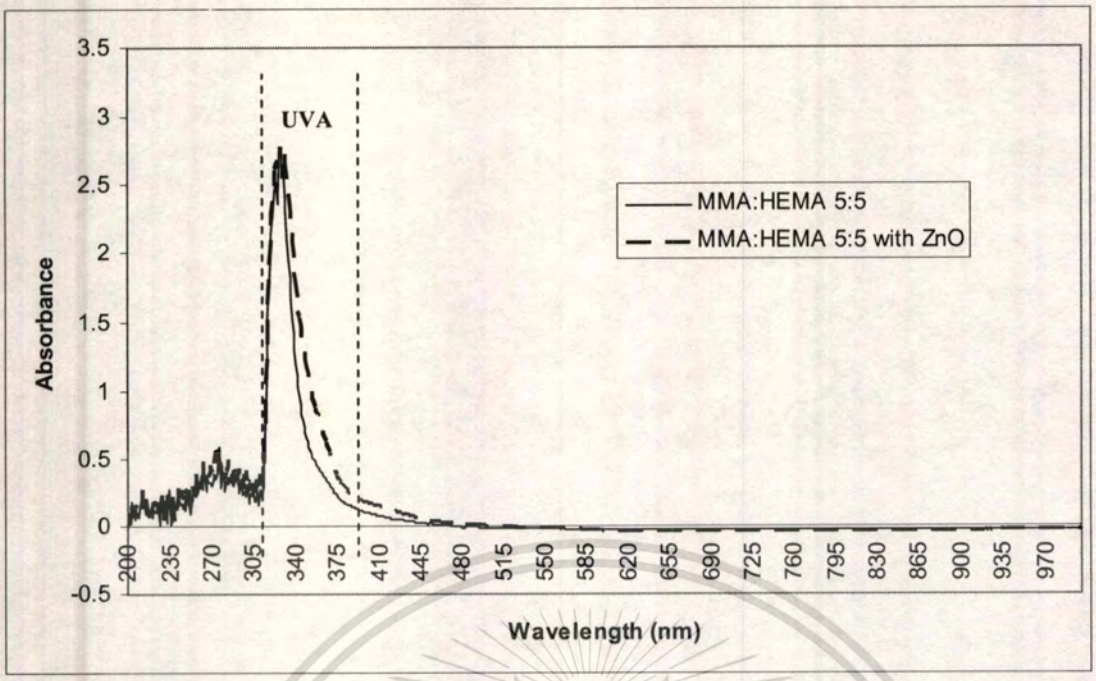


(b) Transmittance spectrum of MMA:HEMA 6:4

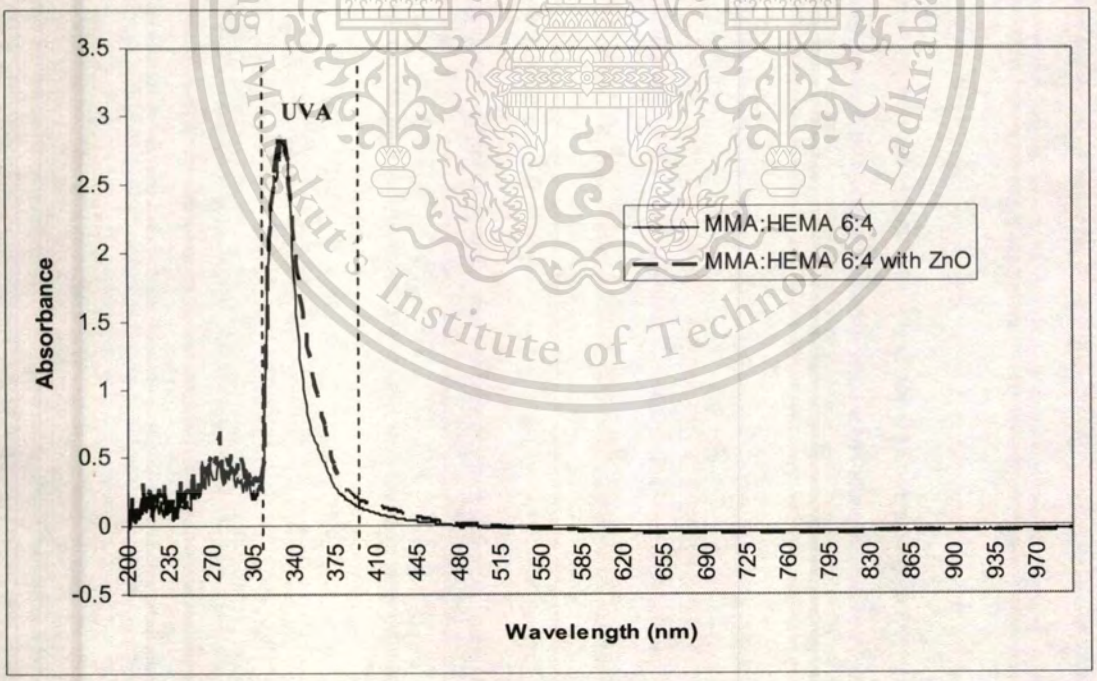


(c) Transmittance spectrum of MMA:HEMA 7:3

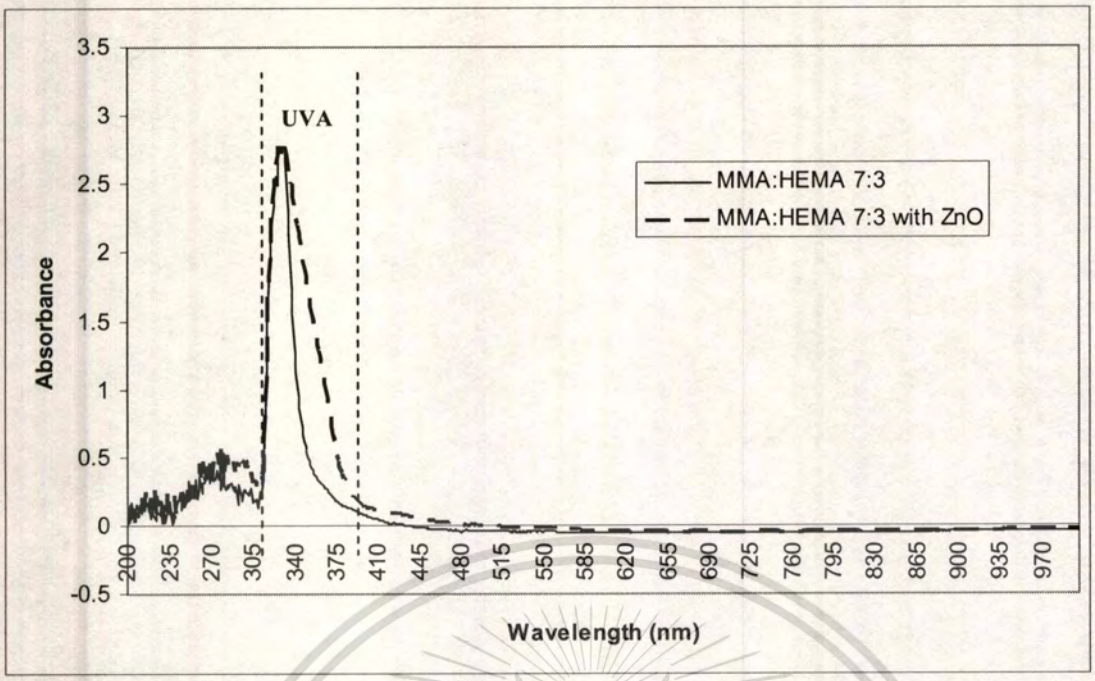
Figure 4.9 Transmittance spectrum of the polymer film



(a) Absorbance spectrum of MMA:HEMA 5:5



(b) Absorbance spectrum of MMA:HEMA 6 :4



(c) Absorbance spectrum of MMA:HEMA 7:3

Figure 4.10 Absorbance spectrum of the polymer film

Table 4.1 The ratio of MMA: HEMA with average thickness of the polymer film

Sample	Average Thickness of the Polymer Film(mm)
MMA:HEMA 5:5	0.3494
MMA:HEMA 5:5 with ZnO	0.4564
MMA:HEMA 6:4	0.5388
MMA:HEMA 6:4 with ZnO	0.5464
MMA:HEMA 7:3	0.3704
MMA:HEMA 7:3 with ZnO	0.3940

The ratio of MMA: HEMA as 8:2 with and without ZnO nanoparticle cannot cast to film. So, the result was not available.

The ratios of MMA: HEMA as 5:5, 6:4 and 7:3 gave no difference in transmittance and absorbance pattern.

Chapter 5

Conclusion and Recommendation

5.1 Conclusion

ZnO nanoparticles were obtained by hydrothermal treatment of $Zn(OH)_2$ in ethylene glycol or poly vinyl alcohol under various conditions. The effect of treatment conditions on the formation of ZnO nanoparticles could be concluded as follows:

- When the concentrations of starting materials increased and/or volume of dispersion media decreased, the particle size of ZnO increased.

- When the treatment temperature increased, the particle size of ZnO increased.

- The sonication technique could generate ZnO nanoparticles at low treatment temperature and short aging time.

The most suitable condition for synthesize of ZnO nanoparticles was the condition which used 0.1 mol/l of starting materials (i.e. $Zn(NO_3)_2 \cdot 6H_2O$ and NH_4OH) and hydrothermal treated in 100ml of EG at 75° C.

The ZnO nanoparticles/P(MMA-co-HEMA) films were successfully prepared by polymerization during casting. The ability of UV absorption of ZnO nanoparticles/P(MMA-co-HEMA) film was better than that of pure P(MMA-co-HEMA) film.

5.2 Recommendation

- ZnO can agglomerate during prolonged storage. Therefore, ZnO should be immediately use after synthesis or ground before use.

- Various properties of polymer film should be tested, such as mechanical properties, optical properties, etc.

- Improve the casting method for preparation of polymer nanocomposite film.

References

[1] [Online] , Available : www.en.wikipedia.org/wiki/Nanoparticle

[2] [Online], Available: www.azonano.com

[3] [Online], Available: www.malvern.com/labeng/industry/nanotechnology

[4] [Online], Available: www.dialog-nanopartikel.de

[5] [Online], Available: www.galleries.com/minerals

[6] [Online], Available: www.navbharat.co.in/clients.htm

[7] [Online], Available: www.reade.com/products/oxides

[8] [Online], Available: www.en.wikipedia.org/wiki/Tetrahydrofuran

[9] [Online], Available: www.basf.com/diol/pdfs/thf-brochur.pdf

[10] [Online], Available: www.en.wikipedia.org/wiki/Polycarbonate

[11] [Online], Available: www.bpf.co.uk/bpfindustry/plastics_material

[12] [Online], Available: www.med.univangers,fr/discipline/lab_histo/page _phema.htm

[13] [Online], Available: www.en.wikipedia.org.wiki.Methy_methacrylate

[14] [Online], Available:http://chemicalland21.com/industrialchem/functional %20Monomer/2-HYDROXY ETHYL%20METHACRYLATE.htm

[15] Naofumi Uekawa, Shunsuke Iahii, Takashi Kojima, Kazuyuki Kakegawa. Formation of porous sperical aggregated structure of ZnO nanoparticles by low-temperature heating of $Zn(OH)_2$ in diol solution, (2006)

[16] C. Hariharan. Photocatalytic degradation of organic contaminants in water by ZnO nanoparticles: Revisited, 304(2006): 55-61

[17] Changle Wu, Xueliand Qiao, Jianguo Chen, Hongshui Wand, Fatang Tan, Shitoa Li. A novel chemical route to prepare ZnO nanoparticles, 60(2006): 1828-1832

[18] Ruoyu Hong, Tingting Pan, Jianzhong Qian, Hongzhong Li. Synthesis and surface modification of ZnO nanoparticles, 119(2006): 71-81

[19] J.Lee, D. Bhattacharyya,A.J. Easteal, and J.B. Metson. Properties of nano-ZnO/poly(vinyl alcohol)/poly(ethylene oxide) composite thin films,(2007)

Appendix A

X-ray fluorescence (XRF)

Table A-1 shows the percentage of (a) Zn and (b) ZnO in polymer film

Sample	The percentage of Zn in polymer film
MMA:HEMA = 5:5 with ZnO	49.7%
MMA:HEMA = 6:4 with ZnO	42.3%
MMA:HEMA = 7:3 with ZnO	43.7%
MMA:HEMA = 8:2 with ZnO	37.2%

(a)

Sample	The percentage of ZnO in polymer film
MMA:HEMA = 5:5 with ZnO	61.9%
MMA:HEMA = 6:4 with ZnO	52.6%
MMA:HEMA = 7:3 with ZnO	54.4%
MMA:HEMA = 8:2 with ZnO	46.4%

(b)