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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

PREPARATION OF ZINC OXIDE/BUTYL ACRYLATE NANOCOMPOSITE
LATEX FOR COATING APPLICATION



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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer

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พรศักดิ์ รักษายศ: การเตรียมนาโนคอมพอสิตเลเทกซ์ของซิงค์ออกไซด์/บิวทิลอะคริเลต เพื่อใช้ในงานเคลือบ (PREPARATION OF ZINC OXIDE/BUTYL ACRYLATE NANOCOMPOSITE LATEX FOR COATING APPLICATION) อ.ที่ปริกษาวิทยานิพนธ์หลัก: ผู้ช่วยศาสตราจารย์ ดร.วราวุฒิ ตั้งพสุธาคล, อ.ที่ปริกษาวิทยานิพนธ์ร่วม: อาจารย์ ดร.สิริวรรณ พัฒนาฤดี, 61 หน้า.

นาโนคอมพอสิตเลเทกซ์ของซิงค์ออกไซด์/พอลิ(บิวทิล อะคริเลต) เพื่อใช้ในงานเคลือบ สามารถเตรียมจากกระบวนการพอลิเมอไรเซชัน โดยทำให้เกิดพอลิเมอร์แบบอิมัลชันภายในของ บิวทิลอะคริเลตในระบบที่มีอนุภาค ซิงค์ออกไซด์ที่ปรับสภาพแล้ว ในขั้นแรก สารคู่ควบ 3-เมทาคริโลออกซิล โพรพิล ไทเรทออกซีไซเลน (MPS) ถูกเติมลงไปเพื่อใช้เป็นสารยึดเกาะ (graft) บน ซิงค์ออกไซด์เพื่อปรับพื้นผิวของซิงค์ออกไซด์ให้เข้ากับ PBA ซึ่งเป็นสารอินทรีย์ได้มากขึ้น โดยที่ ด้านหนึ่งของโมเลกุล MPS ทำหน้าที่เป็นจุดเริ่มต้นเพื่อให้เกิดการกราฟต์ด้วย PBA ด้วยการใส่ โปแทสเซียมเปอร์ซัลเฟตเป็นตัวริเริ่ม และใช้สารลดแรงตึงผิว แบบไม่มีประจุ ลักษณะเอนแคปซูล เชนในนาโนคอมพอสิตเลเทกซ์ของ ZnO/PBA สามารถยืนยันด้วยเทคนิคฟูเรียร์ทรานสฟอร์มอินฟราเรดสเปกโทรสโกปี (FT-IR) และกล้องจุลทรรศน์อิเล็กตรอนแบบส่องผ่าน (TEM) ซึ่งในเลเทกซ์ พบว่าเกิดการกราฟต์ด้วย PBA ถึง 162% และคอมโพสิตเลเทกซ์ที่มีนาโน ZnO 0.3 % โดยน้ำหนัก สามารถคงตัวที่อุณหภูมิห้องได้นานถึง 4 สัปดาห์ นอกจากนี้ แผ่นฟิล์มนาโนคอมพอสิตเลเทกซ์ ZnO/PBA สามารถดูดกลืนแสงทั้งช่วงยูวีและวิซิเบิล แต่กลับพบว่านาโนคอมพอสิตเลเทกซ์ที่ เตรียมได้ไม่มีฤทธิ์ยับยั้งเชื้อแบคทีเรีย อี. โคไล (แกรมลบ) และ เอส. ออเรียส (แกรมบวก)

ศูนย์วิทยทรัพยากร จุฬาลงกรณ์มหาวิทยาลัย

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ปีการศึกษา 2552

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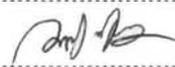
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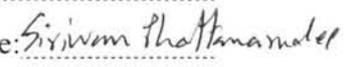
5073416923: MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
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PORNSAK RAKSAYOT: PREPARATION OF ZINC OXIDE/BUTYL
 ACRYLATE NANOCOMPOSITE LATEX FOR COATING
 APPLICATION. THESIS ADVISOR: ASST. PROF. VARAWUT
 TANGPASUTHADOL, Ph.D., THESIS CO-ADVISOR: SIRIWAN
 PHATTANARUDEE, Ph.D., 61 pp.

Nanocomposite latex of zinc oxide/poly(butyl acrylate) (ZnO/PBA) for coating on fabric was prepared by *in situ* emulsion polymerization of butyl acrylate in the presence of treated ZnO particles. The ZnO nanoparticles were first grafted with a silane coupling agent, 3-methacryloxypropyltrimethoxy silane (MPS), in order to improve the interface compatibility between the ZnO and the organic PBA. One end of MPS was facilitated as an initiating point for PBA grafting by using potassium persulfate as an initiator in the presence of nonionic surfactant. The ZnO/PBA composite latex encapsulation was assured by Fourier transform infrared spectroscopy (FT-IR) and transmission electron microscopy (TEM). In the latex, about 162% of PBA were successfully grafted on the surface of ZnO nanoparticles. The composite latex containing 0.3% by wt. of ZnO was fairly stable at room temperature for up to 4 weeks. Furthermore, the ZnO/PBA nanocomposite film displayed UV-shielding properties in both of UV and visible range. But the composite latex did not show any antibacterial activities against both of *E. coli* (gram negative) and *S. aureus* (gram positive) bacteria.

Field of Study: Petrochemistry and Polymer Science Student's Signature: 

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ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

CONTENT

	PAGE
ABSTRACT THAI.....	iv
ABSTRACT ENGLISH.....	v
ACKNOWLEDGEMENTS.....	vi
CONTENTS.....	vii
LIST OF TABLES.....	ix
LIST OF FIGURES.....	xi
CHAPTER I: INTRODUCTION.....	1
1.1 Statement of problem.....	1
1.2 Objective.....	2
1.3 Scope of the investigation.....	2
CHAPTER II: THEORY AND LITERATURE REVIEW.....	3
2.1 Preparation of zinc oxide particles.....	3
2.2 Surface grafting as a way to modify inorganic metal oxide particles.....	4
2.2.1 Silane coupling agents.....	4
2.2.2 Graft mechanism.....	6
2.3 Nano-ZnO/Polymer composite latex.....	7
2.3.1 Preparation of composite latex by in situ emulsion polymerization.....	7
2.4 Testing application.....	9
2.4.1 UV property.....	9
2.4.2 Antibacterial property.....	11
CHAPTER III: EXPERIMENTALS.....	14
3.1 Materials	14
3.2 Procedures.....	14
3.2.1 Preparation of ZnO/PBA composite latex.....	14
3.2.1.1 Grafting of MPS onto ZnO particles.....	14
3.2.1.2 Emulsion polymerization of butyl acrylate.....	15

CONTENTS (continued)

	PAGE
3.2.2 Characterization of ZnO grafted with MPS and ZnO/PBA nanocomposite latex.....	15
3.2.2.1 Chemical functional group of grafted with MPS and ZnO/PBA nanocomposite particle.....	15
3.2.2.2 Latex stability determination.....	16
3.2.2.3 Grafting efficiency.....	16
3.2.2.4 Micro- and nano-scale morphology analysis.....	17
3.2.3 UV shielding property.....	18
3.2.4 Antibacterial property.....	19
CHAPTER IV: RESULTS AND DISCUSSION.....	20
4.1 Modification of nano-ZnO with MPS.....	20
4.2 Emulsion polymerization of butyl acrylate on MPS-grafted ZnO nanoparticles.....	25
4.3 Latex stability determination.....	30
4.4 Scanning electron microscopy analysis.....	31
4.5 UV-shielding properties.....	33
4.6 Antibacterial property.....	34
CHAPTER V: CONCLUSIONS AND SUGGESTION.....	40
5.1 Conclusions.....	40
5.2 Suggestion.....	41
REFERENCES.....	42
APPENDIX A.....	46
APPENDIX B.....	56
VITAE.....	61

LIST OF TABLES

TABLE	PAGE
2.1 Antibacterial Activity Test of the Coated Bandages against <i>E. coli</i> and <i>S.aureusa</i> [28].....	12
2.2 Antibacterial rate of films added ZnO/polystyrene nanocomposite latexes in light and in dark [33].....	13
3.1 The emulsion polymerization recipe of ZnO/PBA nanocomposite latex.	15
4.1 Preparation condition and FTIR spectroscopy results of MPS-grafted nano-ZnO.....	23
4.2 Formulation of BA emulsion polymerization process in the presence of MPS-g-ZnO.....	25
4.3 The effect of BA content on the percentage of conversion, grafting, and grafting efficiency of BA in the emulsion polymerization process with MPS-g-ZnO particles.....	28
4.4 The effect of reaction time on the percentage of conversion, grafting, and grafting efficiency of BA in the emulsion polymerization process with MPS-g-ZnO particles.....	28
4.5 The effect of initiator amount on the percentage of conversion, grafting, and grafting efficiency of BA in the emulsion polymerization process with MPS-g-ZnO particles.....	29
4.6 Antibacterial rate of antibacterial test by agar dilution susceptibility method against <i>S. aureus</i> and <i>E. coli</i>	38
A-1 The surface modification recipe of nano-ZnO with MPS.....	47
A-2 The dry solids of MPS-g-ZnO after sohxlet.....	47
A-3 The %graft of MPS onto the surface of nano-ZnO.....	47
A-4 The emulsion polymerization recipe of ZnO/PBA nanocomposite latex in reaction time of 3 hr.(<i>standard condition</i>).....	48
A-5 Dry solid in latex in the effect of BA content.....	48
A-6 The effect of BA content on the percentage of conversion.....	49
A-7 The dry solids of latex after centrifuge in the effect of BA content.....	49
A-8 Dry solid latex after sohxleted.....	50

LIST OF TABLES (continued)

TABLE		PAGE
A-9	The effect of BA content on the percentage of grafting, and grafting efficiency of BA in the emulsion polymerization process with MPS-g-ZnO particles.....	50
A-10	The effect of reaction times on the percentage of conversion.....	51
A-11	The effect of reaction times on the percentage of grafting, and grafting efficiency of BA in the emulsion polymerization process with MPS-g-ZnO particles.....	51
A-12	The effect of initiator amount on the percentage of conversion.....	52
A-13	The effect of initiator amount on the percentage of grafting, and grafting efficiency of BA in the emulsion polymerization process with MPS-g-ZnO particles.....	52
A-14	. Latex stability determination: bare nano-ZnO in mixed-solvent between MeOH:H ₂ O (4:1) (BZ), MPS-g-ZnO 0.3% w/w in MeOH:H ₂ O (4:1) (ZGM), ZnO/PBA latex prepared from 1% KPS 5% BA (ZPBA), 0.5% KPS 5% BA (ZBA0.5), 1% KPS and 10% BA (Z10BA), 1% KPS and 20% BA (Z20BA), and commercial nano-ZnO latex for fabric coating (ZAB; ZnO 0.3 wt% with negative acrylic binder 1 wt%).....	53

LIST OF FIGURES

FIGURE		PAGE
2.1	Mechanism of the FSP process for ZnO particles synthesis.....	3
2.2	3-Methacryloxypropyltrimethoxysilane (MPS), a coupling agent used in this study.....	4
2.3	Reaction schemes for the grafting of MPS onto oxidic particles [10].....	5
2.4	Schematic process for graft of silane coupling agent onto ZnO nanoparticles [11].....	6
2.5	Steps for preparing nano-ZnO/PBA composite by in situ emulsion polymerization.....	7
2.6	Polyoxyethylene nonylphenyl ether (OP-10).....	8
2.7	ZnO on the cotton fabric [25].....	10
2.8	Diagrammatic representation for erythema index after UV light exposure for optimum coated fabrics [26].....	11
4.1	Synthesis step of nano-ZnO/poly(butylacrylate) composite by <i>in situ</i> emulsion polymerization.....	20
4.2	Synthesis of nano-ZnO particles by spray pyrolysis [26].....	21
4.3	FTIR spectra of nano-ZnO particles type A (A0) and type B (B0).....	22
4.4	Comparison of the FTIR spectra of nano-ZnO particles type A (A0) and type B (B0); nano-ZnO particles modified by MPS in type A (A1) and type B (B1).....	24
4.5	Comparison between the FT-IR spectra for MPS-g-ZnO particles (type B) before and after emulsion polymerization process of butyl acrylate.....	26
4.6	TEMs of nano-ZnO particles type A (a), type B (b), nano-ZnO particles type B modified by MPS (c), and ZnO/PBA composite particles (d).....	27

LIST OF FIGURES (continued)

FIGURE		PAGE
4.7	Comparison of suspension stability: bare nano-ZnO in mixed-solvent between MeOH:H ₂ O (4:1) (BZ), MPS-g-ZnO 0.3% w/w in MeOH:H ₂ O (4:1) (ZGM), ZnO/PBA latex prepared from 1% KPS 5% BA (ZPBA), 0.5% KPS 5% BA (ZBA0.5), 1% KPS and 10% BA (Z10BA), 1% KPS and 20% BA (Z20BA), and commercial nano-ZnO latex for fabric coating (ZAB; ZnO 0.3 wt% with negative acrylic binder 1 wt%).....	30
4.8	Scanning electron micrographs of (A)nano-ZnO type A, (B)nano-ZnO type B, and (C)MPS-g-ZnO from ZnO type B. [left- 500 ×, right- 5,000 ×].....	32
4.9	Scanning electron micrographs of cross-section (left) and top viewed (right) of film samples prepared from (A)unmodified ZnO particles mixed into commercial PBA latex and (B)ZnO/PBA nanocomposite latex prepared in this study. [left- 100 magnification, right- 500 magnification].....	33
4.10	Absorbance spectra of (a) nano-ZnO/PBA composite latex compared to (b) PBA latex- Both analyses were performed by coating the latex on dry quartz cuvette.....	34
4.11	Disk diffusion method using filter papers to test the antibacterial activity of PBA and ZnO/PBA composite latex compared with ampicillin positive control.....	35
4.12	Disk diffusion method using cotton clothes to test the antibacterial activity against <i>E. coli</i> of ZnO/PBA composite latex, nano-ZnO type A, and type B, compared with ampicillin positive control.....	36
4.13	Disk diffusion method using cotton clothes to test the antibacterial activity against <i>S. aureus</i> of ZnO/PBA composite latex, nano-ZnO type A, and type B, compared with ampicillin positive control.....	37

LIST OF FIGURES (continued)

FIGURE		PAGE
B-1	FT-IR images of preparation condition of MPS-grafted nano-ZnO...	57-60
B-2	FT-IR spectra for MPS-g-ZnO particles (type B) after emulsion polymerization process of butyl acrylate.....	60



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CHAPTER I

INTRODUCTION

1.1 Statement of problem

Zinc oxide nanoparticles (nano-ZnO) has drawn increasing attention in recent years due to its many significant physical and chemical properties, such as chemical stability, high luminous transmittance, high catalysis activity, effective antibacterial and bactericide function, intensive ultraviolet and infrared absorption [1-6]. Therefore, nano-ZnO can be potentially applied to UV-shielding material, catalyst, antibacterial material, for example [5]. When applied in coating fabrics and construction materials, ZnO is generally used in a form of ZnO/polymer composite. The inorganic ZnO particle is quite hydrophilic and possesses a large amount of hydroxyl group (-OH) on the particle surface. It generally came together to form cluster of various sizes when the particles are mixed with low polar organic matrix, such as polymers.

To prevent the nanoparticles to aggregate in polymers, the combination of inorganic particles with polymers is usually accomplished by surface modification. The grafting of organic polymers onto inorganic nanoparticle is one of the most effective and versatile methods for this modification purpose. It can significantly enhance the stability of nanoparticles dispersing in polymer matrix by increasing the affinity of the surface for organic substances [5]. A wide variety of organic polymers have been employed in the syntheses of organic-inorganic hybrid materials [2,5], especially of metal oxides, such as ZnO and SiO₂. The type of polymer employed is one of the main features affecting microstructure and macroscopic characteristics of hybrids because they depend essentially on chemical interactions established between organic and inorganic moieties. Poly(butyl acrylate) (PBA) is an attractive polymer for this study due to its low glass transition temperature and one of the water-based coating matrix.

The ZnO/polymer nanocomposites are usually in the form of emulsion, in which the nano ZnO/polymer particles must be dispersed homogeneously. One way to achieve this is to modify the ZnO particles by changing its polar surface

(Zn-OH) to hydrophobic chemical groups. The method used is to graft an organic polymer on the metal-oxide surface. In general a coupling agent, such as 3-methacryloxypropyltrimethoxy silane (MPS), is needed as a link between the metal oxide and the organic polymer. The methoxy silane end of MPS can chemically link with ZnO, while the double bond end can become an initiating point for polymerization of vinyl monomers in the emulsion; hence the process is called *in situ* emulsion polymerization.

1.2 Objective

The aim of this work was to prepare nano-composite latex of ZnO and butyl acrylate via emulsion polymerization by the use of 3-methacryloxypropyltrimethoxy silane (MPS) as a coupling agent.

1.3 Scope of the investigation

The stepwise investigation was carried out as follows:

1. Literature review for methods to prepare ZnO/PBA nanocomposite latex.
2. Surface grafting modification of ZnO with MPS.
3. Emulsion polymerization of butyl acrylate on surface-grafted ZnO particles to prepare ZnO/PBA nanocomposite latex.
4. Characterization of the latex stability, percent of conversion, percent of grafting, percent of grafting efficiency, the morphology, UV-shielding property and antibacterial property of the ZnO/PBA nanocomposites.
5. Summarizing the results and writing the thesis.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Preparation of zinc oxide particles

ZnO nanoparticle have been used increasingly as emulsion for coating on materials such as fabrics and construction materials, since they were shown to suppress bacteria and block UV radiation, for example [1-6].

ZnO particles can be prepared by several existing methods, such as homogeneous precipitation [7], mechanical milling [8], and spray pyrolysis [9]. In this research the nano-ZnO were prepared by the spray pyrolysis method.

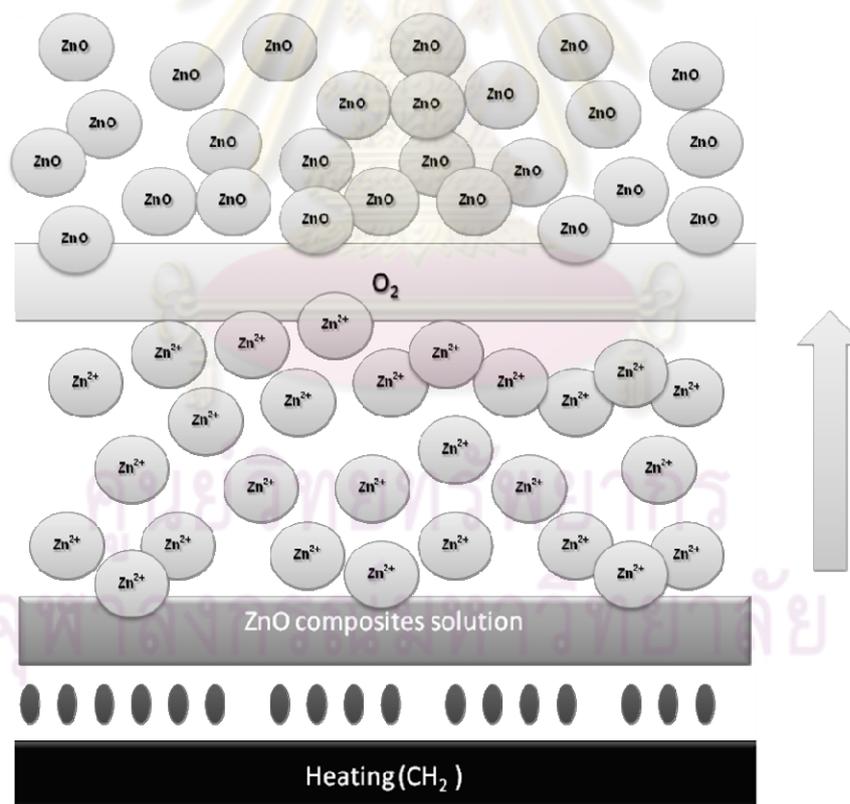


Figure 2.1. Mechanism of the FSP process for ZnO particles synthesis.

Flame spray pyrolysis (FSP) (Fig.2.1) is the use of heat allows for solvent to evaporation and oxidation with the air to be ZnO nanoparticles. At first material solution is various contaminated zinc composites such as zinc acrylate or zinc acetate. The zinc solution was the inductance to produce a zinc vapor by heating a carbon additive (e.g. methane) at various temperatures or stable temperature. Then, the zinc vapor that is then instantaneously reacting with oxygen in the air to be ZnO nanoparticles that the average primary particle diameter can be controlled by the solution feed rate [9]. Because of the lower purity of the source material, the final product will still have some organic group on the surface. This shows that the hydrophobic properties out.

2.2 Surface grafting as a way to modify inorganic metal oxide particles

2.2.1 Silane coupling agents

It has been known that the active polar surface of metal oxide nanoparticles results in agglomeration rather easily. Therefore one way to overcome this is to modify the ZnO particles by changing its polar surface (Zn-OH) to hydrophobic chemical groups. The method used is to graft an organic polymer on the metal-oxide surface. In general a coupling agent, such as 3-methacryloxypropyltrimethoxy silane (MPS) (Fig. 2.2), is needed as a link between the metal oxide and the organic polymer.

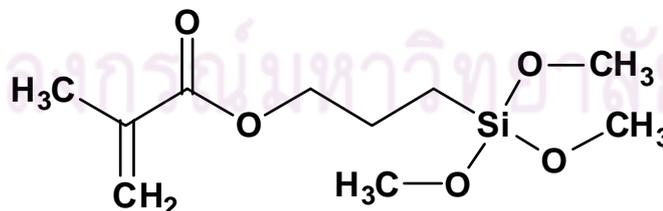
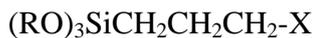


Figure 2.2. 3-Methacryloxypropyltrimethoxysilane (MPS).

Silane coupling agents are silicon-based chemicals that contain two types of reactivity– inorganic and organic–in the same molecule. A typical general structure is



where RO is a hydrolyzable group, such as methoxy, ethoxy, or acetoxy, and X is an organofunctional group, such as amino, methacryloxy, epoxy, etc.

A silane coupling agent will act at an interface between an inorganic substrate (such as glass, metal or mineral) and an organic material (such as an organic polymer) to bond, or couple, the two dissimilar materials.

In 2004, W. Posthumus et al. [10] studied grafting of MPS onto SiO₂, tin oxide (TO), and antimony-doped tin oxide (ATO). They found that the treatment of TO and SiO₂ particles with sufficient MPS resulted in a monolayer coverage of the particles. For ATO the maximum amount of grafted MPS was low. When the maximum surface coverage was reached, excessive MPS did not bind to the particles but did form homocondensates.

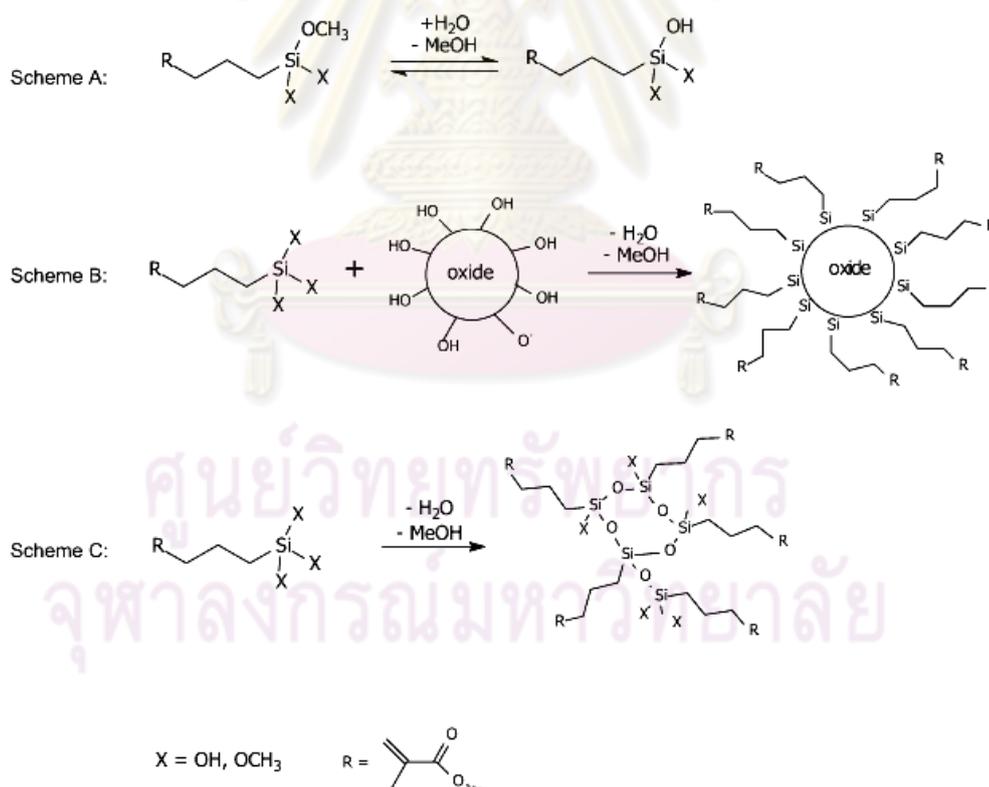


Figure 2.3. Reaction schemes for the grafting of MPS onto oxide particles [10].

2.2.2 Graft mechanism

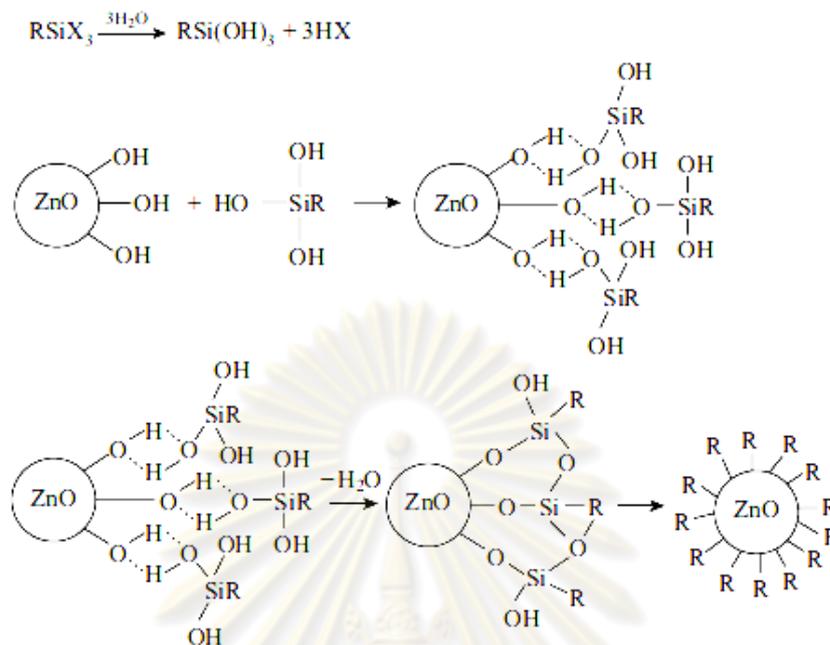


Figure 2.4. Schematic process for graft of silane coupling agent onto ZnO nanoparticles [11].

Figure 2.4 illustrated the graft mechanism of ZnO nanoparticles with silane coupling agent MPS. First, the methoxy groups of MPS undergoes hydrolysis to result in silanol groups with methanol molecule ejection. Second, the silanol groups may bind the hydroxy of the ZnO surface by hydrogen bonds and condense to form Zn-O-Si linkage with the release of water molecule. Thus, the MPS is successfully grafted on the surface of ZnO nanoparticles [11]. This process is catalyzed by heat and acid/base condition. Change of particle polarity and a small amount of water and methanol release from the reaction might somewhat affect the stability of emulsion. A proper uses of surfactant and water content are therefore crucial for sustaining latex stability.

2.3 Nano-ZnO/Polymer composite latex

2.3.1 Preparation of composite latex by in situ emulsion polymerization

In this work MPS was used as coupling agent. The methoxy silane end of MPS can chemically link with ZnO, while the double bond end can become an initiating point for polymerization of the vinyl monomer in the emulsion; hence the process is called in situ emulsion polymerization. The process can be explained in Fig. 2.5.

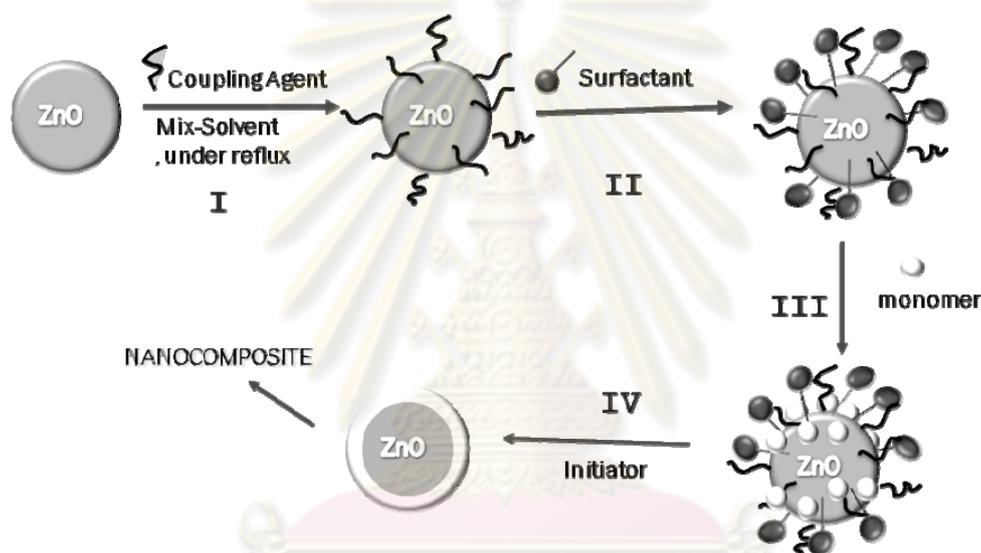


Figure 2.5. Steps for preparing nano-ZnO/PBA composite by in situ emulsion polymerization.

First, MPS as a silane coupling agent is grafted on the ZnO particles. Second, surfactant such as OP-10 (a nonionic surfactant) (Fig. 2.5) is needed in order to stabilize the functionalized ZnO nanoparticles in aqueous system. The amount of surfactant is generally lower than the one corresponding to saturation of the surface. The purpose is to avoid the formation of emulsifier micelles. The hydrophilic terminal of surfactant points to the water phase to ensure the stable suspension of the nanoparticles in the aqueous system during emulsion polymerization. The other terminal (hydrophobic end) points to the MPS phase (grafted on oxide surface) where they form a layer in which further polymerization takes place. Third, the monomers (BA) are adsorbed on the

stabilized ZnO particles, which should result in a very high monomer concentration in the vicinity of the particles compared with the relative limited one in bulk. In the end, the main chain propagating was carried out on the surface of the nano- ZnO particle on which encapsulated composite was formed [12].

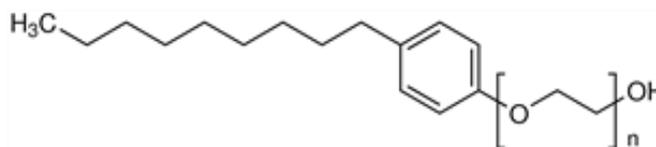


Figure 2.6. Polyoxyethylene nonylphenyl ether (OP-10).

Till now there have been a number of reports on the preparation of composite latex of ZnO and various polymer types, as follows.

In 2002 Shim et al. [13] studied the preparation and morphology of the nanocomposite materials ZnO/poly(methyl methacrylate) (PMMA) prepared by the in situ emulsion polymerization. The SEM image illustrated the spherical structure of nano-ZnO particles that were embedded homogeneously with PMMA. Shim reported that the heart of composite material preparation was to modify the surface of the inorganic substances from hydrophilic (due to $-OH$) to be more hydrophobic.

In 2006 Tang et al. [14] synthesized ZnO/PMMA nanocomposite latex by in situ emulsion polymerization of MMA in the presence of nano ZnO particles that were pre-grafted with MPS. The double bond in the molecule of MPS was used to induce the polymerization for MMA, resulting in the composite latex containing ZnO particles grafted with MPS-PMMA. By TEM technique, the modified nano ZnO particles looked spherical with blockades of PMMA. The FT-IR analysis results helped confirm the chemical link between ZnO and MPS, as well as the existence of PMMA in the particles. The modified ZnO nanoparticles were fairly dispersed in PVC matrix, as indicated by SEM. The increase of ZnO nano materials improved the UV-light resistance of the material.

In addition Peng et al. [15] successfully grafted ZnO with a water-soluble polymer, poly(hydroethyl acrylate) (PHEA) via the copper-mediated surface-initiated atom transfer radical polymerization (SI-ATRP) technique with the bromo-acetamide modified ZnO nanoparticles (BrA-ZnO) as macroinitiators. 1,10-Phenanthroline and Cu(I)Br in water were used as catalysts. PHEA-ZnO

nanoparticles had better dispersibility than the bare ZnO nanoparticles because of the water soluble grafted PHEA on their surfaces. The product, poly(hydroethyl acrylate) grafted ZnO nanoparticles (PHEA-ZnO), were also characterized with Fourier transform infrared spectroscopy (FT-IR), UV-vis spectroscopy, thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM).

2.4 Testing application

2.4.1 UV shielding property

ZnO produces an efficient blue-green luminescence and displays excitonic ultraviolet (UV) laser action at room temperature (band gap energy of 3.37 eV, excitation banding energy of 60 meV). These attributes make ZnO/polymer composite materials potentially interesting for photonic applications in the UV region of the spectrum [16-19]. ZnO can also be used in UV light-emitting diodes, transparent UV-protection coatings, luminescent devices, solar cells, piezoelectric devices, etc [20-22].

In addition, the inorganic nanoparticles (ZnO) have a higher density than the organic monomer, so a density gradient of nanoparticles may be formed in nanocomposite films during a long curing process, which would result in the optical inhomogeneity of the nanocomposite films. Both of absorbance and transmittance properties of the ZnO/polymer nanocomposites can be increased by control of the content of the MPS-capped ZnO particles in the matrix [23].

The UV-blocking property of a fabric is enhanced when a dye [24], pigment, delustrant, or ultraviolet absorber finish is present. The molecule can absorb ultraviolet radiation and block its transmission through a fabric to the skin. Metal oxides like ZnO as UV-blocker are more stable when compared to organic UV-blocking agents. Hence, nano ZnO can enhance the UV-blocking property due to their increase surface area (increasing ZnO content) and intense absorption in the UV region. Zinc oxide (ZnO) nanoparticles embedded in polymer matrices are can be used as UV-protection in textiles by coating the surface of textiles and clothing with nanoparticles active surfaces [25].

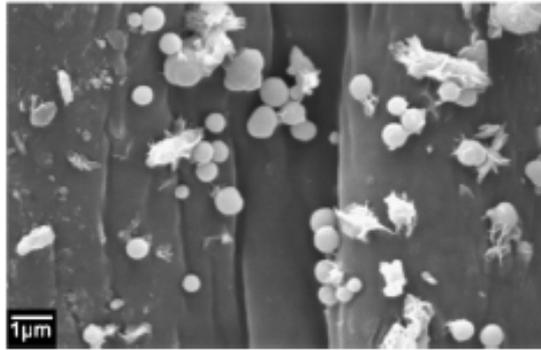


Figure 2.7. ZnO on the cotton fabric [25].

In Maged's study [26], the novel UV-protective formulations for cotton, poly(ethylene terephthalate) (PET) and cotton/PET fabrics were prepared. Gamma rays as an ionizing radiation was utilized for surface curing. Natural occurring aluminum potassium sulfate (alum) was used individually and in binary coat with ZnO, to induce the UV-blocking properties. Fig. 2.8 showed that alum and ZnO fitted the definition of UV absorbent agents, whether in an individual or binary form (with no change in surface color). Inorganic UV blockers are more preferable to organic UV blockers as they are non toxic and chemically stable under exposure to both high temperatures and UV.

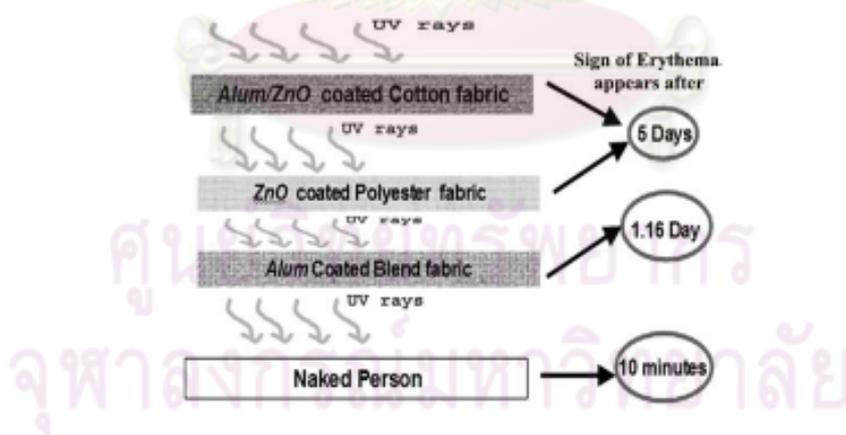


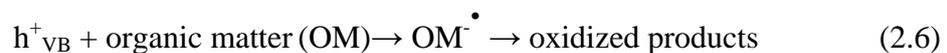
Figure 2.8. Diagrammatic representation for erythema index after UV light exposure for optimum coated fabrics [26].

2.4.2 Antibacterial property

At present, fabrics with antibacterial property has increasingly attracted attention. Nanosized particles have a larger surface area per unit mass and hence higher efficiency than bulk materials. Nanoparticles are used in textile finishing altering surface properties and imparting textile function.

Antibacterial agents can be broadly classified into two types, organic and inorganic. Organic antibacterial materials are often less stable particularly at high temperatures and/or pressures compared to inorganic antibacterial agents. Indeed, inorganic materials such as metal and metal oxides have attracted a lot of attention because of their ability to withstand harsh processing conditions. One of these inorganic materials is zinc oxide (ZnO).

The photocatalytic process of ZnO is initiated when a ZnO absorb photons with energy equal or superior to their band gap, promoting the valence band electrons to the conduction band energy level (Eq. (2.1)). The electrons in the conduction band (e^-_{CB}) can recombine with the photo-generated vacancies (holes, h^+_{VB}) decreasing the efficiency of the photocatalytic process (Eq. (2.2)). On the other hand, electrons can migrate to the surface of the ZnO particle being trapped by adsorbed oxygen molecules, thus forming the superoxide anion (O_2^-) increasing the efficiency of the photocatalytic process (Eq. (2.3)). In parallel, the vacancies generated in the valence band (h^+_{VB}) can be trapped on the ZnO surface promoting the splitting of adsorbed water molecules or hydroxide anions generating hydroxyl radicals (HO^\bullet) (Eqs.(2.4) and (2.5)). These hydroxyl radicals have been considered as responsible for the oxidation of organic matter due to their high oxidation capability. Finally, the holes can directly oxidize the adsorbed organic matter conducting to oxidized intermediates (Eq. (2.6)) :



The oxidation reactions that will occur between the active oxygen and many kinds of organic matters in bacteria will kill bacteria [27].

Perelshtein studied [28], ZnO nanoparticles deposited on the surface of cotton fabrics using ultrasound irradiation. Optimization of the process resulted in a homogeneous distribution of ZnO nanocrystals on the fabric surface.

From Table 2.1, the performance of fabrics coated with 0.75 wt% ZnO nanoparticles as an antibacterial agent was investigated and their excellent bactericidal effect demonstrated.

Table 2.1. Antibacterial activity test of the coated bandages against *E. coli* and *S.aureus*^a [28].

<i>E.coli</i>						
sample	duration of treatment					
	1h			2h		
	CFU, mL ⁻¹	N/N ₀	% reduction in viability	CFU, mL ⁻¹	N/N ₀	% reduction in viability
clean fabric	1.02 x 10 ⁷	0.98	2.4	1.34 x 10 ⁷	1.28	-28.23
no fabric	1.17 x 10 ⁷	1.14	-28.57	1.23 x 10 ⁷	1.35	-35.16
0.75% ZnO (sample 5)	1.71 x 10 ⁷	1.58 x 10 ⁻³	99.84	0	-0.9 x 10 ⁻⁸	100
<i>S.aureus</i>						
sample	duration of treatment					
	1h			2h		
	CFU, mL ⁻¹	N/N ₀	% reduction in viability	CFU, mL ⁻¹	N/N ₀	% reduction in viability
clean fabric	0.7 x 10 ⁷	0.71	20.46	0.99 x 10 ⁷	1.125	-12.5
no fabric	0.89 x 10 ⁷	1.1	-10.11	0.67 x 10 ⁷	0.75	24.72
0.75% ZnO (sample 5)	3.9 x 10 ⁶	3.36 x 10 ⁻¹	66.4	7.6 x 10 ³	6.55 x 10 ⁻⁴	99.93

^aThe viable bacteria were monitored by counting the number of colony-forming units (CFU); N/N₀=survival fraction.

Ming [29] found that antibacterial effects of six inorganic antibacterial agents including basic magnesium hypochlorite, two zinc oxide whisker (ZnOw) antibacterial complexes and three silver containing compounds (following Table 2.2) were assessed using broth dilution and agar dilution tests on six pathogenic bacteria associated with oral infectious diseases: Streptococcus mutans (ATCC 25175), S. mutans (Ingbritt), Actinomyces viscosus (ATCC 15987), Lactobacillus casei (ATCC 393), Staphylococcus aureus (ATCC 29213) and Candida albicans (ATCC 90028).

The six inorganic antibacterial agents can significantly inhibit the growth of six common oral bacteria in vitro. Both silver ion and zinc ion-containing agents can effectively kill the tested oral pathogenic bacteria. The broth dilution test showed a better performance than the agar dilution test for the insoluble compounds tested. The author confirmed that the mechanism of antibacterial activity on the surface nano-ZnO are the same as shown in Eqs.2.1 to 2.6.

Tang [30] studied the nano-ZnO embedded in polystyrene in the form of ZnO/polystyrene nanocomposite latex via miniemulsion polymerization. The ZnO nanoparticles in the composite latex exhibited good dispersion ability in the polymer coating film. The composite obtained from the nanocomposite latex still exhibited antibacterial activity, with the antibacterial rate increased when the ZnO content increased from 0.5 to 5.0 wt%. At low ZnO content, the antibacterial rate under UV-light was higher than the rate under dark condition.

Table 2.2. Antibacterial rate of films added ZnO/polystyrene nanocomposite latexes under UV-light and dark condition [30].

The amount of ZnO among composite coatings (wt.%)	Antibacterial rate (%)			
	Colibacillus		<i>Staphylococcus aureus</i>	
	Light	Dark	Light	Dark
0	0	0	0	0
0.5	52	23	49	21
1.0	83	56	85	57
2.0	89	75	90	73
3.0	99	87	99	86
4.0	99	95	99	94
5.0	99	99	99	99

CHAPTER III

EXPERIMENTALS

3.1 Materials

Butylacrylate monomer and 3-methacryloxypropyltrimethoxy silane (MPS, AR) were purchased from Sigma-Aldrich, Germany. Zinc oxide (ZnO) type A (ZoNoP® Zinc Oxide Nano Particles) was donated from Nano Materials Technology Co., Ltd. (Thailand). ZnO type B (ZP 20L) was donated from Nanoscience Technology Co., Ltd. (Thailand). Potassium persulfate (KPS, production grade) was purchased from China. Polyoxyethylene nonylphenyl ether (IGEPAL CA-630, cmc = 0.083 mM or 0.005 % v/v, production grade) was purchased from Rhodia, India. Hydrophobic acrylic binder (PRIMAL ECO-36) was purchased from DOW chemical, USA. Methanol (AR) and isopropyl alcohol (AR) were purchased from Merck, Thailand. Deionized water was used throughout this work.

3.2 Procedures

3.2.1 Preparation of ZnO/PBA composite latex

3.2.1.1 Grafting of MPS onto ZnO particles

ZnO nanoparticles (2 g) were mixed with a mixture (50 mL) of water and methanol (ratio 1:4), followed by the addition of MPS (1 g). The mixture was first dispersed for 20 min through an ultrasonic instrument (2800HT, Thailand) at room temperature. The mixture was then heated to reflux for at least 4 h. At the end of the reaction, the mixture was cooled down and diluted 4 or 5 times with iso-propanol. This mixture was vacuum-filtered through poly(vinylidene fluoride) membrane (size 0.45 micron) and the ZnO powder was dried at 50°C in vacuum until dry [11].

3.2.1.2 Emulsion polymerization of butyl acrylate

The aqueous solution of 0.004 % of surfactant (CA-630) was mixed with MPS-grafted ZnO in a beaker. The content of MPS-g-ZnO was 0.3% by weight per volume. The mixture was then sonicated by ultrasonic instrument for 30 min at room temperature. The dispersion was then poured into a four-neck flask that equipped with a stirrer. The flask was heated to 65°C under N₂ atmosphere. Liquid BA monomer was prepared in the amount of 5-20 % by weight compared to total latex solution. The monomers were introduced by drill-feeding into the flask and kept in the react for 1.30 hr. The flask was then heated to 75°C, followed by the addition of initiator solution (0.25-3% by weight of monomer) [6]. During the polymerization, the reaction mixture was maintained at 75°C for 2-6 h. After that the latex was cooled down to room temperature, it was analyzed for latex stability, monomer conversion, percentage of grafting, and grafting efficiency. The emulsion polymerization recipe of ZnO/PBA nanocomposite latex is shown in Table 3.1.

Table 3.1. The emulsion polymerization recipe of ZnO/PBA nanocomposite latex.

Chemical Name	% wt
Butylacrylate monomer	5-20
Modified ZnO	0.3
IGEPAL CA-630	0.004
KPS	0.05-0.2
Deionized water	94.7

3.2.2 Characterization of ZnO grafted with MPS and ZnO/PBA nanocomposite latex

3.2.2.1 Chemical functional group of grafted with MPS and ZnO/PBA nanocomposite particle

A Fourier transform infrared spectrophotometer (FT-IR) analysis was performed on IR spectrophotometer (Spectrum100, Perkin Elmer). FT-IR was used to characterize the functional groups of the two types of ZnO particles (type

A and B) and modified ZnO particles. ZnO powder samples were compressed with KBr into disks for IR analysis. The prepared ZnO/PBA composite latex after soxhleted was analyzed by casting the latex on NaCl cell.

3.2.2.2 Latex Stability determination

The latex was left standing in a clear screw thread vials (size: 21×70 mm, 15 mL tall) for 4 weeks. The depth of sedimentation from the surface of suspension was recorded every day for a total time of 30 days. The sedimentation percentage of the composite latex was determined by the following equation:

$$\% \text{ Sedimentation} = H/H_0 \times 100\% \quad (3.1)$$

where H (cm) is the depth of sedimentation from the surface of suspension, and H_0 (cm) is the total depth of suspension. The value shown in the result was averaged from 3 sets of experiments.

3.2.2.3 Grafting efficiency

The resulting BA-grafted ZnO particles were separated from the mixture by centrifugation at 15,000 rpm for 30 min and washed with water. The BA-grafted ZnO was then subject to soxhlet extraction using acetone as solvent, since PBA was able to dissolve in acetone. The soxhlet was performed 1 times with a total extraction time of 2 hrs.

The monomer conversion was determined by conventional gravimetric method by the following equation:

$$\text{Conversion (\%)} = [(A-B)/C] \times 100 \quad (3.2)$$

where A is the weight of total resulting particle which is the weight of ZnO plus grafted polymers, B is the weight of charged nano-ZnO particles, and C is the weight of charged monomer.

The amount of PBA grafted onto the nano-ZnO surface was also determined by gravimetric method. The percentage of grafting and its efficiency were calculated by the following equations:

$$\text{Grafting (\%)} = [D/E] \times 100 \quad (3.3)$$

$$\text{Grafting efficiency (\%)} = [D/F] \times 100 \quad (3.4)$$

where D (g) is the weight of grafted PBA, E (g) is the weight of charged ZnO particles, and F (g) is the total PBA (grafted and ungrafted polymers) formed in the system.

3.2.2.4 Micro- and nano-scale morphology analysis

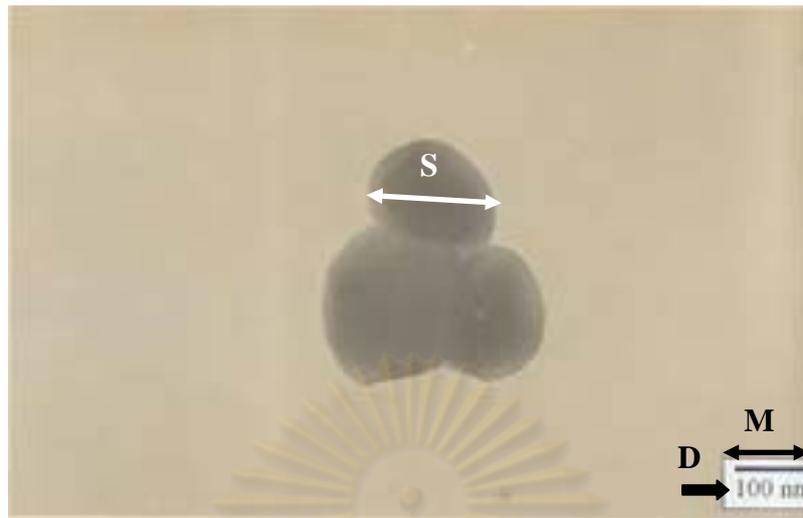
Size and dispersion behavior of nano ZnO type A and type B, MPS-g-ZnO and ZnO/PBA nanocomposite particles were studied using transmission electron microscope (TEM) and scanning electron microscope (SEM). Initially, 1% wt of either each type of the nano ZnO or ZnO-g-MPS was diluted in 98% ethanol. The mixtures were dispersed for 20 min through an ultrasonic bath at room temperature. The mixtures were then dropped on a grid and dried for 1 hour before TEM analysis. For ZnO/PBA nanocomposite latex, it was directly dropped on a grid and let dry before analysis. SEM photographs were used to determine the dispersion of the nano-ZnO in the composite latex. By the adding bare nano-ZnO type B 0.3%w of latex in commercial PBA latex and ZnO/PBA composite latex that consist of 0.3%w of latex were dry on aluminum trays in diameter 1 cm. for 3 times. Then, the films on aluminum trays were cut-off in cross-section and put on sputter .The sputters were coated with gold before the scanning electron micrographs were taken. The sample size and growing number were calculated from electron microscope images by

$$\text{Sample size} = D \times S/M \quad (3.5)$$

$$\text{Growing number} = M/S \quad (3.6)$$

where D is Directed numbers, S is length of subject and M is length of micron bar.

Example



From image

$$\begin{aligned} \text{So} \quad \text{Sample size} &= D \times S/M \\ &= 10 \mu\text{m} \times 6.0 \text{ cm}/4.2 \text{ cm} \\ &= 14.2 \mu\text{m} \end{aligned}$$

$$\begin{aligned} \text{and} \quad \text{Growing number} &= M/S \\ &= 4.2 \text{ cm} / 10 \mu\text{m} \\ &= 4200 \text{ or } 4200 \times \end{aligned}$$

where D is multiplier numbers, S is length of subject, and M is length of micron bar.

3.2.3 UV shielding property

The ZnO/PBA nanocomposite latex and PBA latex were dip-coated to the 3/4 of total length of both sides of each quartz cuvettes. Then the latex-coated cuvettes were dried at 60°C for 5 min. The coated cuvettes were then analyzed in a UV spectrometer, using bare quartz cuvette as blank.

3.2.4 Antibacterial property

The antibacterial test was performed according to the agar dilution susceptibility method. *E. coli* and *S. aureus* were two bacterial strains selected for testing. Ampicillin 50 mg/mL was used as a positive control. First, fresh culture of spawn raising under $37\pm 1^\circ\text{C}$ over 24 h was washed down by physiological saline and used as bacterial suspension. The growth medium was agar mixed with the ZnO samples in different concentration. Second, the bacterial suspension of 100 μL was dropped on to the agar in growth medium plates. All plates were kept at $37\pm 1^\circ\text{C}$. After 24 h, the bacteria were washed off using physiological saline. The colony forming units (CFU) of bacteria were counted. The antibacterial concentration was calculated via the conventional calculation.

For example: Calculation of *S. aureus* type.

In spread there is 100 μL of bacterial suspension. If the concentration of dilute is 10^{-6} , the content of bacteria can be calculated as follows.

In a bacterial suspension of 100 μL , the amount of bacteria is 72 colonies.

So in bacterial suspension of 1 mL, the content of bacteria is

$$(1 \times 10^{-3}) \times 72 / (100 \times 10^{-6}) = 720 \text{ CFU/mL}$$

After 10^{-6} dilution, the bacteria content in the suspension is $720 / (1 \times 10^{-6})$

$$= 720 \times 10^6 \text{ CFU/mL}$$

The antibacterial rate (*R*) was calculated via the following equation:

$$R(\%) = [(B-A)/B] \times 100 \quad (3.7)$$

where *B* is the CFU of blank sample and *A* is the CFU of sample films.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Modification of nano-ZnO with MPS

In order to obtain stable composite latex of ZnO-PBA, the nano-ZnO particles must be modified by attaching hydrophobic group on the particle surface with the purpose to reduce polar-polar interaction among the particles. In the first step, ZnO particles were reacted with MPS, so that the surface of ZnO was chemically linked with MPS via zinc-oxygen-silicon bonding (Fig. 4.1). On the other end of MPS molecule, a double-bond group (C=C) became an initiation point for butylacrylate polymerization which was carried out in the next step.

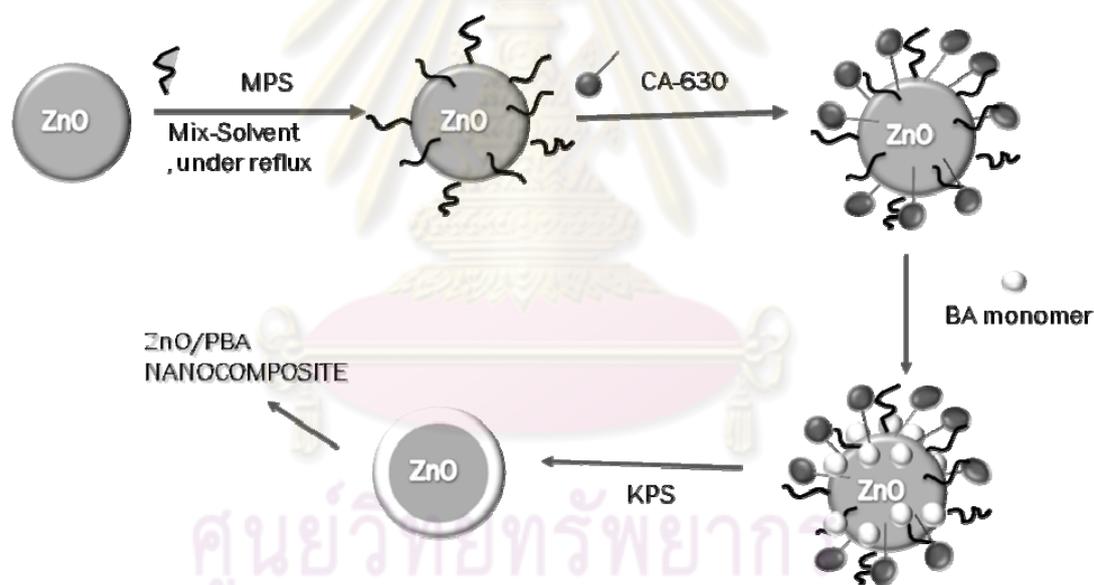


Figure 4.1. Synthesis step of nano-ZnO/poly(butylacrylate) composite by *in situ* emulsion polymerization.

Two types of ZnO particles were compared for its ability to be grafted by MPS. ZnO type A was prepared by spray-drying process (Fig. 4.2) at 600-1,000 °C. The zinc acetate aqueous solution was ultra-sonicated becoming droplets and transported into a reaction furnace using air as a carrier gas. The reaction furnace consisted of four independent heating zones, of which temperatures were set at

600, 700, 800, and 1000 °C, respectively [29]. ZnO type B was obtained from the spray-drying at one fixed temperature of 600°C.

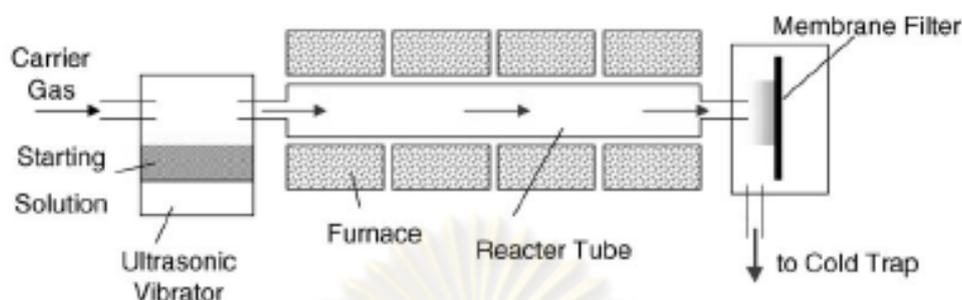


Figure 4.2. Synthesis of nano-ZnO particles by spray pyrolysis [26].

The two ZnO types, as analyzed by FTIR, possess different functional group features especially at a region from 800 to 1700 cm^{-1} (Fig. 4.3). There are more organic functional groups remained in the ZnO type B than those found in type A. In the spectra of both types, the broad absorption band at 3436 cm^{-1} indicates the presence of -OH which is generally found on the surface of ZnO particles. And for only ZnO type B, the peaks at 1738, 1508, 1383, 1217, and 836 cm^{-1} belonging to C=O str, C=C str, CH bending, C-O bending, and CH_2/CH_3 bending, respectively, were clearly observed. This can be explained by the fact that both ZnO particles were prepared from zinc acetate that was subjected to pyrolysis process to prepare the ZnO particles [9, 29]. At low temperature (600 °C), some organic functional groups evidently remained in the particles type B.

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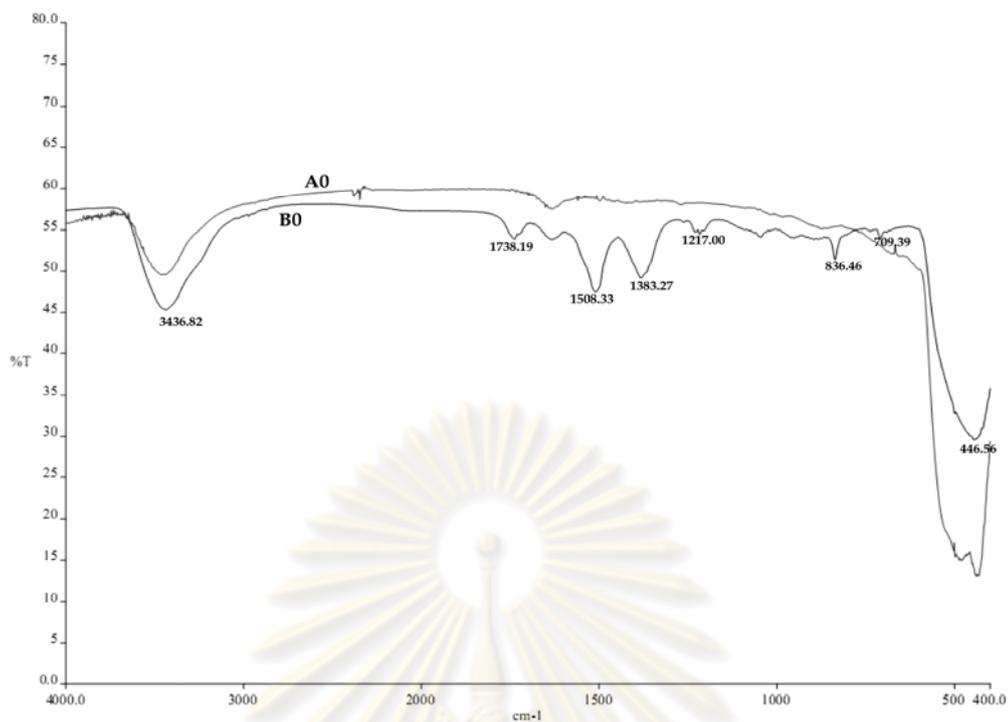


Figure 4.3. FTIR spectra of nano-ZnO particles type A (A0) and type B (B0).

The success of MPS-grafting on nano ZnO type A and B was followed by FTIR analysis. Results and MPS-grafting conditions are listed in Table 4.1.

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Table 4.1. Preparation condition and FTIR spectroscopy results of MPS-grafted nano-ZnO.

No.	ZnO(g)	Solvent (total 50 ml)	MPS (g)	Method	FT-IR Spectrum band detection ¹					Remark
					-OH	Si-O Stretch	Si-O- Zn	C=O	CH ₃ ,CH ₂ of silane	
					3400 cm ⁻¹	900- 1100 cm ⁻¹	1130, 1010 cm ⁻¹	1725 cm ⁻¹	2800- 3000 cm ⁻¹	
A0	2	0	0	0	✓	✗	✗	✗	✗	ZnO type A
A1	6	MeOH	1.5	reflux	✓	✗	✗	✗	✗	Amount test
A2	2	MeOH	0.5	reflux	✓	✗	✗	✗	✗	
A3	2	MeOH	0.5	reflux@low temp (<100°C)	✓	✗	✗	✗	✗	Method Test
A4	2	MeOH	0.5	Stir for 12h.	✓	✗	✗	✗	✗	
A5	2	MeOH	1	reflux@low temp (<100°C)	✓	✗	✗	✗	✗	Vary MPS' amount
A6	2	MeOH	1	Stir for 12h.	✓	✗	✗	✗	✗	
A7	2	MeOH+H ₂ O 40:10	1	reflux@low temp (<100°C)	✓	✗	✗	✗	✗	Good solvent test
A8	2	MeOH+H ₂ O 40:10	1	Stir for 12h.	✓	✗	✗	✗	✗	
A9	2	MeOH	2	reflux@low temp (<100°C)	✓	✗	✗	✗	✗	Vary MPS' amount
A10	2	MeOH	2	Stir for 12h.	✓	✗	✗	✗	✗	
A11	2	MeOH+H ₂ O 40:10	2	reflux@low temp (<100°C)	✓	✗	✗	✗	✗	Vary MPS' amount
A12	2	MeOH+H ₂ O 40:10	4	reflux@low temp (<100°C)	✓	✗	✗	✗	✗	
A13	2	MeOH+H ₂ O 40:10	8	reflux@low temp (<100°C)	✓	✗	✗	✗	✗	
A14	2	MeOH+H ₂ O 40:10	2	reflux in water bath	✓	✗	✗	✗	✗	Method test
A15	2	MeOH+H ₂ O 40:10	1	reflux@low temp (<70°C)	✓	✗	✗	✗	✗	
B0	2	0	0	-	✓	✗	✗	✗	✗	ZnO type B
B1	2	MeOH + H ₂ O 40:10	1	reflux@low temp (<60°C)	✓	✓	✓	✓	✓	Vary MPS' amount
C	2	MeOH + H ₂ O 40:10	2	reflux@low temp (<60°C)	✓	✓	✓	✓	✓	

¹ ✓ = detected ✗ = non-detected

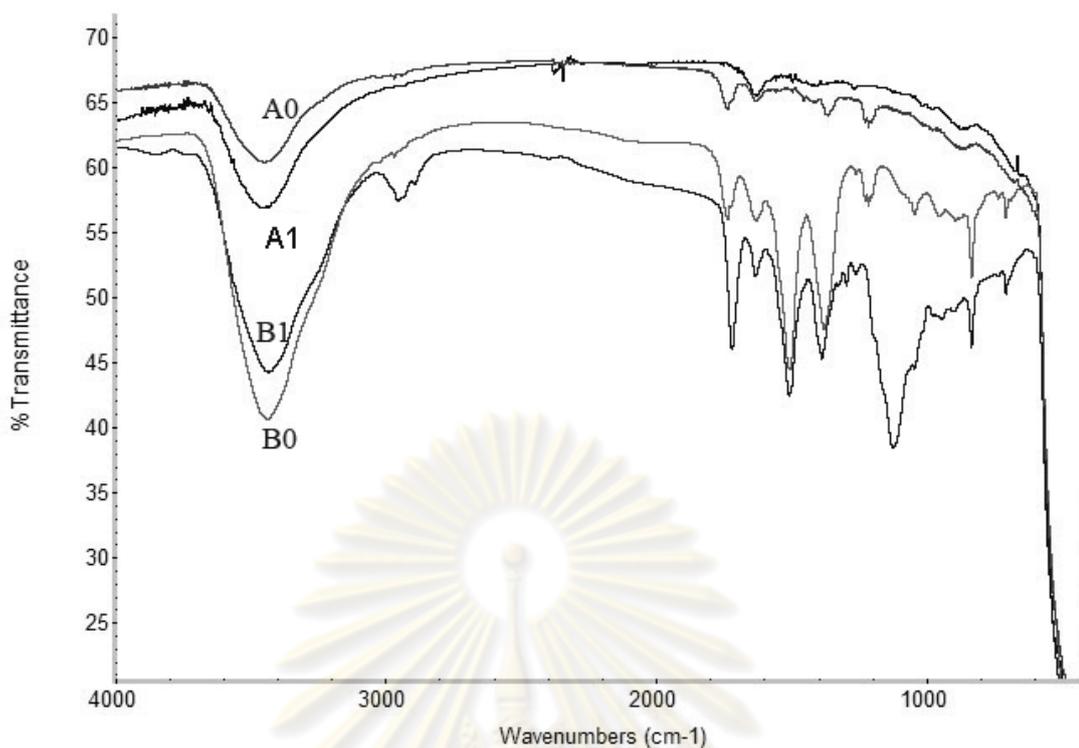


Figure 4.4. Comparison of the FTIR spectra of nano-ZnO particles type A (A0) and type B (B0); nano-ZnO particles modified by MPS from type A (A1) and type B (B1).

From Table 4.1 and Fig. 4.4, only ZnO B1 shows IR band at $1,127\text{ cm}^{-1}$, belonging to Zn-O-Si or Si-O-Si bond. In addition, an increase of C-H stretching signal (from MPS molecule) was observed at $2,955\text{ cm}^{-1}$. These two evidences suggest that the chemical bonding between ZnO and MPS is achieved for the ZnO type B. It should be noted here that any non-bonded MPS was washed away from these two modified particles by extraction before the IR analysis.

In conclusion ZnO type B was preferably used in this work. The grafting of MPS on nano-ZnO was successfully carried out with the grafting content of 37% by weight of ZnO type B as determined by sohxlet extraction. The MPS-g-ZnO particles were then subjected to the emulsion polymerization of butylacrylate.

4.2 Emulsion polymerization of butyl acrylate on MPS-grafted ZnO nanoparticles

An optimal condition to prepare stable nano ZnO latex was investigated. The amounts of chemicals used to carry out the emulsion polymerization are shown in Table 4.2.

Table 4.2. Formulation of BA emulsion polymerization process in the presence of MPS-g-ZnO (B).

No	Monomer to water ratio	Ingredient (% w/w)					% Residual solid	Remark
		Butylacrylate (%)	Water (%)	IGEPAL CA-630 (%)	KPS (1% of monomer)	Modified ZnO (%)		
1	20:80	20	80	0.03	0.2	0.3	2	over CMC and vary ZnO content
2	20:80	20	80	0.03	0.2	0.15	2	
3	5:95	5	95	0.004	0.05	0.3	0.3	under CMC and vary monomer concentration
4	10:90	10	90	0.004	0.1	0.3	0.5	
5	20:80	20	80	0.004	0.2	0.3	0.8	

To ensure the dispersion of nano-ZnO system in water, the amount of surfactant (IGEPAL CA-630) used was critical toward latex stability [14]. As shown in Table 4.3, the amount of surfactant was varied at 0.03 and 0.004%, which were over and under its CMC (CMC = 0.083 mM or 0.005 % v/v), respectively. At the high surfactant content, the latex tended to be unstable. Aggregation of latex particles was observed. However, when the amount of CA-630 was reduced to 0.004%, the latex was quite stable and homogeneous. It was expected that the grafted ZnO particles were surrounded by the surfactant. One end of CA-630 is hydrophilic; helping nano-ZnO suspending in the emulsion. The other hydrophobic end of CA-630 points to the MPS layer that was previously grafted on the ZnO particles. This can create a suitable environment for the fairly hydrophobic butyl acrylate monomer to be later adsorbed on the MPS layer, which is also an initiating point for further polymerization of the BA. Chain propagation can then take place from the MPS-grafted on the ZnO surface, and finally becoming a thin layer of PBA covering the core ZnO particles. This was proven by the results of FT-IR and TEM shown in Fig. 4.5 and 4.6.

Figure 4.5 illustrates the spectrum from FTIR analysis, providing information of the frequency of absorbed band of PBA on the surface of the nano ZnO. It can be clearly seen that the intensities of carbonyl peak at $1,730\text{ cm}^{-1}$ and C-H stretching peak at $2,885$ and $2,953\text{ cm}^{-1}$ increase dramatically after the BA polymerization. This is caused by the long chain length of PBA that are present on the surface of nano-ZnO possibly anchoring via the grafted MPS molecules.

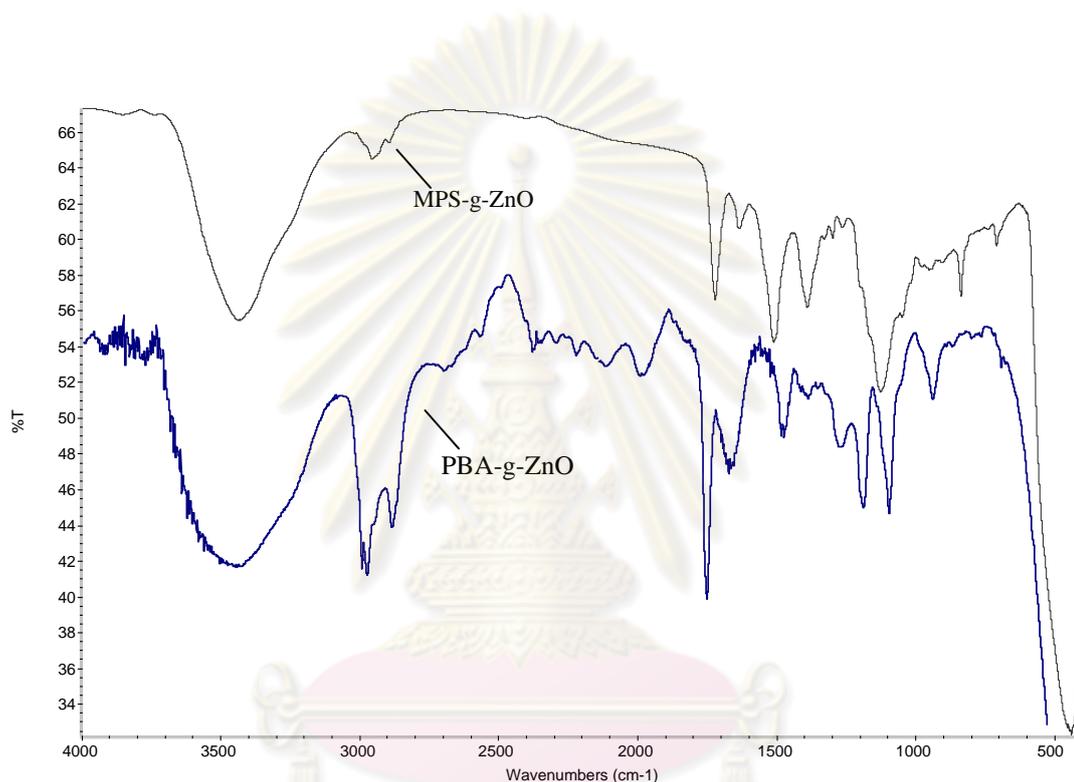


Figure 4.5. Comparison between the FT-IR spectra of MPS-g-ZnO particles (type B) before and after emulsion polymerization process of butyl acrylate.

This method led to an encapsulation of the ZnO particle by PBA layer. Visualization of the nanocomposite ZnO particle was carried out by TEM (Fig. 4.6). Figure 4.6 shows the spherical morphology of nano-ZnO particles type A, type B, and MPS-g-ZnO type B, with the mean size of 20–80 nm. In Figure 4.6d, light-toned shell layer surrounding the dark-toned ZnO particle can be observed. This outer shell is most likely the PBA layer that was grafted on the ZnO particles via the MPS coupling agent. The mean size is ~100 nm as determined by measuring the length of objects in the electron microscope images, multiplied by

the direct number that under micron bar, and dividing by the length of the micron bar shown.

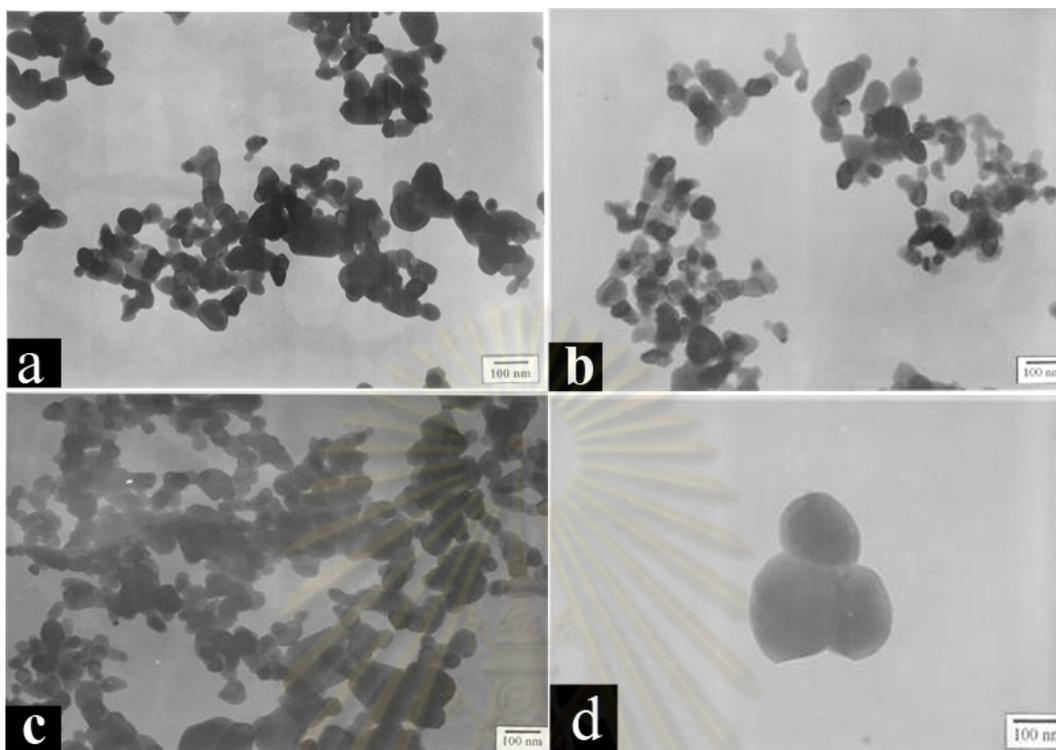


Figure 4.6. TEMs of nano-ZnO particles type A (a), type B (b), nano-ZnO particles type B modified by MPS (c), and ZnO/PBA composite particles (d).

It was found that the emulsion polymerization of BA (5 wt% of latex weight) in the presence of MPS-g-ZnO resulted in the grafting weight of PBA on the particles of 162% with a grafting efficiency of 36%. The calculation method of grafting weight and efficiency is listed in Chapter III under section 3.3. The conversion of the monomer to PBA in this system was only 42%. This was possibly due to the fact that BA monomer was rather hydrophobic and therefore did not mix well with the emulsion.

Table 4.3-4.5 show the improvement of grafting weight of PBA on the MPS-modified ZnO by varying BA monomer content in latex, reaction time, and the ratio of KPS to monomer.

The effect of initial BA content on the degree of grafting was listed in Table 4.3. Increasing the initial amount of BA from 5-10% resulted in an increase of degree of grafting and grafting efficiency, as well as the conversion of monomer. The grafting of PBA chains embedded into the surface of nano-ZnO increased from 162% to as high as 3905% with grafting efficiency value of up to

92%. This means that the weight of organic polymers grafted on ZnO particles was increased to over 39 folds. Also, 92% of all PBA chains formed were successfully grafted onto the surface of MPS-g-ZnO particles. Nevertheless the conversion of BA monomer to polybutylacrylate was at the maximum of 65%.

Table 4.3. The effect of BA content on the percentage of conversion, grafting, and grafting efficiency of BA in the emulsion polymerization process with MPS-g-ZnO particles.

%BA monomer	%Conversion	Graft(%)	Grafting efficiency(%)	%Homo PBA
5	43	162	36	64
10	50	1395	81	19
20	65	3905	92	8

¹The amount of BA is in percentage by weight of latex. The polymerization was carried out using KPS (1% of monomer) as initiator and reaction time of 3 hr in 0.3%w of MPS-g-ZnO particles.

In the polymerization of PBA on the nano-ZnO surface by using 5%wt BA and KPS (1% of monomer) as initiator in 0.3%w of MPS-g-ZnO particles, the reaction times (from 120-360 min) did not affect the degree of BA grafting and monomer conversion (Table 4.4).

Table 4.4. The effect of reaction time on the percentage of conversion, grafting, and grafting efficiency of BA in the emulsion polymerization process with MPS-g-ZnO particles.

Time (min.)	%Conversion	Graft(%)	Grafting efficiency(%)	%Homo PBA
120	43	168	36	64
180	43	162	36	64
240	45	161	35	65
360	47	166	35	65

¹The polymerization was carried out using 5%wt BA and KPS (1% of monomer) as initiator in 0.3%w of MPS-g-ZnO particles.

In this study, the amounts of KPS added were varied from 0.25, 0.5, 1 and 3% of BA weight. The correlation between the added KPS amount and degree of grafting was not, however clear. It was found that when the amount of KPS was 0.5% of BA monomers, the grafting weight of PBA on MPS-g-ZnO, and the graft efficiency were at the maximum. In general increasing the initiator content would result in an increasing of initiating point, in this work, at the olefinic end of MPS and on the BA monomer. In the formal case, the grafting content will increase, where in the later case, free homo PBA would be obtained at a higher yield. However in this work the conversion of BA to PBA in this system was rather low (from < 56%). The low conversion suggested that a portion of monomers could not take part in the emulsion polymerization. Although the initiator content was adjust from 0.25–3% of monomers weight. Two explanations that can be made at this point are, the initiator was not active due to improper control of N₂, and improper missing of BA monomers in the emulsion. From these results, it is possible that the amount of KPS of 0.5% is the highest initiator concentration that can be absorbed on the nano-ZnO surface for initiating the C=C bond of MPS [31].

Table 4.5. The effect of initiator amount on the percentage of conversion, grafting, and grafting efficiency of BA in the emulsion polymerization process with MPS-g-ZnO particles.

KPS (% of monomers)	%Conversion	Graft(%)	Grafting efficiency(%)	%Homo PBA
0.25	37.27	189.27	39.99	60
0.5	55.82	647.99	81.70	18
1	42.52	161.85	36.03	64
3	40.12	157.83	34.80	65

¹The amount of KPS is in percentage by weight of BA monomer. The polymerization was carried out using 5% BA and reaction time of 3 hr in 0.3%w of MPS-g-ZnO particles.

In conclusion, the optimal condition to prepare the nanocomposite latex of ZnO-poly(butylacrylate) was to use initial BA contents of 0.5 wt%, the reaction time of 180 hr, the initiator concentration of 0.5 wt% of monomer wt, MPS-g-ZnO of 0.3 wt%, and surfactant amount of 0.0004 wt%.

4.3 Latex Stability determination

In this section, the stability of latex was investigated by means of measuring the height of sedimentation when the latex was stored undisturbed for 4 weeks. The results are reported in terms of the ratio between the height of sediment and the suspension as shown in Fig. 4.7.

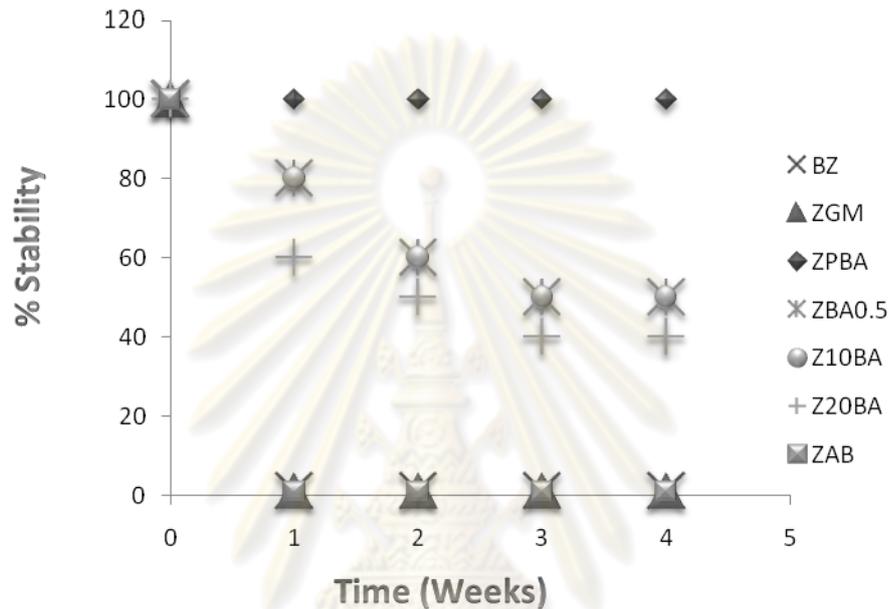


Figure 4.7. Comparison of suspension stability: bare nano-ZnO in mixed-solvent between MeOH:H₂O (4:1) (BZ), MPS-g-ZnO 0.3% w/w in MeOH:H₂O (4:1) (ZGM), ZnO/PBA latex prepared from 1% KPS 5% BA (ZPBA), 0.5% KPS 5% BA (ZBA0.5), 1% KPS and 10% BA (Z10BA), 1% KPS and 20% BA (Z20BA), and commercial nano-ZnO latex for fabric coating (ZAB; ZnO 0.3 wt% with negative acrylic binder 1 wt%).

From Fig. 4.7, the non-modified ZnO particles in MeOH-water (4:1) mixed medium (BZ), MPS-g-ZnO particles in MeOH:H₂O (ZGM), and commercial nano-ZnO latex (ZAB) settled to the bottom of medium almost immediately. The ZnO/PBA composite latexes prepared from MPS-g-ZnO particles in this work; sample ZBA0.5, Z10BA, and Z20BA, slowly settled during the studied period (4 weeks). On the other hand, sample ZPBA which was the ZnO/PBA composite latex prepared from using 1% KPS and 5% BA, remained stable without any observable sedimentation for as long as 4 weeks. In this

sample, the degree of BA grafting was 162%. It should be emphasized here that the most stable latex sample *ZPBA* was not the one prepared by using the optimal condition of BA grafting (0.5% KPS, 5% BA, 0.3% MPS-g-ZnO), as reported in Table 4.5, section 4.2. The result of latex stability test suggests that, for the latex prepared by using the optimal method, the amount of organic polymer PBA grafted on MPS-g-ZnO particles was as high as 648%. This amount of organic polymer was somewhat too much to retain the latex stability in this latex system.

Since the goal of this work was to prepare composite latex that can be used commercially, the stability of latex during storage was a major requirement. Therefore the composite latex sample *ZPBA* was further investigated for its UV-shielding and antibacterial activity.

4.4 Scanning electron microcopy analysis

In order to determine the dispersibility of the prepared nano ZnO particles in the prepared composite PBA latex, the ZnO/PBA composite latex was cast as films were investigated by SEM. For comparison, a film prepared from non modified ZnO nanoparticles (0.3 wt %) mixed with PBA commercial-grade latex was also studied.

Figure 4.8 shows microscopic images of nano-ZnO type A and B and MPS-g-ZnO. In general the morphology of ZnO type A, type B, and the MPS grafted ZnO type B particles was not distinctively different.

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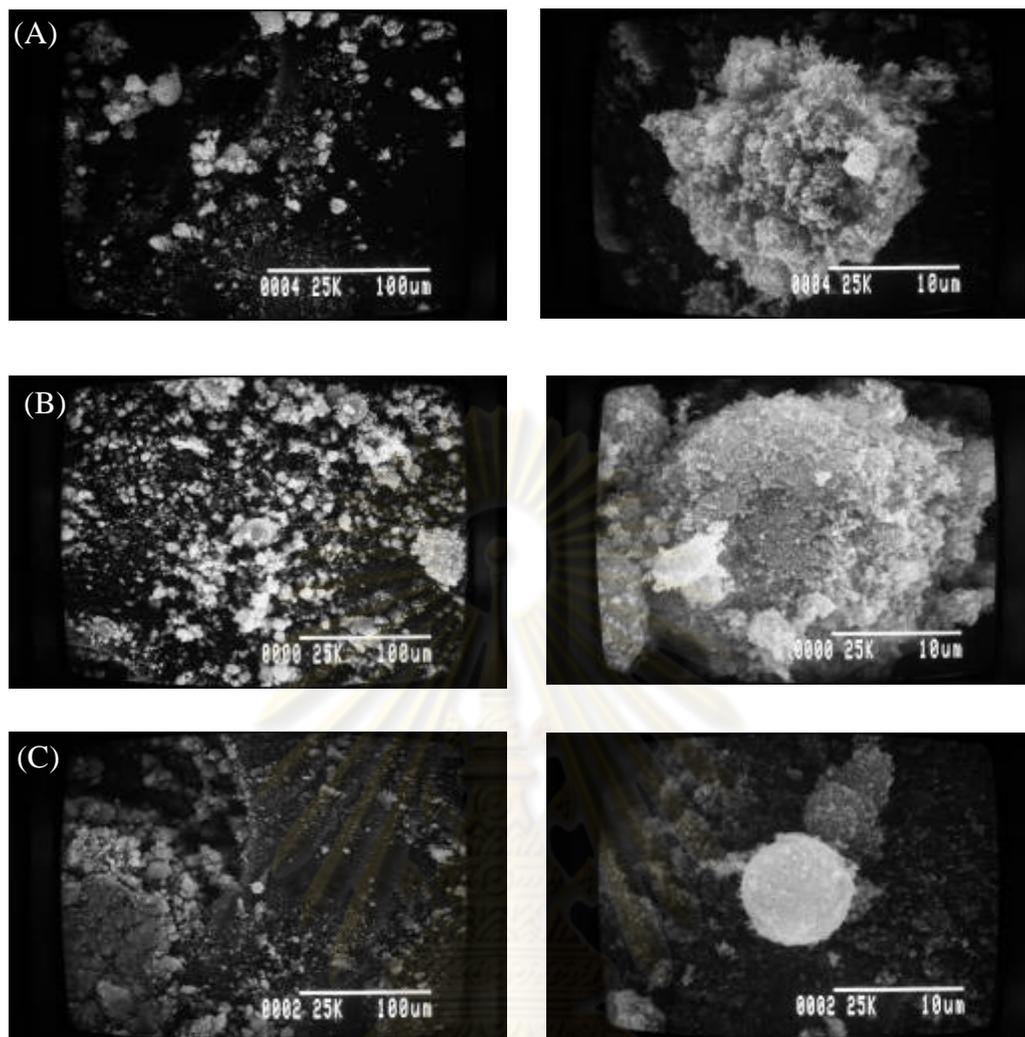


Figure 4.8. Scanning electron micrographs of (A) nano-ZnO type A, (B) nano-ZnO type B, and (C) MPS-g-ZnO from ZnO type B. [left- 500 ×, right- 5,000 ×].

The dispersion of treated and untreated ZnO nanoparticles in PBA matrix is displayed in Fig. 4.9. Dark toned area is PBA matrix from the scissor-cut cross section of the film obtained from the untreated ZnO particle in PBA latex [Fig. 4.9(A)] and the prepared ZnO/PBA composite latex (Fig. 4.9(B)). The ZnO particles in Fig. 4.9(A) were clearly observed on the organic matrix, whereas the particles were rarely seen in Fig. 4.9(B). The more homogeneous dispersion of treated ZnO nanoparticles in the PBA was probably the consequence of MPS and PBA grafting steps, which caused the reduction of highly polar hydroxyl groups on the ZnO particles. Therefore the polymer chain grafted on the composite particle supported the dispersion stability of ZnO nanoparticles.

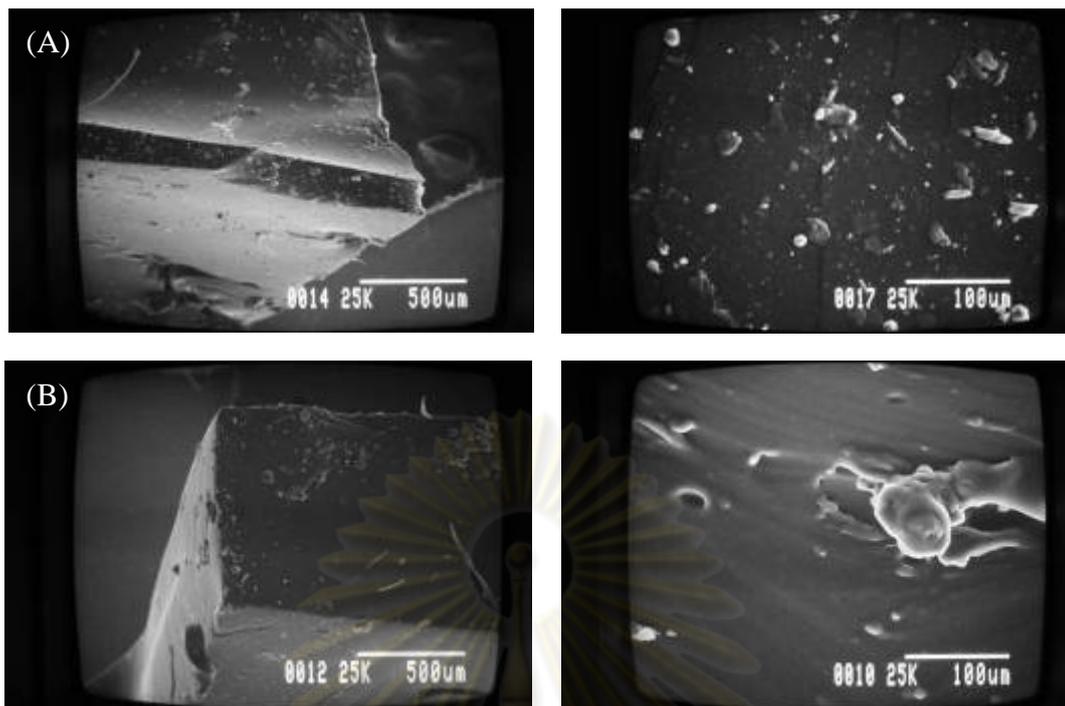


Figure 4.9. Scanning electron micrographs of cross-section (left) and top viewed (right) of film samples prepared from (A) unmodified ZnO particles mixed into commercial PBA latex and (B) ZnO/PBA nanocomposite latex prepared in this studied. [left- 100 ×, right- 500 ×].

4.5 UV-shielding properties

The light absorbing properties of ZnO/PBA nanocomposite particles were measured. The tested latex was cast into a thin film layer coated on the both of the side panels of cuvette that used in a UV spectrophotometer. The coated films of both ZnO/PBA nanocomposite and ZnO-free PBA were hazy and pale white.

The absorbance spectra of ZnO/PBA composite film and ZnO-free PBA film were compared as shown in Fig. 4.10. It is clearly seen that the ZnO/PBA nanocomposite (a) possesses higher absorption in both UV (<400 nm.) and visible region (400-750 nm.) than the PBA films (b). This is most likely a result of the presence of nano-ZnO at the amount of 0.3 wt% in the latex. As reported by others [6,2], UV shielding property of polymer films can be improved by the addition of ZnO nano-particles. Thus the nanocomposite latex prepared in this work can be used as a UV absorbance material for coating.

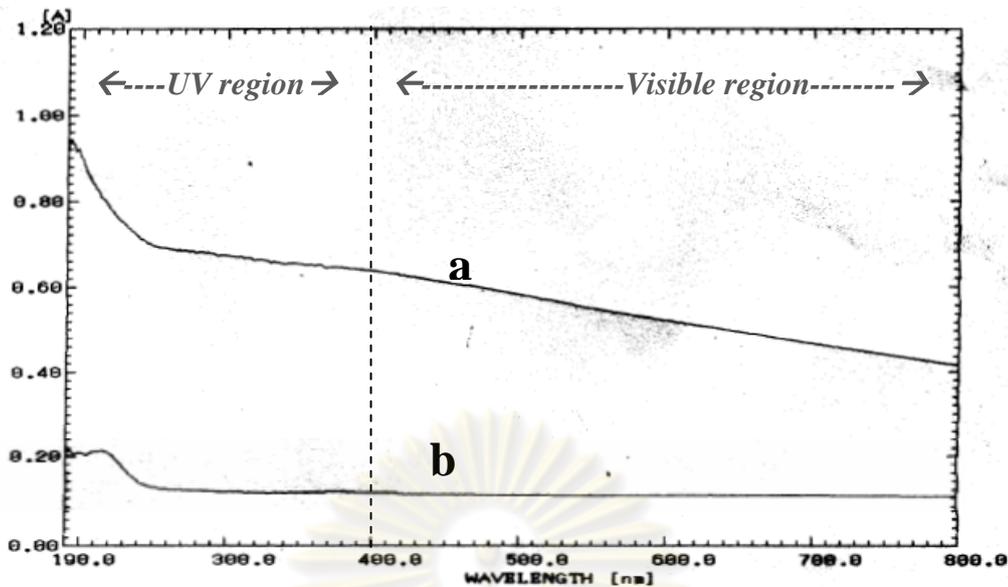


Figure 4.10. Absorbance spectra of (a) nano-ZnO/PBA composite latex compared to (b) PBA latex- Both analyses were performed by coating the latex on dry quartz cuvette.

4.6 Antibacterial property

The antibacterial property was investigated by 2 methods- disk diffusion and agar dilution.

In the disk diffusion method, the tests were performed by dropping the tested latex on round filter papers (Fig. 4.11) and squared cotton clothes (Fig. 4.12). From Fig. 4.11, there was no 'clear zone' indicating antibacterial activity surrounding the filter papers on which ZnO-free PBA and ZnO/PBA composite latexes were spotted on. This implies that the tested samples do not show antibacterial activity.

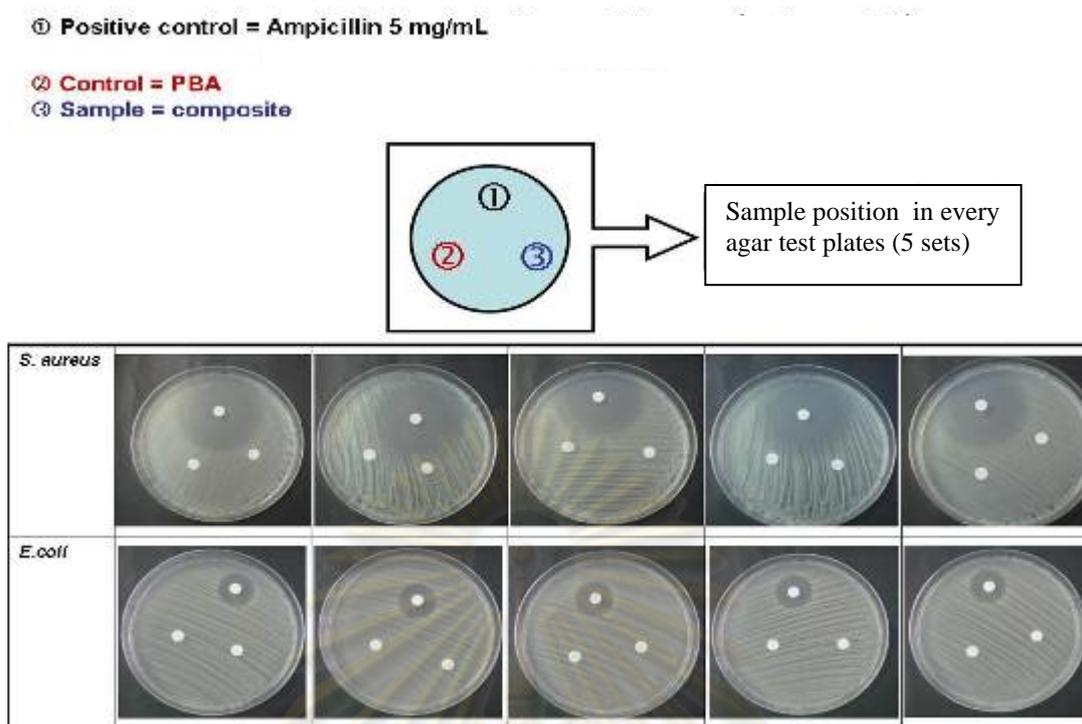
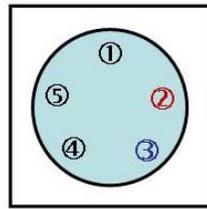


Figure 4.11. Disk diffusion method using filter papers to test the antibacterial activity of PBA and ZnO/PBA composite latex compared with ampicillin positive control.

In Fig.4.12, again, the prepared ZnO/PBA composite latex, nano-ZnO type A, and B showed *no* antibacterial activity against *E. coli*. It was, however, found that in the case of *S. aureus* (Fig. 4.13), only the unmodified ZnO type A and B showed some antibacterial activity since small areas of clear zones were observed surrounding the samples at position 4 & 5 in the agar plates, but the ZnO/PBA composite latex also did not have any activity as in the *E. coli* testing. The reason behind this unexpected result is that the organic polybutylacrylate can possibly block the contact between the ZnO nanoparticles and the bacteria. Without this contact, ZnO cannot react with the cell wall of the bacteria, which was reported to be an important step toward bactericide activity. In the next test, an agar dilution susceptibility method was used to support this assumption.

- ① Control = Blank cotton
- ② Positive control = Ampicillin 5 mg/mL
- ③ Sample = composite
- ④ ZnO₂ A
- ⑤ ZnO₂ B



Sample position in every agar test plate.

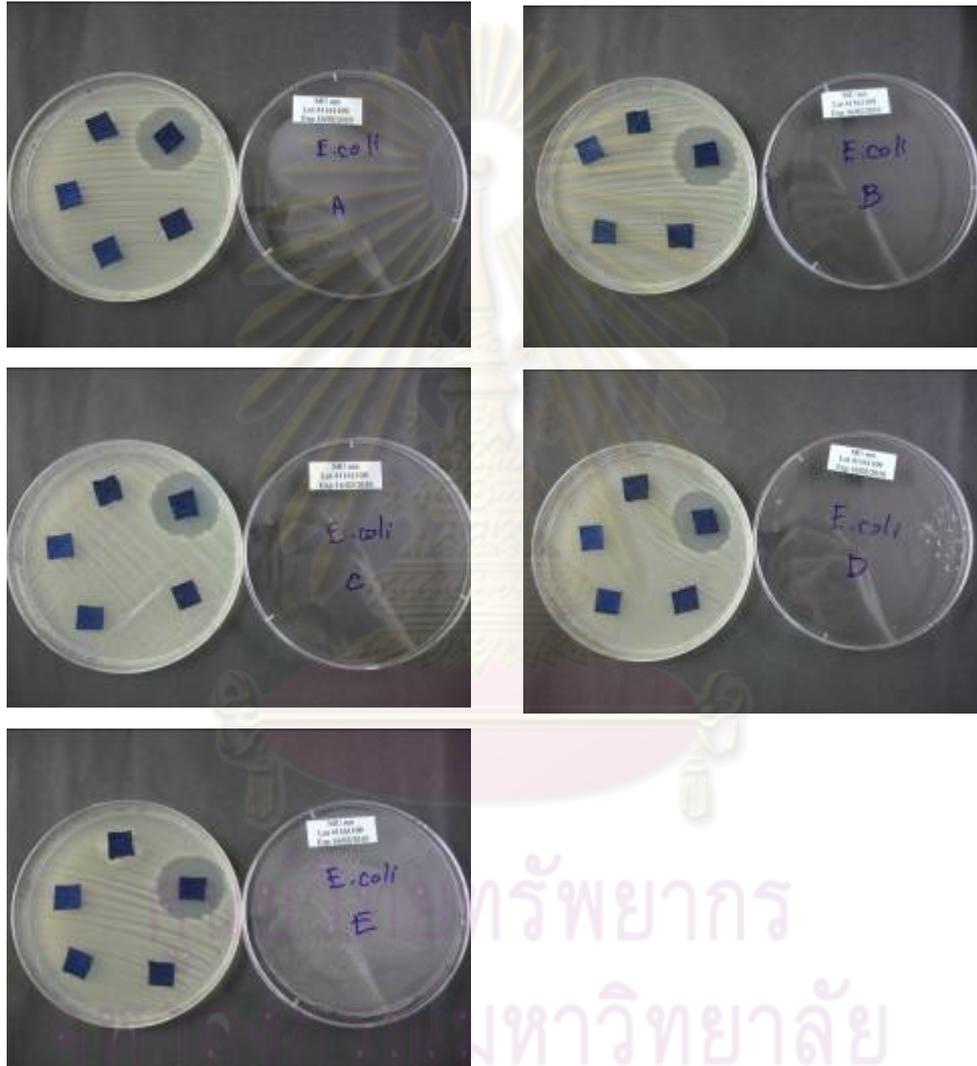
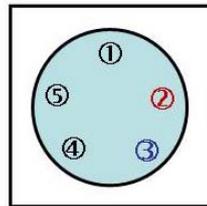


Figure 4.12. Disk diffusion method using cotton clothes to test the antibacterial activity against *E. coli* of ZnO/PBA composite latex, nano-ZnO type A, and type B, compared with ampicillin positive control.

- ① Control = Blank cotton
- ② Positive control = Ampicillin 5 mg/mL
- ③ Sample = composite
- ④ ZnO₂ A
- ⑤ ZnO₂ B



Sample position in every agar test plate.

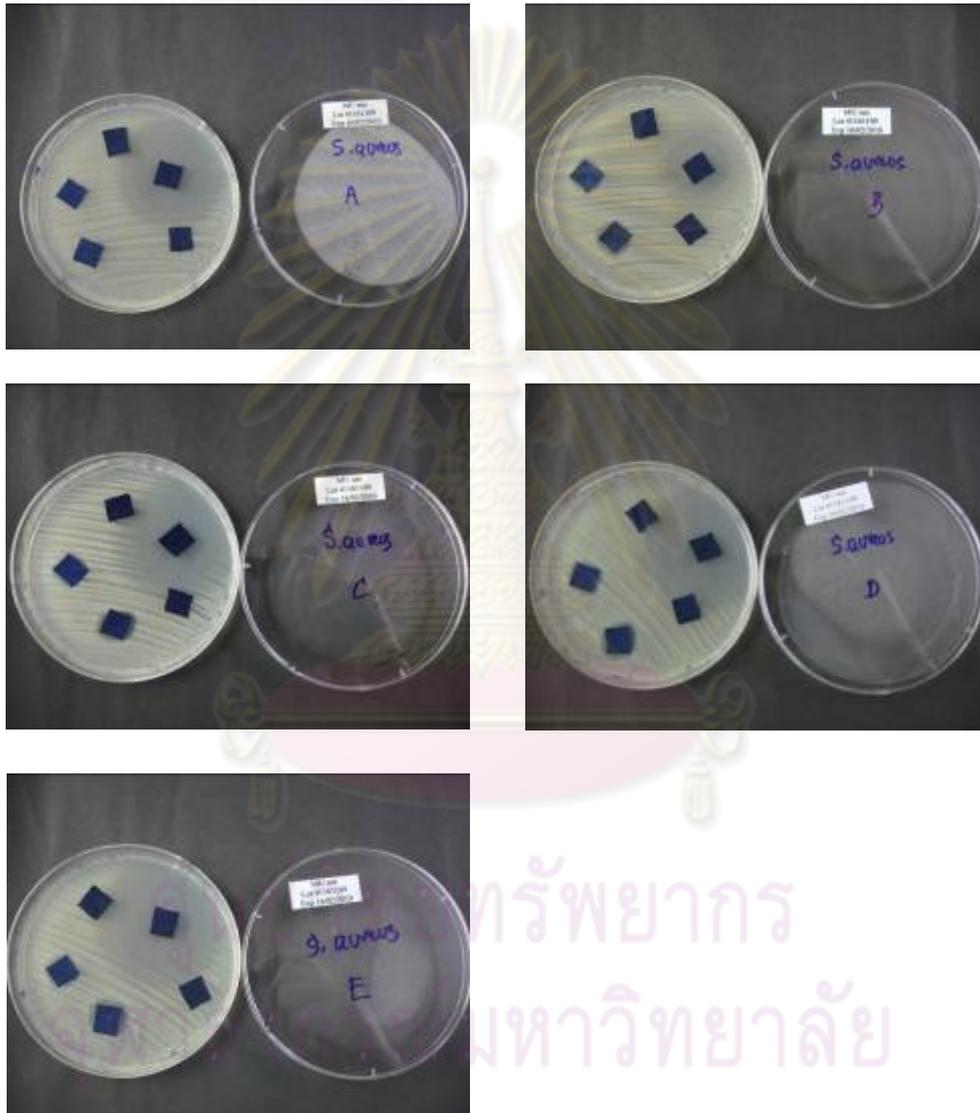


Figure 4.13. Disk diffusion method using cotton clothes to test the antibacterial activity against *S. aureus* of ZnO/PBA composite latex, nano-ZnO type A, and type B, compared with ampicillin positive control.

Table 4.6. Antibacterial rate of antibacterial test by agar dilution susceptibility method against *S. aureus* and *E. coli*.

[The lower the CFU value, the higher the antibacterial activity]

<i>S. aureus</i>	CFU/mL $\times 10^6$	%R	<i>E. coli</i>	CFU/mL $\times 10^6$	%R
negative control	830	0	negative control	1183	0
10% composite	927	-11.65	10% composite	2093	-76.90
20% composite	1270	-53.01	20% composite	1987	-67.89
30% composite	1283	-54.62	30% composite	1963	-65.92
40% composite	917	-10.44	40% composite	2033	-71.83
50% composite	823	0.80	50% composite	2047	-72.96
10% ZnO ₂ A	0	100	10% (v/v) ZnO ₂ A	1860	-57.18
20% ZnO ₂ A	0	100	20% (v/v) ZnO ₂ A	1780	-50.42
30% ZnO ₂ A	0	100	30% (v/v) ZnO ₂ A	1330	-12.39
40% ZnO ₂ A	0	100	40% (v/v) ZnO ₂ A	1383	-16.90
50% ZnO ₂ A	0	100	50% (v/v) ZnO ₂ A	1300	-9.86
10% ZnO ₂ B	0	100	10% (v/v) ZnO ₂ B	1220	-3.10
20% ZnO ₂ B	0	100	20% (v/v) ZnO ₂ B	613	48.17
30% ZnO ₂ B	0	100	30% (v/v) ZnO ₂ B	0	100
40% ZnO ₂ B	0	100	40% (v/v) ZnO ₂ B	0	100
50% ZnO ₂ B	0	100	50% (v/v) ZnO ₂ B	0	100
positive control	0	100	positive control	0	100

By agar dilution susceptibility method, the antibacterial property of the composite latex was carried out by determining CFU value (The colony forming units) of the latex, compared with unmodified ZnO particles (Table 4.6). It was found that the CFU value of every concentration of the prepared ZnO/PBA latex was quite high and almost equaled to the value of negative control (only agar in growth medium). This indicated that the composite latex did not have any antibacterial properties against both *S. aureus* and *E. coli* bacteria strains as also concluded from the disk diffusion method. However both the untreated ZnO type A and B in fact showed *strong* antibacterial effect. This finding confirms published reports [28, 33] that bare ZnO particles possess antibacterial activity. Here, in this work, it is most likely that the modified ZnO particles in the ZnO/PBA nanocomposite are covered by polybutylacrylate. There was no contact between ZnO nanoparticle and the tested bacteria [33]. Therefore the composite

latex did not show antibacterial activity under the test condition performed in this work.



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CHAPTER V

CONCLUSIONS AND SUGGESTION

5.1 Conclusions

Nanocomposite latex of polybutylacrylate and zinc oxide nanoparticles was prepared by means of emulsion polymerization of butyl acrylate monomer. The nano ZnO particles were enclosed by PBA shell with the help of MPS acting as a coupling agent between the inorganic ZnO and organic PBA. Parameters including initial feed of surfactant (OP-10), monomer (BA), initiator (KPS), and reaction time were investigated. At high surfactant content, aggregation of latex particles was observed. The optimum amount of CA-630 was found to be 0.004%, resulting in stable and homogeneous latex. Increasing the initial amount of BA from 5-10% resulted in an increase of degree of grafting and grafting efficiency, as well as the conversion of monomer. When the amount of added KPS was 0.5% of monomer weight, the grafting weight of PBA on MPS-g-ZnO and the graft efficiency were at the maximum. The reaction times (from 120-360 min) did not, however, affect the degree of BA grafting and monomer conversion.

The latex containing 0.3 wt% of ZnO and 5 wt% of PBA remained stable for up to 4 weeks of storage at room temperature. Mixing of ZnO/PBA nanocomposite latex and PBA latex resulted in a PBA film with well-dispersed ZnO aggregates. This was probably the consequence of MPS-PBA grafting on the ZnO, causing a reduction of highly polar groups on the ZnO particles. The ZnO/PBA film obtained from the composite latex displayed UV-shielding properties. The ZnO/PBA nanocomposite possessed higher absorption in both UV and visible region than the PBA films. Nevertheless the ZnO/PBA latex did not exhibit any antibacterial activity. It is possible that the ZnO needs to be exposed to the microorganisms in order to achieve antibacterial effect. From these results, the ZnO/PBA composite latex obtained from this work can be potentially used as a coating agent.

5.2 Suggestion

From this work, it was found that the content of ZnO in the latex was somewhat low (0.3 wt %). One may need to explore other routes or coupling agents to increase the ZnO content in the latex. In addition, reduction of the amount of initiator KPS would be worth investigated, so that the amount of organic polymer (PBA) can be increased. The amount of PBA in the latex can affect the film forming ability of the latex as well.



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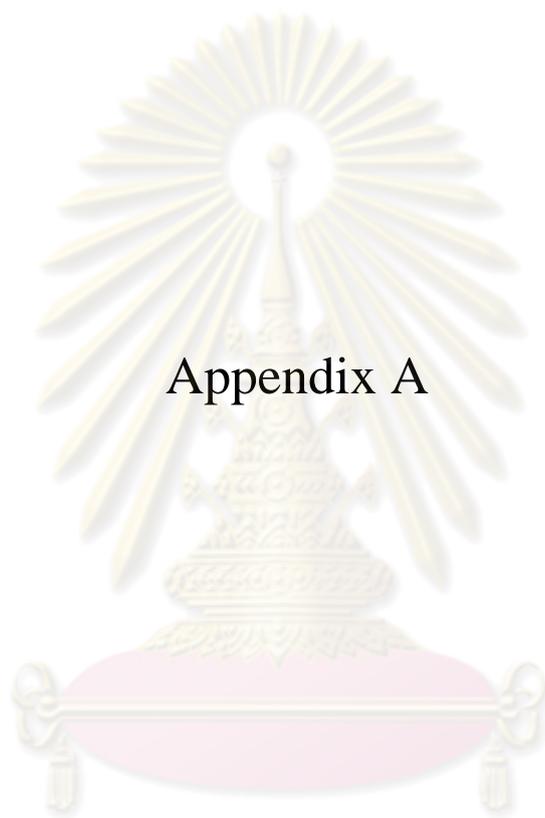
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Appendix A

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

APPENDEX A

A1 Preparation of ZnO/PBA composite latex

A1.1 Modification of nano-ZnO with MPS

Table A-1: The surface modification recipe of nano-ZnO with MPS

ZnO	MPS	total solid
2	1	3

Table A-2: The dry solids of MPS-g-ZnO after sohxlet.

No.	Trimble (g)	trimble + drysolid (g)	Dry Solid before sohxlet(g) (G+UG+Z)	Grafted polymer after sohxlet(g) (G+Z)		Dry solid after sohxlet
				1	2	
1	3.38914	4.0075	0.6184	3.9600	3.9600	0.5709
2	3.38922	4.0065	0.6173	3.9544	3.9544	0.5652
3	3.3946	4.0256	0.6310	3.9656	3.965	0.5704

The % graft of MPS onto the surface of nano-ZnO was determined by the following equation:

$$\text{Grafting (\%)} = [(Dm - Em) / Em] \times 100$$

where Dm (g) is the weight of dry modified nano-ZnO after sohxlet, Em (g) is the weight of charged ZnO particles in dry modified before sohxlet.

Table A-3: The %graft of MPS onto the surface of nano-ZnO.

No.	ZnO	MPS	Dry Solid before sohxlet(g) (G+UG+Z)	Dry solid after sohxlet	Graft %
1	0.4122	0.2061	0.6184	0.5709	38
2	0.4115	0.2058	0.6173	0.5652	37
3	0.4207	0.2103	0.6310	0.5704	36

A1.2 Emulsion polymerization of butyl acrylate on MPS-grafted ZnO nanoparticles

Table A-4: The emulsion polymerization recipe of ZnO/PBA nanocomposite latex in reaction time of 3 hr.(*standard condition*)

Chemical Name	% wt
Butylacrylate monomer	5
Modified ZnO	0.3
IGEPAL CA-630	0.004
KPS	0.05
Deionized water	94.7

Weight latex form Table A-3 that show in Table A-4 to determine the dry solid in latex.

Table A-5: Dry solid in latex in the effect of BA content.

%BA monomer ¹	Latex (g)	%Solid	Dry Solid(g) in latex
5	5.080	2.44	0.12
	5.299	2.49	0.13
	5.060	2.51	0.13
10	5.012	7.39	0.37
	5.030	6.32	0.32
	5.133	6.35	0.33
20	3.138	13.72	0.43
	3.311	13.43	0.44
	3.237	13.56	0.44

¹The amount of BA is in percentage by weight of latex. The polymerization was carried out using KPS (1% of monomer) as initiator and reaction time of 3 hr in 0.3%w of MPS-g-ZnO particles.

Use Table A-4 to calculated the BA monomers content and nano-ZnO content of dry solid in dry latex by conventional calculation as using Table A-3 in a compared. And using these data to calculate the conversion(%) as follow

equation:

$$\text{Conversion (\%)} = [(A-B)/C] \times 100 \quad (\text{A.1})$$

where A is the weight of total resulting particle which is the weight of ZnO plus grafted polymers, B is the weight of charged nano-ZnO particles, and C is the weight of charged monomer.

Table A-6: The effect of BA content on the percentage of conversion.

%BA monomer	Total result particle in latex (G+UG+Z)	%Conversion
5	0.12	41.72
	0.13	42.72
	0.12	43.12
Average	0.12	42.52
10	0.37	56.69
	0.31	45.72
	0.32	48.02
Average	0.33	50.14
20	0.42	66.08
	0.44	64.63
	0.43	65.28
Average	0.43	65.33

Table A-7: The dry solids of latex after centrifuge in the effect of BA content.

%BA monomer	Vial	Latex (g) to centrifuge	Glass dish(g)	Glass dish+solid(g)	Dry solid after centrifuge (g)			
					1	2	3	Dry solid
5	1	20.4932	15.1997	16.5344	16.2353	16.1385	16.1385	0.9388
	2	18.6068						
	3	17.7402						
	sum	56.8402						
10	4	-	15.2684	18.937	18.5871	18.5899	18.5898	3.3214
	5	19.0729						
	6	19.8254						
	sum	38.8983						
20	7	-	15.1433	23.2347	22.9988	22.9056	22.9056	7.7623
	8	19.2488						
	9	-						
	sum	19.2488						

Take these dry solid to sohxleted for 24 hr. the result in Table A-7.

Table A-8: Dry solid latex after sohxleted.

%BA monomer	Trimble (g)	trimble + drysolid (g)	Dry Solid before sohxlet(g) (G+UG+Z)	Grafted polymer after sohxlet(g) (G+Z)					
				0	1	2	3	4	Dry solid
5	3.1927	4.1291	0.9364	4.1291	3.9542	3.7745	3.6392	3.6392	0.4465
10	3.4771	5.6055	2.1284	5.6055	5.2819	5.2351	5.2214	5.2214	1.7443
20	3.1265	5.6470	2.5205	5.634	5.533	5.445	5.4390	5.4393	2.3128

The percentage of grafting and its efficiency were calculated by the following equations:

$$\text{Grafting (\%)} = [D/E] \times 100 \quad (\text{A.2})$$

$$\text{Grafting efficiency (\%)} = [D/F] \times 100 \quad (\text{A.3})$$

where D (g) is the weight of grafted PBA, E (g) is the weight of charged ZnO particles, and F (g) is the total PBA (grafted and ungrafted polymers) formed in the system.

Table A-9: The effect of BA content on the percentage of grafting, and grafting efficiency of BA in the emulsion polymerization process with MPS-g-ZnO particles.

%BA monomer	Latex (g)	Modified ZnO	Dry Solid before sohxlet(g) (G+UG+Z)	Grafted polymer after sohxlet(g) (G+Z)	Total polymer (G+UG)	Graft(%)	Grafting efficiency(%)
5	56.8402	0.17	0.9364	0.4465	0.7659	161.85	36.03
10	38.8983	0.12	2.1284	1.7443	2.0117	1394.75	80.91
20	19.2488	0.06	2.5205	2.3128	2.4628	3905.10	91.57

As the same in the effect of BA content, the effect of reaction¹ time the percentage of conversion, grafting, and grafting efficiency as follow in Table A-9 and Table A-10 respectively. ¹The polymerization was carried out using 5%wt BA and KPS (1% of monomer) as initiator in 0.3%w of MPS-g-ZnO particles.

Table A-10 : The effect of reaction times on the percentage of conversion.

Time (min.)	Total result particle in latex (G+UG+Z)	%Conversion
120	0.12	41.72
	0.12	42.72
	0.12	43.12
Average	0.12	42.52
180	0.12	41.72
	0.13	42.72
	0.12	43.12
Average	0.12	42.52
240	0.13	43.92
	0.13	44.62
	0.13	45.32
Average	0.13	44.62
360	0.13	46.02
	0.13	46.72
	0.14	47.42
Average	0.13	46.72

Table A-11: The effect of reaction times on the percentage of grafting, and grafting efficiency of BA in the emulsion polymerization process with MPS-g-ZnO particles.

Time (min.)	Latex (g)	Modified ZnO	Dry Solid before sohxlet(g) (G+UG+Z)	Grafted polymer after sohxlet(g) (G+Z)	Total polymer (G+UG)	Graft(%)	Grafting efficiency(%)
120	54.4323	0.16	0.9342	0.4378	0.7709	168.10	35.61
180	56.8402	0.17	0.9364	0.4465	0.7659	161.85	36.03
240	56.4420	0.17	0.9453	0.4413	0.7760	160.62	35.05
360	55.83	0.17	0.9635	0.4463	0.79601	166.46	35.03

As the same in the effect of BA content, the initiator amount¹ the percentage of conversion, grafting, and grafting efficiency as follow in Table A-11 and Table A-12 respectively. ¹The amount of KPS is in percentage by weight of BA monomer. The polymerization was carried out using 5% BA and reaction time of 3 hr in 0.3%w of MPS-g-ZnO particles

Table A-12 : The effect of initiator amount on the percentage of conversion.

KPS (% of monomers)	Total result particle in latex (G+UG+Z)	%Conversion
0.25	0.09	39.27
	0.06	35.87
	0.06	36.67
Average		37.27
0.5	0.10	59.82
	0.12	53.62
	0.12	54.02
Average		55.82
1	0.12	41.72
	0.13	42.72
	0.12	43.12
Average		42.52
3	0.07	39.92
	0.07	40.32
	0.07	40.12
Average		40.12

Table A-13: The effect of initiator amount on the percentage of grafting, and grafting efficiency of BA in the emulsion polymerization process with MPS-g-ZnO particles.

KPS (% of monomers)	Latex (g)	Modified ZnO	Dry Solid before sohxlet(g) (G+UG+Z)	Grafted polymer after sohxlet(g) (G+Z)	Total polymer (G+UG)	Graft(%)	Grafting efficiency(%)
0.25	53.73	0.16	0.9242	0.4663	0.7630	189.27	39.99
0.5	57.74	0.17	1.5472	1.2958	1.3740	647.99	81.70
1	56.84	0.17	0.9364	0.4465	0.7659	161.85	36.03
3	56.85	0.17	0.9442	0.4398	0.7736	157.83	34.80

A1.3 Latex Stability determination

The latex was left standing in a clear screw thread vials (size: 21×70 mm, 15 mL tall) for 4 weeks. The depth of sedimentation from the surface of suspension was recorded every day for a total time of 30 days. The sedimentation percentage of the composite latex was determined by the following equation:

$$\% \text{ Sedimentation} = H/H_0 \times 100\% \quad (\text{A.4})$$

where H (cm) is the depth of sedimentation from the surface of suspension, and H_0 (cm) is the total depth of suspension. The value shown in the result was averaged from 3 sets of experiments.

Table A -14: Latex stability determination: bare nano-ZnO in mixed-solvent between MeOH:H₂O (4:1) (BZ), MPS-g-ZnO 0.3% w/w in MeOH:H₂O (4:1) (ZGM), ZnO/PBA latex prepared from 1% KPS 5% BA (ZPBA), 0.5% KPS 5% BA (ZBA0.5), 1% KPS and 10% BA (Z10BA), 1% KPS and 20% BA (Z20BA), and commercial nano-ZnO latex for fabric coating (ZAB; ZnO 0.3 wt% with negative acrylic binder 1 wt%)

Time(day)	sample	No.	H ₀ (cm.)	H (cm.)	% Sedimentation
1-7	BZ	1	5	0.05	1
		2	5	0.05	1
		3	5	0.05	1
	ZGM	1	5	0.05	1
		2	5	0.05	1
		3	5	0.06	1.2
	ZPBA	1	5	5	100
		2	5	5	100
		3	5	5	100
	ZBA0.5	1	5	4	80
		2	5	4	80
		3	5	4	80
	Z10BA	1	5	4	80
		2	5	4	80
		3	5	4	80
	Z20BA	1	5	3	60
		2	5	3	60
		3	5	3	60
	ZAB	1	5	0.05	1
		2	5	0.05	1
		3	5	0.06	1.2

Table A -14: Latex stability determination (*continued2*)

Time(day)	sample	No.	H ₀ (cm.)	H (cm.)	% Sedimentation
8-14	BZ	1	5	0.05	1
		2	5	0.05	1
		3	5	0.05	1
	ZGM	1	5	0.05	1
		2	5	0.05	1
		3	5	0.05	1
	ZPBA	1	5	5	100
		2	5	5	100
		3	5	5	100
	ZBA0.5	1	5	3	60
		2	5	3	60
		3	5	3	60
	Z10BA	1	5	3	60
		2	5	3	60
		3	5	3	60
	Z20BA	1	5	2.5	50
		2	5	2.5	50
		3	5	2.5	50
	ZAB	1	5	0.05	1
		2	5	0.05	1
		3	5	0.05	1
15-21	BZ	1	5	0.05	1
		2	5	0.05	1
		3	5	0.05	1
	ZGM	1	5	0.05	1
		2	5	0.05	1
		3	5	0.05	1
	ZPBA	1	5	5	100
		2	5	5	100
		3	5	5	100
	ZBA0.5	1	5	2.5	50
		2	5	2.5	50
		3	5	2.5	50
	Z10BA	1	5	2.5	50
		2	5	2.5	50
		3	5	2.5	50
	Z20BA	1	5	2	40
		2	5	2	40
		3	5	2	40
	ZAB	1	5	0.05	1
		2	5	0.05	1
		3	5	0.06	1.2

Table A -14: Latex stability determination (*continued3*)

Time(day)	sample	No.	H ₀ (cm.)	H (cm.)	% Sedimentation
22-30	BZ	1	5	0.05	1
		2	5	0.05	1
		3	5	0.05	1
	ZGM	1	5	0.05	1
		2	5	0.05	1
		3	5	0.06	1.2
	ZPBA	1	5	5	100
		2	5	5	100
		3	5	4.8	96
	ZBA0.5	1	5	2.5	50
		2	5	2.5	50
		3	5	2.5	50
	Z10BA	1	5	2.5	50
		2	5	2.5	50
		3	5	2.5	50
	Z20BA	1	5	2	40
		2	5	2	40
		3	5	2	40
	ZAB	1	5	0.05	1
		2	5	0.05	1
		3	5	0.06	1.2

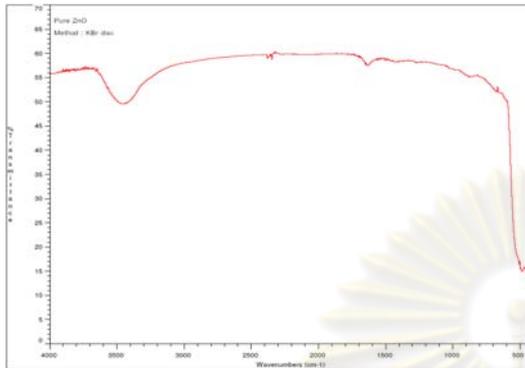
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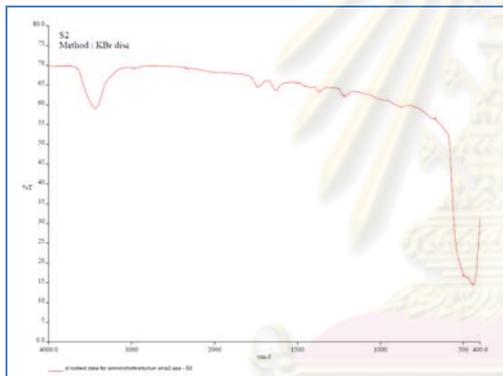
Appendix B

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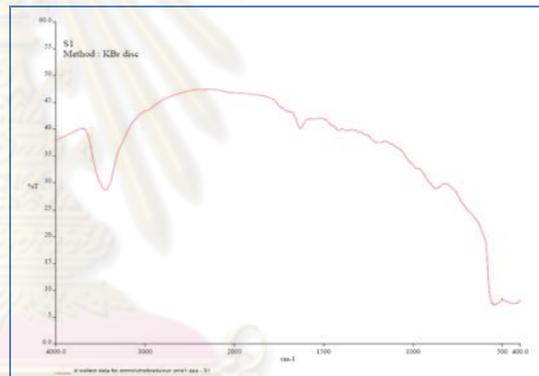
APPENDIX B

B1 Preparation of ZnO/PBA composite latex**B1.1 Modification of nano-ZnO with MPS**

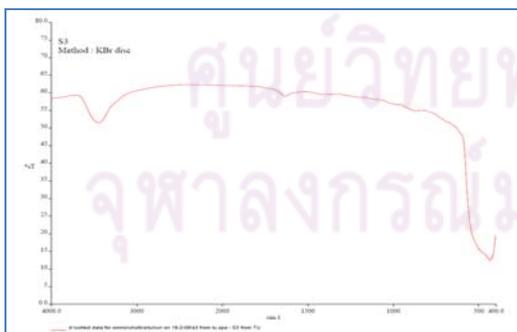
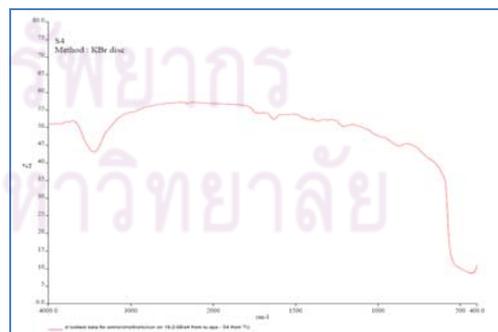
A0 = pure ZnO type A



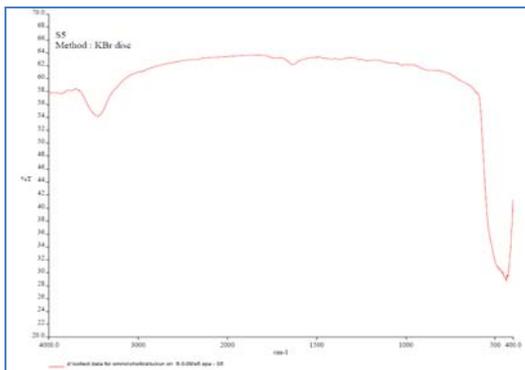
A1 = ZnO 6 g



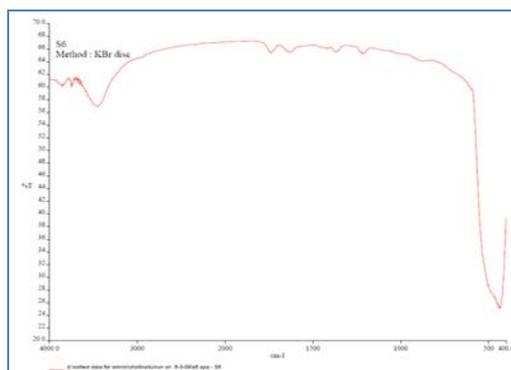
A2 = ZnO 2 g

A3 = MPS 0.5 g /Reflux in
low temp (<100°C)

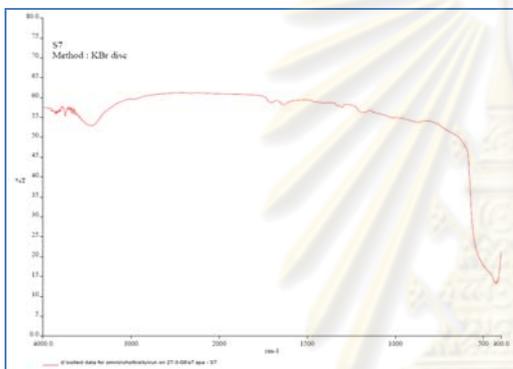
A4 = MPS 0.5 g /Stirr for 12h.



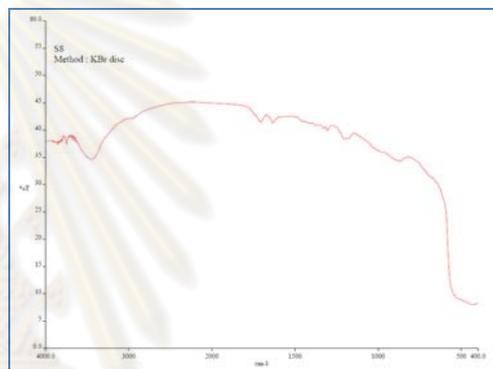
A5 = MPS 1 g / MeOH/ Reflux
in low temp (<100°C)



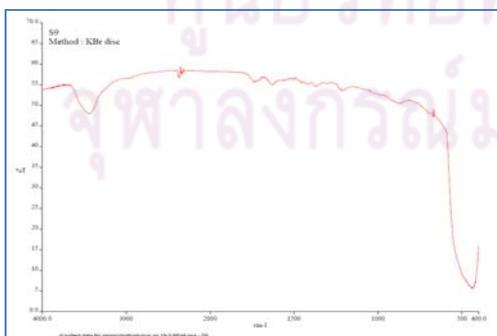
A6 = MPS 1 g / MeOH/ Stirr for
12h.



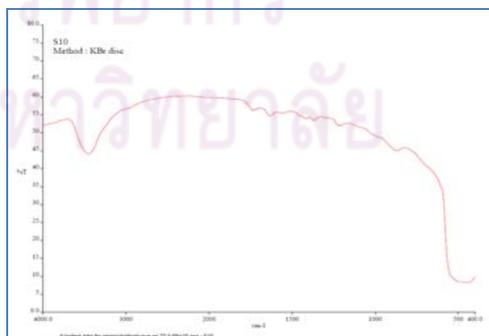
A7 = Solvent (total 50ml); MeOH +
H₂O 40:10 /Reflux in low temp
(<100°C)



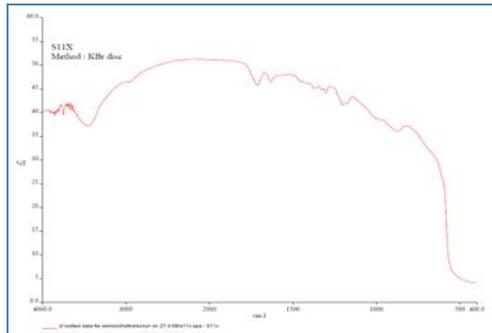
A8 = Solvent (total 50ml); MeOH +
H₂O 40:10 / Stirr for 12h.



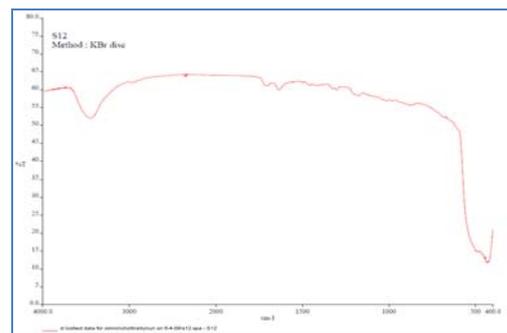
A9 = MPS 2g/MeOH /Reflux in
low temp (<100°C)



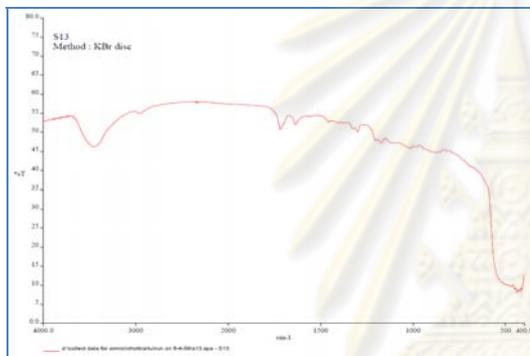
A10 = MPS 2 g/MeOH/ Stirr for
12h.



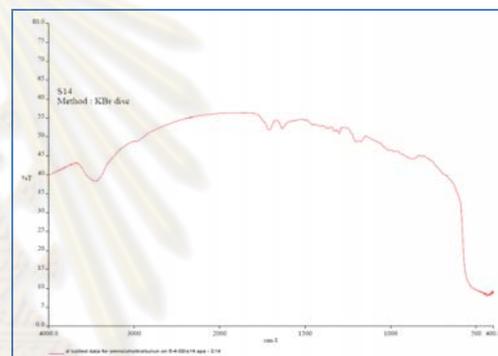
A11 = MPS 2g/ MeOH + H₂O
40:10 /Reflux in low temp (<100°



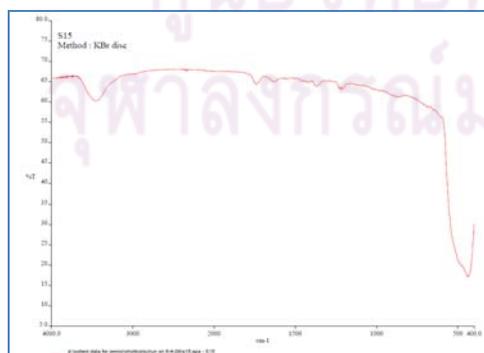
A12 = MPS 4 g/ MeOH + H₂O
40:10 /Reflux in low temp
(<100°C)



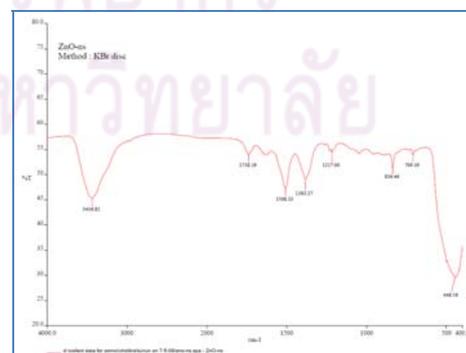
A13 = MPS 8 g/ MeOH + H₂O
40:10 /Reflux in low temp (<100°C)



A14 = MPS 4 g/ MeOH + H₂O
40:10 /Reflux in water bath



A15 = MPS 8 g/ MeOH + H₂O 40:10
/Reflux in low temp (<70°C)



B0 = nano- ZnO type B

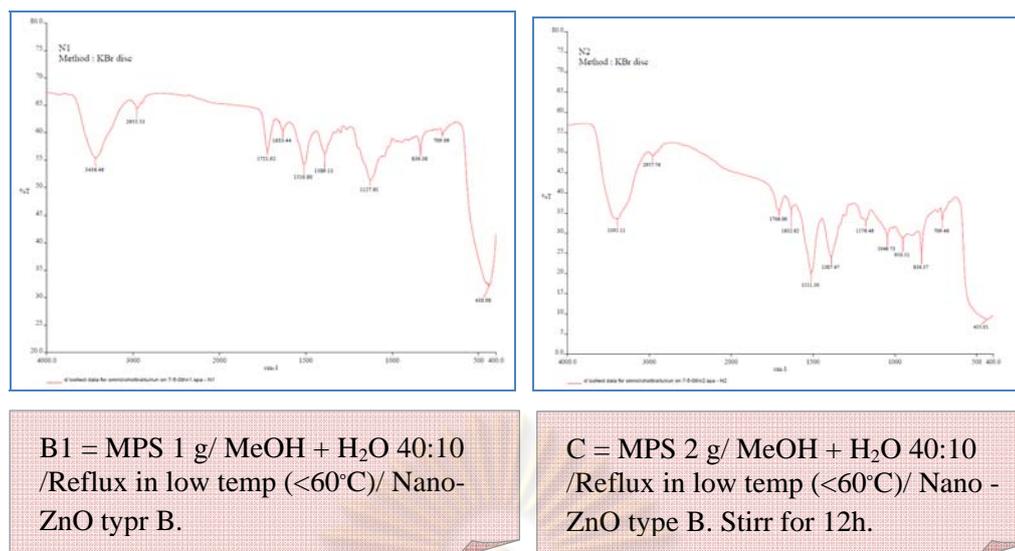


Figure B-1: FT-IR images of preparation condition of MPS-grafted nano-ZnO.

B1.2 Emulsion polymerization of butyl acrylate on MPS-grafted ZnO nanoparticles

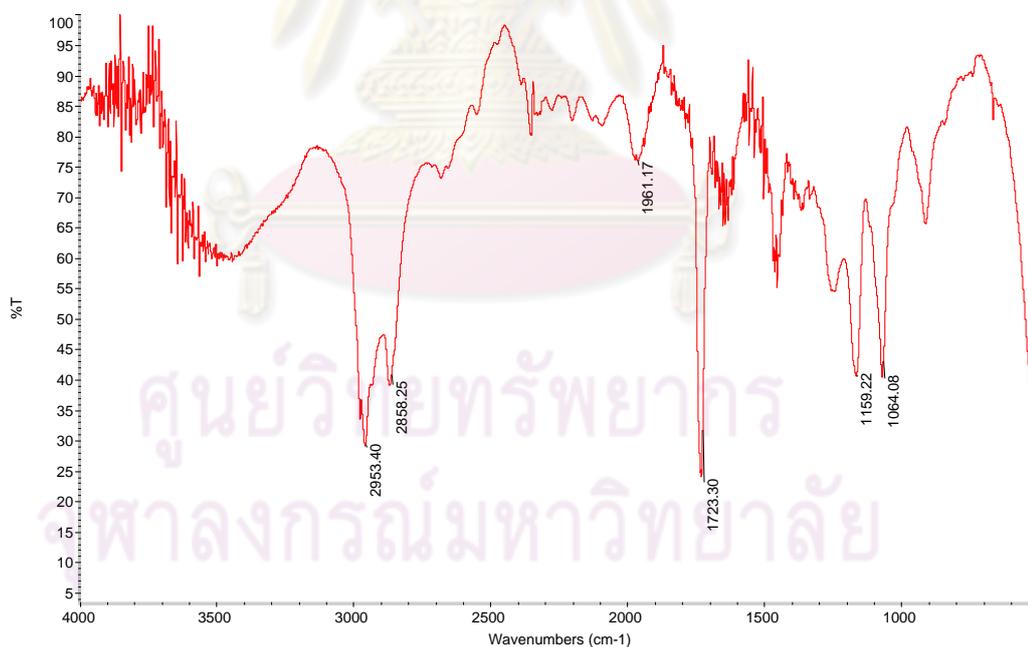


Figure B-2: FT-IR spectra for MPS-g-ZnO particles (type B) after emulsion polymerization process of butyl acrylate.

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