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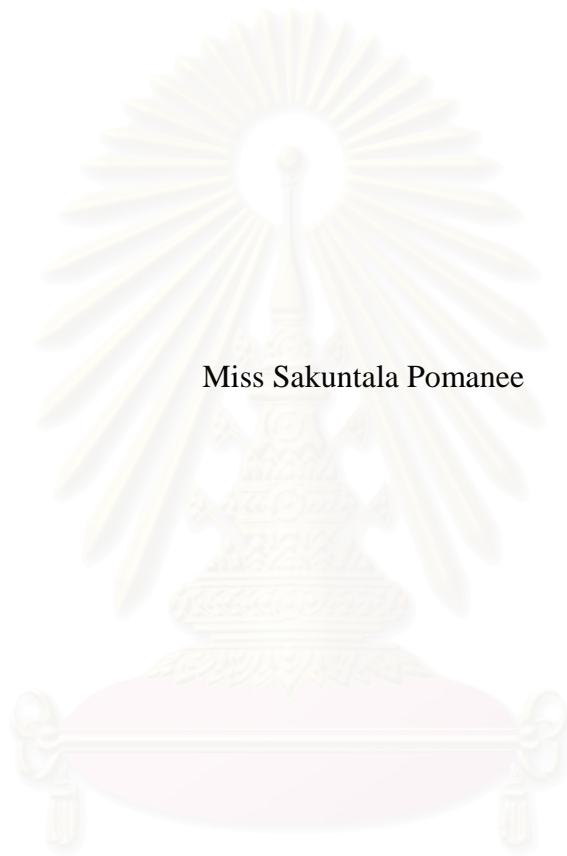
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SYNTHESIS AND CHARACTERIZATION OF PANI/PU/PMMA LATEXES



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Faculty of Science

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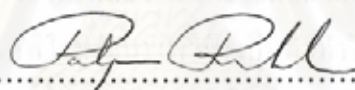
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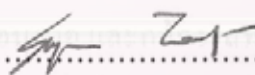


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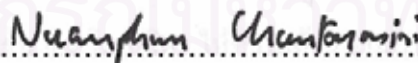
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ได้สังเคราะห์พอลิเอสเทอร์พอลิออลโดยปฏิกิริยาการเกิดพอลิเมอร์แบบควบแน่นจาก 1,6-
 เฮกเซนไดออล แอดิพิกแอซิด และ ไอโซทาลิกแอซิด ที่โมลอัตราส่วน 5:3:1 วัตถุประสงค์และ
 ค่าความเป็นกรดของพอลิเอสเทอร์พอลิออลได้เป็น 140 มิลลิกรัม KOH/กรัม และ 3.7 ตามลำดับ
 แล้วนำพอลิเอสเทอร์พอลิออลมาทำปฏิกิริยากับ 2,4-โทลูอินไดไอโซไซยานต และไดเมทิลโพรพิ
 ออนิกแอซิด เพื่อให้เกิดเป็นพอลิยูรีเทนพริพอลิเมอร์ ที่มีหมู่กรดคาร์บอกซิลิก หลังจากทำให้เป็น
 กลางด้วยไตรเอทิลเอมีน ได้นำไปกระจายตัวในน้ำและเติมเอทิลีนไดเอมีน เพื่อให้เกิดเป็นพอลิยูรี
 เทนดิสเพอร์ชันในน้ำ แล้วใช้พอลิยูรีเทนดิสเพอร์ชันในน้ำเป็นตัวกลางในการสังเคราะห์พีเอ็มเอ็ม
 เอ เพื่อผลิตพียู/พีเอ็มเอ็มเอลาเท็กซ์ ที่อัตราส่วน โดยน้ำหนักแตกต่างกัน ได้แก่ 2:1, 1:1, และ 1:2 ที่
 สองอัตราส่วนแรกได้ขนาดอนุภาคเฉลี่ยของ พียู/พีเอ็มเอ็มเอ เป็น 182 นาโนเมตร ในขณะที่อัตรา
 ส่วนสุดท้ายได้ขนาดอนุภาคใหญ่กว่าเป็น 206 นาโนเมตร ได้เลือกใช้พียู/พีเอ็มเอ็มเอลาเท็กซ์ (1:1)
 ในการเตรียมพีเอเอ็นไอ/พียู/พีเอ็มเอ็มเอลาเท็กซ์ พีเอเอ็นไอ/พียู/พีเอ็มเอ็มเอลาเท็กซ์เกิดขึ้นได้ด้วย
 การเกิดพอลิเมอร์ของแอนิลีนไฮโดรคลอไรด์ โดยใช้แอมโมเนียมเปอร์ออกซิไดซัลเฟต เป็นตัวออก
 จิแดนซ์ และพอลิ (เอ็น - ไวนิลพิโรลิโดน) (พีวีพี) เป็นตัวทำให้เสถียรในพียู/พีเอ็มเอ็มเอลาเท็กซ์ ได้
 ปรับเปลี่ยนความเข้มข้นของแอนิลีนไฮโดรคลอไรด์ และพีวีพี เพื่อให้ได้พีเอเอ็นไอ/พียู/พีเอ็มเอ็ม
 เอลาเท็กซ์ที่เสถียร ได้วิเคราะห์ลาเท็กซ์เหล่านี้ด้วยฟูเรียทรานฟอร์มอินฟราเรดสเปกโทรสโกปี
 (เอฟทีไออาร์) เครื่องวัดขนาดอนุภาค และกล้องจุลทรรศน์อิเล็กตรอนแบบส่องผ่าน สุดท้ายได้
 ศึกษาความสามารถในการต้านทานการกักร้อนของพีเอเอ็นไอ/พียู/พีเอ็มเอ็มเอลาเท็กซ์ ด้วยการแช่
 ชั้นทดสอบซึ่งเป็นชั้นหลักที่เคลือบด้วยลาเท็กซ์ ในสารละลายเกลือโซเดียมคลอไรด์ (3.5 ร้อยละ
 โดยน้ำหนัก) เป็นเวลา 30 วัน แล้ววิเคราะห์ด้วยกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด ได้
 ทดสอบฟิล์มพีเอเอ็นไอ/พียู/พีเอ็มเอ็มเอโดยวิธีเดียวกันและได้วิเคราะห์เอฟทีไออาร์สเปกตรัมของ
 ฟิล์มด้วย ผลการทดลองแสดงให้เห็นว่าพีเอเอ็นไอ/พียู/พีเอ็มเอ็มเอลาเท็กซ์ที่เตรียมได้จาก แอนิลีน
 ไฮโดรคลอไรด์ที่ความเข้มข้น 0.4 โมล/ลิตร ให้ความต้านทานการกักร้อนที่ดี

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477 24904 23: MAJOR PETROCHEMISTRY AND POLYMER SCIENCE

KEY WORD: POLYURETHANE DISPERSION / POLYANILINE / LATEX

SAKUNTALA POMANEE: SYNTHESIS AND CHARACTERIZATION OF
 PANI/PU/PMMA LATEXES. THESIS ADVISOR: ASSOC. PROF. SUPAWAN
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Polyester polyol was synthesized by condensation polymerization of 1,6-hexanediol, adipic acid, and isophthalic acid at 5:3:1 mole ratio. The hydroxyl value and acid value of polyester polyol were found to be 140 mg KOH/g and 3.7, respectively. Polyester polyol was then reacted with 2,4-toluene diisocyanate and dimethylolpropionic acid to form polyurethane prepolymer containing pendant carboxylic acid group. After neutralizing with triethylamine, it was dispersed in water and ethylene diamine was added to obtain aqueous polyurethane dispersion. Then, aqueous polyurethane dispersion was used as medium in the synthesis of PMMA to generate PU/PMMA latexes at different weight ratios; 2:1, 1:1, and 1:2. At the first two ratios, the same average particle size of PU/PMMA was 182 nm, while at the last ratio larger particle size of 206 nm was resulted. PU/PMMA latex (1:1) was selected for preparing as PANI/PU/PMMA latex. The formation of PANI/PU/PMMA latex occurred by polymerization of aniline hydrochloride using ammonium peroxydisulfate as an oxidant and poly (*N*-vinylpyrrolidone) (PVP) as stabilizer in PU/PMMA latex. The concentration of aniline hydrochloride and PVP was varied in order to obtain stable PANI/PU/PMMA latex. These latexes were characterized by Fourier transform infrared spectroscopy (FTIR), particle size analyzer, and transmission electron microscopy. Finally, the corrosion protection performance of PANI/PU/PMMA latex was studied by immersion the tested samples, which were steel pieces coated with latex, in NaCl solution (3.5 wt. %) for 30 days and then investigated by scanning electron microscopy. PANI/PU/PMMA film was also subjected to the same test and its FTIR spectrum was analyzed. The results indicated that PANI/PU/PMMA latex prepared from aniline hydrochloride at a concentration of 0.4 mol L⁻¹ gave good corrosion resistance.

Field of student Petrochemistry and polymer science Student's signature *Sakuntala Pomanee*
 Academic year2006..... Advisor's signature *Supawan Tantayanon*

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สถาบันวิทยบริการ
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CONTENTS

	Page
ABSTRACT IN THAI	iv
ABSTRACT IN ENGLISH	v
ACKNOWLEDGEMENTS	vi
CONTENTS	vii
LIST OF TABLES	x
LIST OF FIGURES	xi
LIST OF SCHEMES	xiii
LIST OF ABBREVIATION AND SIGNS	xiv
CHAPTER I INTRODUCTION	1
1.1 Introduction.....	1
1.2 Objectives of Research.....	2
1.3 Scope of Research.....	2
CHAPTER II THEORY AND LITERATURE REVIEWS	3
2.1 Theory.....	3
2.1.1 Introduction to Polyurethane.....	3
2.1.2 Polyurethane Coating.....	5
2.1.3 Aqueous Polyurethane Dispersion.....	7
2.1.4 Emulsion Polymerization.....	10
2.1.5 Polyaniline.....	11
2.2 Literature Reviews.....	13
CHAPTER III EXPERIMENTAL	16
3.1 Chemicals.....	16
3.2 Glasswares and Equipments.....	17
3.3 Instruments.....	17
3.4 Purification and Preparation of Materials.....	18
3.5 Synthesis of PANI/PU/PMMA Latexes.....	18
3.5.1 Synthesis of Polyester Polyol.....	18

	Page
3.5.2 Synthesis of Aqueous Polyurethane Dispersion.....	19
3.5.3 Synthesis of PU/PMMA Latex.....	20
3.5.4 Synthesis of PANI/PU/PMMA Latex.....	21
3.6 Corrosion Study.....	21
3.7 Determination of Properties of Resins.....	22
3.7.1 Determination of Nonvolatile Matter (NV).....	22
3.7.2 Determination of Hydroxyl Value (OHV).....	22
3.7.3 Determination of Acid Value (AV).....	23
3.7.4 Determination of Isocyanate Groups (NCO) Content.....	4
3.8 Characterization.....	25
3.8.1 FTIR Analysis.....	25
3.8.2 Characterization of Molecular Weight Distribution by GPC....	25
3.8.3 Particle Size and its Distribution	25
3.8.4 Morphology of Particles.....	26
3.8.5 Morphology of the Coating Degradation.....	26
CHAPTER IV RESULTS AND DISCUSSION.....	27
4.1 Aqueous Polyurethane Dispersion.....	27
4.1.1 Synthesis and Characterization of Polyester Polyol.....	27
4.1.2 Synthesis and Characterization of Aqueous Polyurethane Dispersion.....	30
4.2 PU/PMMA Latex.....	35
4.2.1 Synthesis and Characterization of PU/PMMA Latex.....	35
4.2.2 Size and Distribution of PU/PMMA Particle.....	39
4.3 PANI/PU/PMMA Latex.....	42
4.3.1 Synthesis and Characterization of PANI/PU/PMMA Latex.....	42
4.3.2 Size and Distribution of PANI/PU/PMMA Particle.....	44
4.4 Corrosion Study.....	49
4.4.1 FTIR Analysis.....	49
4.4.2 Morphology of the Coating Degradation.....	51

	Page
CHAPTER V CONCLUSIONS AND SUGGESTIONS	55
5.1 Further Works.....	56
REFERENCES	57
APPENDICES	60
APPENDIX A	61
APPENDIX B	66
VITAE	73



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

LIST OF TABLES

	Page
Table 4.1 The study of acid value of the synthesis of polyester polyol.....	28
Table 4.2 Diameter and polydispersity of PU/PMMA particles.....	40
Table 4.3 The effect of PVP concentration on diameter and polydispersity of PANI/PU/PMMA particle (aniline hydrochloride 0.1 mol L^{-1}).....	44
Table 4.4 The effect of concentration of aniline hydrochloride on diameter and polydispersity at PVP 1.3 wt. %.....	45



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

LIST OF FIGURES

	Page
Figure 2.1 Types of aliphatic diisocyanate.....	6
Figure 2.2 Types of aromatic diisocyanate.....	6
Figure 2.3 Schematic of micelles formed by cationic (a) and anionic (b) polyurethane ionomers in water [2].....	9
Figure 3.1 The apparatus for the synthesis of polyester polyol.....	19
Figure 3.2 The apparatus for the synthesis of aqueous polyurethane dispersion.....	20
Figure 4.1 FTIR spectrum (neat) of polyester polyol.....	29
Figure 4.2 FTIR spectrum (neat) of aqueous polyurethane dispersion.....	33
Figure 4.3 Diagrammatic formation of an aqueous polyurethane dispersion.....	34
Figure 4.4 Particle size distribution of aqueous polyurethane dispersion.....	34
Figure 4.5 Schematic formation of PU/PMMA latex.....	36
Figure 4.6 FTIR spectrum (neat) of PU/PMMA at 1:1 weight ratio.....	37
Figure 4.7 FTIR spectrum (neat) of PU/PMMA at 1:2 weight ratio.....	37
Figure 4.8 Particle size distributions of PU/PMMA latexes at 2:1(a), 1:1(b) and 1:2(c) weight ratios.....	39
Figure 4.9 Schematic representation of the effect of MMA content on PU/PMMA particle size.....	41
Figure 4.10 TEM photographs of PU/PMMA latex at 1:1 weight ratio was stained with phosphotungstic acid (a) and osmium tetroxide (b)....	41
Figure 4.11 FTIR spectra (neat) of PANI, PU/PMMA, and PANI/PU/PMMA (0.1 mol L ⁻¹ of aniline hydrochloride).....	43
Figure 4.12 Polyaniline particle formation in aqueous phase [19, 20].....	44
Figure 4.13 Particle size distribution of PANI (---) and PANI/PU/PMMA latex (—) prepared separately at various concentrations of aniline hydrochloride; 0.1 (a), 0.2 (b), 0.3 (c), and 0.4 (d) mol L ⁻¹	46
Figure 4.14 Diagrammatic representation of PANI/PU/PMMA particle.....	47
Figure 4.15 TEM photographs of latex particles; PANI/PU/PMMA ×50K (a) and ×25K (b), PU/PMMA (c), and PANI (d).....	48

- Figure 4.16** FTIR spectra of PU/PMMA film; initial sample (a),
after 30 days of exposure in NaCl solution (3.5 wt.%) (b).....50
- Figure 4.17** FTIR spectra of PANI/PU/PMMA film; initial sample (a),
after 30 days of exposure in NaCl solution (3.5 wt.%) (b).....50
- Figure 4.18** Photographs and SEM micrographs of the
surface of tested samples; initial sample (a), no coating (b),
coated with PU/PMMA latex (c) and PANI/PU/PMMA latex (d);
(b), (c), and (d) immersed in NaCl solution (3.5 wt. %) for 30 days.....52
- Figure 4.19** Photographs and SEM micrographs of the surface
of tested samples coated with PANI/PU/PMMA latex at
0.1 (a), 0.2 (b), 0.3 (c), and 0.4 (d) mol L⁻¹ of aniline hydrochloride
after immersed in NaCl solution (3.5 wt. %) for 30 days.....53

LIST OF SCHEMES

	Page
Scheme 2.1 Polyurethane reaction.....	4
Scheme 2.2 Reactions of isocyanate.....	5
Scheme 4.1 Synthesis of polyester polyol.....	28
Scheme 4.2 Synthesis of the aqueous polyurethane dispersion.....	32
Scheme 4.3 Corrosion mechanism of steel when attacked by water and oxygen.....	54



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

List of Abbreviation and signs

°C	degree Celsius
g	gram
h	hour
µm	micrometre
mg	milligram
mL	millilitre
mL/ min	millilitre per minute
min	minute
M	molarity
mol L ⁻¹	mol per litre
nm	nanometre
N	normal
W	watt
cm ⁻¹	wave number
wt	weight

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CHAPTER I

INTRODUCTION

The development of raw materials for coatings has been dominated by two major driving forces; improvement in protective properties and improvement in appearance. Nowadays, a third factor is, at least of equal importance; the ecological balance of the coating, starting with the development, continuing with production of the raw materials, application of the paint, lifetime of the coating and ending with the disposal of the coated subject. Most industrial coating manufacturers are still using organic solvents for easy application, thus providing a source of volatile organic compounds (VOCs). In order to improve further the protection of the environment, most industrial nations have issued laws demanding a reduction in the use of organic solvents.

Waterborne systems have been known for many years and their field of application has been predominantly in the building and construction market. However, many industrial applications require a higher performance, the standard having been set by solvent borne systems, especially with polyurethanes, which cannot be fulfilled by this kind of waterborne system. In view of the need to reduce the organic solvent content and increase the performance of waterborne systems, the transfer of polyurethane chemistry to the aqueous coatings was an obvious step. Today, there is a range of waterborne polyurethane coating which meets these higher requirements, and development is still in progress.

Furthermore, acrylic polymer emulsions also have been widely used for coating. Acrylic polymer emulsions and polyurethane dispersions have their own characteristic advantages and disadvantages. Acrylic polymer emulsions have excellent weather resistance, water and alkali resistant films. However, the elasticity and abrasion resistance of acrylic polymer emulsions are inferior to those of urethane resin, which feature excellent elasticity and abrasion resistance and superior low temperature impact resistance, but suffer from poor water and alkali resistance.

Therefore it is of great interest to produce emulsions in which each particle is composed of acrylic polymer and polyurethane components.

In addition, polyaniline is the most popular and recently commercially available conducting polymer. Plenty of information about the synthesis, electrical conductivity and practical application of polyaniline is available. One of the most explored applications of polyaniline is based on its good corrosion protection properties in coatings.

Accordingly, it will be useful if polyurethane, poly (methyl methacrylate) and polyaniline can be synthesized as a core-shell particle for coating application. This will provide not only good coating vehicle but also improve the corrosion protection property of coating.

1.1 Objectives of Research

1. To synthesize a novel ternary latex of PANI/PU/PMMA.
2. To study the corrosion protection of steel coated with PANI/PU/PMMA latex.

1.2 Scope of Research

1. To synthesize polyester polyol by condensation polymerization method.
2. To synthesize aqueous polyurethane dispersion by prepolymer mixing process.
3. To synthesize PU/PMMA latex by soap free emulsion polymerization method. (The weight ratio of PU: PMMA was varied as 2:1, 1:1, and 1:2.).
4. To synthesize PANI/PU/PMMA latex by oxidative polymerization of aniline hydrochloride in the presence of PU/PMMA latex. Poly (*N*-vinylpyrrolidone) and aniline hydrochloride were varied from 0.4-1.3 wt.% and 0.1-0.4 mol L⁻¹, respectively.
5. To investigate the protection performance of PANI/PU/PMMA latex against the corrosion of steel immersed in NaCl solution (3.5 wt. %) for 30 days.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Theory

2.1.1 Introduction to Polyurethane

Polyurethanes are all around us, playing a vital role in many industries-from shipbuilding to footwear; construction to cars. They appear in an astonishing variety of forms, a variety that is continuously increasing.

Polyurethane can be manufactured in an extremely wide range of grades, in densities from 6 kg/m^3 to 1220 kg/m^3 and polymer stiffnesses from very flexible elastomers to rigid, hard plastics.

2.1.1.1 Types of Polyurethanes

Foams

By itself the polymerization reaction produces solid polyurethane. Foams are made by forming gas bubbles in the polymerizing mixture. This is called “blowing”.

Solid polyurethanes

Although foamed polyurethanes form some 90% by weight of the total market for polyurethanes, there is a wide range of solid polyurethanes used in many applications.

Solid polyurethane elastomers

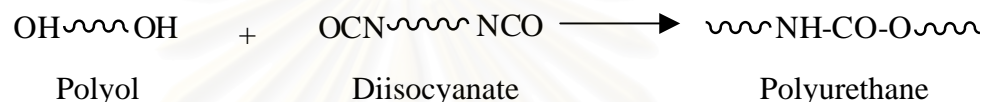
Most polyurethane elastomers have excellent abrasion resistance with good resistance to attack by oil, petrol and many common non-polar solvents. They may be tailored to meet the needs of specific applications, as they may be soft or hard, of high or low resilience, solid or cellular.

Adhesive, binders, coating and paints

Polyurethanes are also used in flexible coatings for textiles and adhesives for film and fabric laminates. Polyurethane paints and coatings give the highest wear resistance to surfaces such as floor and the outer skins of aircraft. They are also becoming widely used for high quality finishes on automobiles [1].

2.1.1.2 Definitions

In general, polyurethanes are produced by the reaction of a diisocyanate with a polyol illustrated below;



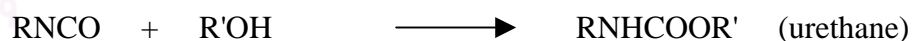
Scheme 2.1 Polyurethane reaction

This reaction is exothermic. The rate of polymerization reaction depends on the structures of both the isocyanate and the polyol. Aliphatic polyols with primary hydroxyl end-groups are the most reactive.

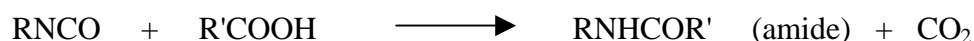
2.1.1.3 Reactions of Isocyanate

The isocyanate group (-NCO) can react with any compounds which contain active hydrogen atoms, i.e., alcohol, carboxylic acid, amine, and water and diisocyanate may therefore be used to modify many other products.

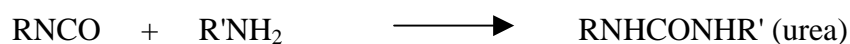
Reaction with an alcohol yields urethane:



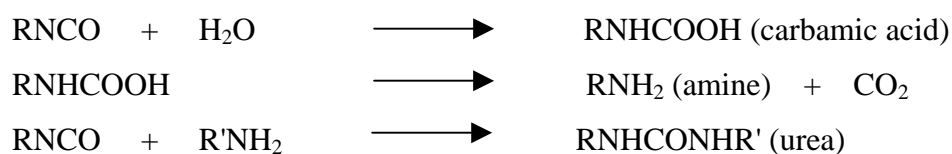
Reaction with a carboxylic acid yields an amide:



Reaction with an amine yields a urea:



Reaction with water produces a carbamic acid:



Scheme 2.2 Reactions of isocyanate

The unstable carbamic acid breaks down into an amine and carbon dioxide. The amines react with a further molecule of isocyanate to form urea. This last reaction is one way of introducing gas to form foams but it is a reaction to be avoided in surface coatings.

2.1.2 Polyurethane Coating

In manufacturing of the polyurethane coating, it needs to be consisted of two main parts, diisocyanate and polyol.

2.1.2.1 Diisocyanate

Aliphatic diisocyanates

Aliphatic diisocyanates are used in the manufacture of color-stable polyurethanes for coating and elastomer applications. Aliphatic diisocyanates afford polyurethane coating with outstanding weatherability.

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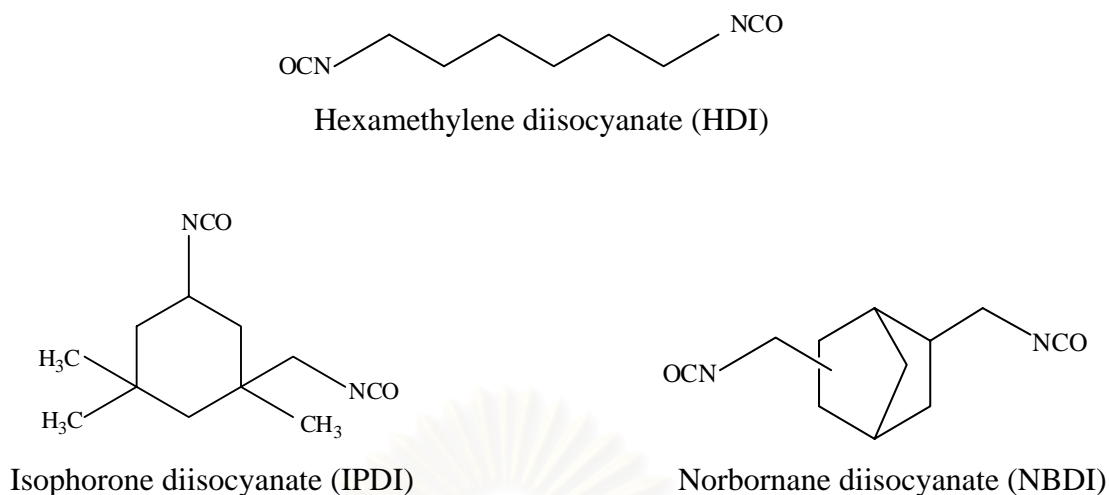
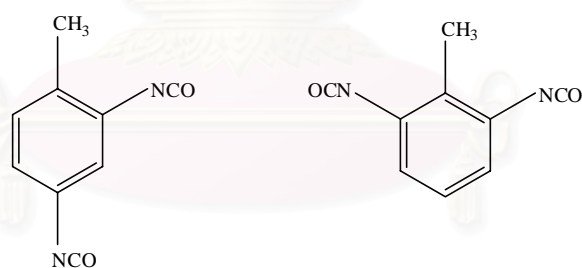


Figure 2.1 Types of aliphatic diisocyanate.

Aromatic diisocyanates

More than 90% of the total world production of isocyanates is accounted for polymeric MDI (PMDI), its co-product 4, 4'-methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI).



2, 4 and 2, 6- toluene diisocyanate (TDI)

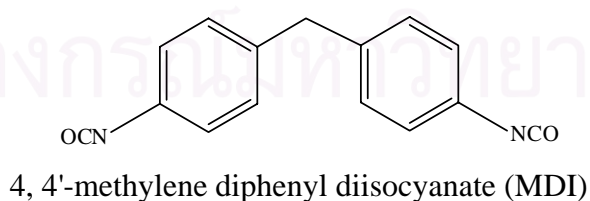


Figure 2.2 Types of aromatic diisocyanate.

2.1.2.2 Polyols

The other component in the production of polyurethane is a polyol. A wide range of polyol is used in polyurethane manufacture. The molecular weight and functionality of the polyol are the main factors, but the structure of the polyol chains is also important. Polyol that use for synthesis of polyurethane such as polyester polyol, polyether polyol, and acrylic polyol.

2.1.3 Aqueous Polyurethane Dispersion

The increase interest in waterborne coatings is due to its low VOC content. Waterborne coating technologies require new types of resins for binder dispersions and additives to fulfill high quality requirements. An aqueous PU dispersion (PUD) is a binary colloidal system in which the particles of PU are dispersed in continuous water phase. The particle size tends to be about 20-200 nm, and the particles have a high surface energy. This results in a strong driving force for film formation after water evaporation. Usually, PU polymers are not soluble in water and the degree of hydrophilicity is one of the key factors determining the particle size distributions in the PUD. The shelf life colloidal stability of PUD is influenced by their particle size distribution. Therefore, a special treatment or structural modification is necessary for the polymer to be dispersible in water. Generally, aqueous PUDs can be prepared by incorporating hydrophilic groups into the polymer backbone or by adding a surfactant. The former material known as a PU ionomer in which the ionic groups act as internal emulsifiers. Therefore, waterborne PU ionomers consist of PU backbones with a minority of pendant acid or tertiary nitrogen groups, which are completely or partially neutralized or quaternized, respectively, to form salts.

Various processes have been developed for the preparation of aqueous PUDs. In all of these processes, a medium molecular weight polymer (the prepolymer) is formed by the reaction of suitable diols or polyols (usually macrodiols such as polyethers or polyesters) with a molar excess of diisocyanates or polyisocyanates in the presence of an internal emulsifier as first step. The emulsifier is a diol with an ionic group (carboxylate, sulfonate, or quaternary ammonium salt) or a non-ionic group [poly (ethylene oxide)] is usually added to allow the dispersion of the polymer

in water. The critical step in which the various synthetic pathways differ is the dispersion of the prepolymer in water and the molecular weight buildup. The most important processes are the acetone process, pre-polymer mixing process, melts dispersion process and ketimine process.

Aqueous PUDs are of three types; non-ionic cationic and anionic depending upon the type of hydrophilic segments present in the PU backbone. Depending on the type of ionic species, a minimum ionic content is required for the formation of a stable PU ionomer. The interaction between ions and their counter ions is responsible for the formation of stable dispersion. The ion-dipole interaction between the ionomer and dispersing media (e.g., water) results in the formation of a solvation sheath, where the ionomer properties depends on the degree of neutralization and content of ionic component.

2.1.3.1 Cationic PU

According to Lorenz et al. [2], cationic PU ionomers in water are stabilized because of the formation of electric double layer. The soft segment of cationic PU is hydrophobic and the hard segment with secondary ammonium cation (NHR_2^+) is hydrophilic. Therefore, the molecular chains of cationic PU can self-organize to micelles when dispersed in water, with positively charged hydrophilic groups at the surface and hydrophobic groups concentrated in the micelle interior. An electric double layer forms around the micelles, which undergo Brownian motion, stabilized against intermicelle aggregation by electrostatic forces. At the same time, there are hydrogen bonds between the hydrophilic groups and water molecules, and the particles are surrounded by a layer of water molecules making a solvation sheath. This phenomena hinder the aggregation of particles. For the preparation of a cationic PUD, 3-dimethylamino-1, 2-propanediol can be used to disperse the medium after neutralizing with a weak protonic acid in water.

2.1.3.2 Anionic PU

Dimethylol propionic acid (DMPA) is commonly incorporated into PU backbones because it is very effective for water dispersion in the subsequent neutralization reaction with triethylamine (TEA). The carboxylic ion of DMPA in the polymer is hydrophilic and serves as an anionic center as well as internal emulsifier. Carboxylic ions are not only stabilizes aqueous PUDs, but may also become the curing site. The carboxyl groups in PUDs provide charges to the surfaces of PU micelles (particles), thereby causing repulsion between PU particles resulting in uniform PU particle size distribution in the water phase. Schematic diagrams of micelles formed by (a) cationic and (b) anionic PU ionomers in water are shown in Figure 2.3. Because of the hydrophilic properties of the carboxyl group. These PUs becomes self-emulsified (or water-reducible) in the water phase. Such conventional aqueous-based PUs has a disadvantage similar to that of a polymer surfactant, in that they exhibit high hydrophilicity after drying into a film. Therefore, the weight percent of DMPA used the prepolymer not only influences the particle size and stability of the dispersion, but also the hydrophobicity of the coatings. For example, the use of higher amount of DMPA results in a smaller average particle size and high hydrophilicity in the film, which reduces the water resistance of the coating. Therefore an optimum amount of DMPA should be used for making a high performance coating [2].

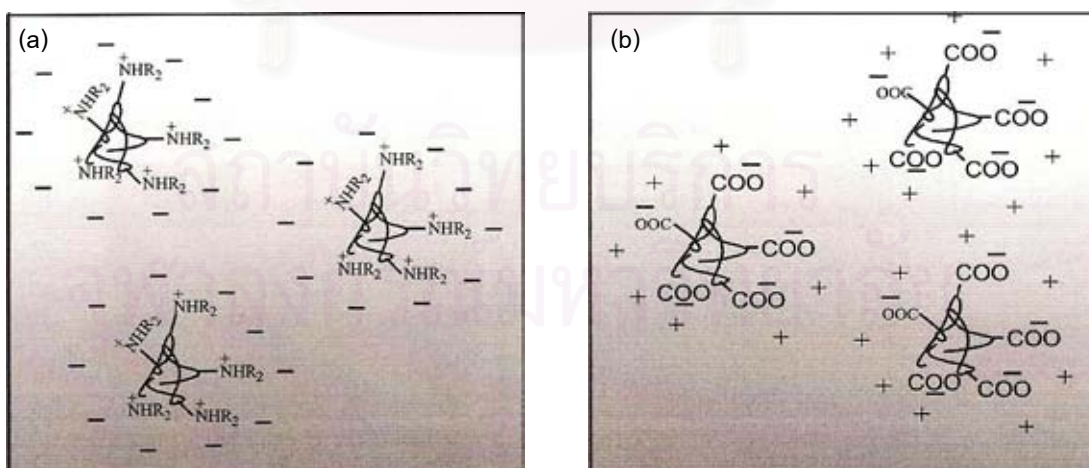


Figure 2.3 Schematic of micelles formed by (a) cationic and (b) anionic polyurethane ionomers in water [2].

2.1.4 Emulsion Polymerization

Emulsion polymerization is a most typical and well-known polymerization method for preparing uniform polymeric microspheres composed of relatively hydrophobic monomers. The monodispersed microspheres with diameters from several tens to hundreds of nanometers can be obtained easily by this technique. The polymerization system usually consists of a hydrophobic monomer, water (medium), an emulsifier such as sodium salt of long-chain aliphatic acid, and a water-soluble initiator. The polymerization procedure is as follows.

After the monomers are dispersed into the aqueous phase where the emulsifier is dissolved. Nitrogen gas is introduced to replace oxygen in the reactor. Then, the temperature is elevated to a desired reaction temperature. Finally, the initiator is added to the system to start polymerization. The advantage of the emulsion polymerization is that the polymerization rate is fast and the size distribution of the obtained particles is very narrow. Usually, the polymerization is nearly complete within 1 h. When the concentration of the emulsifier is above the critical micelle concentration (CMC), the emulsion polymerization of the hydrophobic monomer is well described by the micellar nucleation mechanism (Harkins' theory). Before the initiator is added, the system is composed of monomer-swollen micelles (~ 20 nm, $\sim 10^{17-18}$ /cm³), monomer droplets (1-10 μ m, 10^{8-9} /cm³) stabilized by an emulsifier, and an aqueous phase where free emulsifier molecules ($\sim 10^{18}$ /cm³) and a small part of monomer are dissolved. After a water-soluble initiator such as potassium persulfate (KPS) is added in the system, it decomposes into primary radicals in the aqueous phase. The radical is either captured quickly by the monomer-swollen micelle or captured after growing to an oligomeric radical by adding several monomers dissolved in the aqueous phase. Then, the polymerization proceeds inside monomer-swollen micelles to form monomer-polymer particles. The polymerization does not occur inside the monomer droplets, although most of the monomer is present in the system as monomer droplets. This is because the number and the specific surface area of the monomer droplets are much smaller than those of the micelles. As a result, the possibility of primary radicals or oligomeric radicals entering the droplets is negligibly small. The monomer droplet serves only as a reservoir of the monomers from which the monomer diffuses into the monomer-polymer particles through the

aqueous phase and thus the dynamic equilibrium is maintained among monomer droplets, aqueous phase, and monomer-polymer particles until the monomer droplets disappear. In parallel with the growth of the monomer-polymer particles, free emulsifiers adsorb on the surface of the particles to stabilize the growing polymer particles. After it is consumed completely, no more particles are formed and their number stabilizes at a constant value. The polymerization then proceeds only in the monomer-polymer particles.

Concluding the above description, the polymerization proceeds in the three stages:

In the first state, the particles are generated from the monomer-swollen micelles by radicals entering the micelles from the aqueous phase. After the depletion of the micellar form of emulsifiers, the formation of new particles ends.

In the second state, the particles grow by means of diffusion of the monomer from the monomer droplets until the monomer droplets disappear.

In the last stage, the particles consume the remaining monomer inside until the complete monomer conversion [3].

2.1.5 Polyaniline

Among various materials for anti-corrosion of metals, conductive polymer coatings are one of the most effective, cheapest and also the most environmentally friendly materials.

Research on corrosion protection of steel by conducting polymers gained momentum in the last few decades. The advantage of protection by conducting polymer coating is that the coatings get more tolerance to pin holes due to the passivation ability of conducting polymer. In recent years, studies are being reported on the use of conducting polymer containing paint coatings for the protection of steel [4].

The synthesis of conducting polymers as stable colloidal dispersions overcomes the limitations associated with the intractable nature of these polymers. Such dispersions are readily prepared by chemical oxidation of the monomer (normally pyrrole or aniline) in the presence of a steric stabilizer such as polyvinyl alcohol (PVA) or poly ethylene oxide (PEO).

The use of sterically stabilized latex particles as the basis on which to form core-shell conducting polymer colloids was first reported by DSM Research. The conducting polymer component constitutes the shell layer of the particle without affecting the steric stabilization mechanism. The particle core is the latex particle (e.g. polystyrene or polyurethane).

An alternative approach to conducting polymer colloid formation involves the electrochemical oxidation of monomer in the presence of a stabilizer in flow through electrolytic cell.

Polyaniline (PANI) has been extensively investigated for its ability to protect metals against aqueous corrosion. The PANI dispersions were prepared by an oxidative dispersion polymerization using dodecylbenzene sulfonic acid and poly (sodium-4-styrenesulfonate) as stabilizer and co-dopant. Chattopadhyay and Mandal and Banerjee et al. prepared PANI dispersions by oxidation polymerization with methyl cellulose and poly (vinyl methyl ether), respectively, as stabilizers. Stejskal and Kratochvil prepared similar PANI colloidal dispersions with poly (vinyl alcohol) and poly (*N*-vinylpyrrolidone) as steric stabilizers [5].

2.2 Literature Reviews

In 1997, Hirose [6] studied the structure and properties of core-shell type acrylic-polyurethane hybrid aqueous emulsion. He prepared core-shell type acrylic-polyurethane hybrid emulsions containing reactive groups by soap free polymerization technique. In this emulsion, the shell part is composed of polyurethane polymers containing pendant carboxylic groups and hydrazide end groups and the core part is composed of acrylic copolymer containing ketone groups. The particle size of emulsion varied depending on the core-shell ratio and chemical composition.

In 1999, Dong [7] prepared waterborne polyacrylate-polyurethane microspheres, which polyurethane acts as the shell and acrylic polymer as the core. From transmission electron microscopy (TEM), it was shown that the PU layer was stained by osmium tetroxide and appeared dark, and the core appears white. The increase of the core/shell ratio and the cross-linked structure led to the decrease of water absorption and the contact angles. But when the core/shell is large, the binding strength, impact strength, and adhesive force decrease and their flexibility are bad.

In 2001, Lee [8] modified the aqueous polyurethane by forming latex interpenetrating polymer networks with polystyrene. A polyurethane dispersion was synthesized from poly (propylene glycol) (PPG) (2000 g/mol) and IPDI. To obtain the latex IPNs or semi-IPNs, hydrophilic vinyl terminated prepolymers were first polymerized in the presence of potassium persulfate (KPS), followed by the polymerization of styrene monomers in the cross-linked PUs. PU/PS latex particles formed well defined core (PS)-shell (PU) morphology and positive deviations of the mechanical properties showed that the PU/PS hybrids films form intensive interlocking structures between the two components.

In 2004, Chen [9] synthesized ternary latex of PU/PA/epoxy resin. First, polyurethane dispersion was prepared from polyether polyol, and TDI. After that PU/PA latex was prepared by introduction MA and BA monomer and initiator ($0.03\% \text{K}_2\text{S}_2\text{O}_8$) into PU dispersion acts as seed particle. The average particle size of PU/PA latex becomes larger with the increase of PA content in PU/PA latex.

In 2005, Brown [10] studied and compared the properties of urethane/acrylic hybrids with the corresponding blends of polyurethane dispersions and acrylic emulsions. The mechanical properties of pure polyurethane (PUR) based urethane/acrylic hybrids were found to be superior to those of PUR/acrylic blends of similar composition. The difference in mechanical properties between blends and hybrids are attributed to the increased level of interphase polymer and improved dispersion of phase domains in the hybrids.

In 1997, Bremer [11] prepared core-shell dispersions with a polyurethane (a low T_g) core and a polyaniline shell. The polyurethane-polyaniline dispersions have good coating properties. The nature of the particles having a filmforming core and a thin shell of the conductive polymer guarantees an optimum contact between the metal surface and the active component in the shell, the polyaniline. These type of dispersion are especially suited as binder system in advanced corrosion protection primers.

In 2001, Yang [12] studied nanocomposite of polyaniline and water-based polyurethane. He synthesized polyaniline complexes with polystyrenesulfonic acid and poly (2-acrylamido-2-methyl-1-propanesulfonic acid). Polyaniline complexes were dissolved in water and filtered to make 2% aqueous solution. Water-based polyurethane was added to make polymer blend solution. The stability of polyaniline under air provides the opportunity of various applications. The improvement of the solubility opens the opportunity for solution processing and blending, thus leading to materials with high electrical conductivity and mechanical strength. The adhesive properties and chemical inertness of PU make polyaniline blend suitable for conducting coating.

In 2003, Jeevananda [13] prepared a series of conducting interpenetrating networks (IPNs) by filling polyaniline (PANI) into mixture of polyurethane (PU) with poly (methyl methacrylate) (PMMA) to improve the processability of polyaniline. PU/PMMA IPNs is not aqueous dispersion. The PANI filled IPNs can find applications as an antenna material in cellular phone, as an antistatic paper roller in a printer, and as a fragile, preventive wrapping bag for packing electronic products.

In 2005, Ocampo [14] compared the resistance against marine corrosion of several paints before and after being modified by adding a conducting polymer derived from polythiophene. All the paints showed an excellent adherence to the steel substratum and the smooth and homogenous surface of the film provides a good inter-coat layer for the other applications. An important improvement in the protection was found after adding 0.2% w/w of poly (3-decylthiophene-2, 5-diyl). Thus, corrosion products did not appear in the surface of the metallic piece after 30 days of immersion.

In 2005, Laco [15] compared the corrosion protection of carbon steel with thermoplastic coatings and alkyd resins containing polyaniline as conducting. The results were shown that thermoplastic polymer coatings had a corrosion resistance very lower than alkyd resin modified with polyaniline. Although the characteristics of alkyd resin without conductive polymer are poor in relation to the thermoplastics polymers used in this work, the corrosion resistance is clearly improved by the presence of the conductive polymer.

In 2005, Sapurina [16] modified water-based polyurethane latex with a conducting polymer, polyaniline, in situ during the polymerization of aniline. The colloidal stability is maintained with a polymeric stabilizer, poly (N-vinylpyrrolidone) (PVP). Both the particle size and polydispersity are reduced with increasing concentration of PVP in the reaction mixture. The mechanical properties of composite films are sufficient to be used as the coatings for the anticorrosion protection of metals.

In 2006, Sung [17] synthesized polyaniline/polystyrene latex by oxidative polymerization, which polystyrene acts as the core and polyaniline as the shell. The sedimentation problem and also electrorheological performance by dispersing synthesized hollow polyaniline particles with nano-scale in silicon oil were studied.

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

Chemicals	Suppliers
1, 6-Hexanediol	ACROS
Adipic acid	ACROS
Isophthalic acid	ACROS
Toluene diisocyanate (TDI)	ACROS
<i>N</i> -methyl-2-pyrrolidone (NMP)	ACROS
Dimethylolpropionic acid (DMPA)	ACROS
Methyl methacrylate (MMA)	FLUKA
Triethylamine (TEA)	FLUKA
Tertiary butyl hydroperoxide (TBHP)	FLUKA
Sodium formaldehyde sulfoxylate	FLUKA
Ethylene diamine (EDA)	FLUKA
Poly (<i>N</i> -vinylpyrrolidone) (PVP) (type K90, M = 390,000)	FLUKA
Aniline hydrochloride, 99%	ACROS
Ammonium peroxydisulfate, 98% (APS)	FLUKA
Potassium hydroxide (KOH)	FLUKA
Pyridine	ACROS
Acetic anhydride	ACROS
Chlorobenzene	ACROS
Di- <i>n</i> -butylamine	FLUKA
Toluene	FLUKA
<i>n</i> -Butanol	FLUKA
Phenolphthalein	FLUKA

3.2 Glasswares and Equipments

1. Burette
2. Pipette
3. Ultra turrax disperser (UTD)
4. Mechanical stirrer
5. Thermometer
6. Condenser
7. Five-neck round bottom glass reactor
8. Heating mantle
9. Silicone oil bath
10. Dropping funnel

3.3 Instruments

1. Fourier transform infrared spectrometer, FTIR
2. Transmission electron microscope, TEM
3. Particle size analyzer
4. Gel permeation chromatography (GPC)
5. Scanning electron microscope, SEM

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3.4 Purification and Preparation of Materials

3.4.1 Water was removed from polyester polyol by heating in vacuum oven at 120°C for 2 h.

3.4.2 Water was removed from dimethylolpropionic acid by heating in vacuum oven at 105°C for 2 h.

3.4.3 *N*-methyl-2-pyrrolidine was purified before used by refluxing with calcium hydride (CaH₂) for 2 h and then distilling off.

3.4.4 Di-*n*-butylamine was purified before used by refluxing with calcium hydride (CaH₂) for 2 h and then distilling off.

3.4.5 Water was removed from chlorobenzene by immersing molecular sieve type 4A for 24 h and then distilling off.

3.5 Synthesis of PANI/PU/PMMA Latex

3.5.1 Synthesis of Polyester Polyol

A 500 mL five-neck round bottom glass reactor equipped with a mechanical stirrer, a thermometer, a condenser, and a nitrogen gas inlet was used. Reaction temperature was controlled using a heating mantle. Figure 3.1 shows the apparatus for the synthesis of polyester polyol.

The 1, 6-hexanediol, adipic acid and isophthalic acid, 5:3:1 mole ratio, were introduced into the reactor and stirred with continuous heating that controlled not over 280 °C for 9 h.

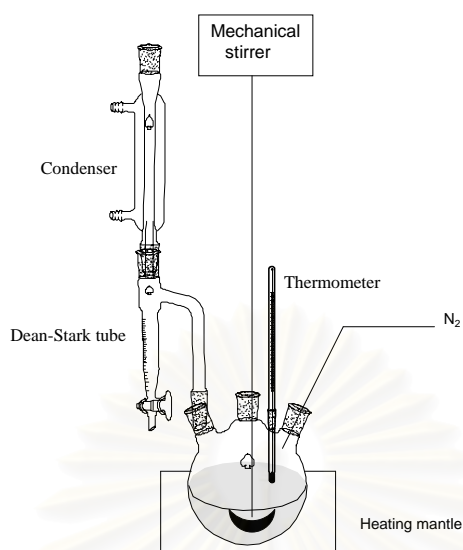


Figure 3.1 The apparatus for the synthesis of polyester polyol.

3.5.2 Synthesis of Aqueous Polyurethane Dispersion

Aqueous polyurethane dispersion was prepared by self-emulsification. Polyaddition reaction was conducted in a 500 ml five-necked round bottom glass reactor equipped with a reflux condenser, a mechanical stirrer, thermometer, a nitrogen gas and dropping funnel. The polyester polyol was introduced into the reactor then slowly adding TDI from the dropping funnel about 2 h. When the TDI addition was completed, add the NMP and DMPA to the reactor, respectively. Then the mixture was heated to 90°C and hold for 1.5 h. The amount of residual NCO groups was determined by the di-*n*-butylamine back titration method.

The prepolymer was then neutralized the carboxylic acid in DMPA by adding TEA. After that the mixture was dispersed in deionized water with Ultra turrax disperser (UTD). The mixture was then chain extended and catalyzed by adding ethylene diamine (EDA) and sodium formaldehyde sulfoxylate, respectively. Figure 3.2 shows the apparatus for the synthesis of aqueous polyurethane dispersion.

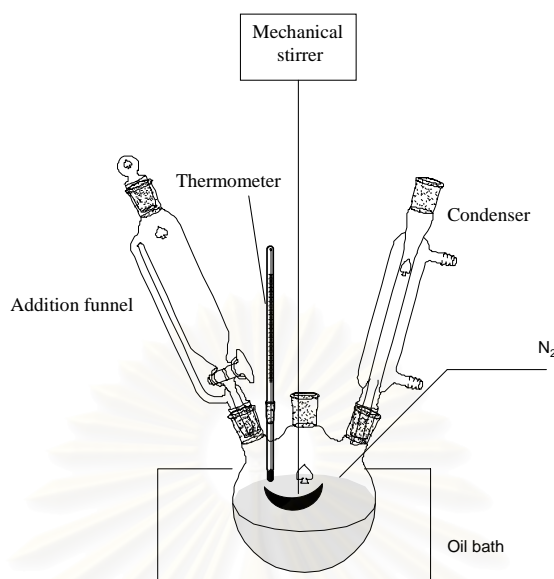


Figure 3.2 The apparatus for the synthesis of aqueous polyurethane dispersion.

3.5.3 Synthesis of PU/PMMA Latex

The polyurethane (PU)/poly (methyl methacrylate) (PMMA) latex emulsion was prepared by soap free emulsion polymerization method. The aqueous polyurethane dispersion was used as seed particle, calculated weight percentages of MMA monomers were dropped into this system in 2 h at room temperature. Then initiator, tertiary butyl hydroperoxide (TBHP) (0.03 wt. %), was introduced into the reactor, the mixture was heated to 65°C and maintained for 2 h.

The weight ratio between PU and PMMA was varied, by changing the amount of MMA introduced while keeping the amount of PU dispersion constant, to be 2:1, 1:1 and 1:2.

3.5.4 Synthesis of PANI/PU/PMMA Latex

The PU/PMMA latex constituted the medium for the polymerization of aniline. The latex was mixed with a 4 wt. % aqueous poly (*N*-vinyl pyrrolidone) (PVP) solution and water was added as needed to adjust the concentrations of both polymer components. The aqueous solution of aniline hydrochloride was then introduced, followed by the aqueous solution of ammonium peroxydisulfate at room temperature for 3 h. The peroxydisulfate-to-aniline molar ratio was 1.25 in all experiments.

First, the amount of polymer steric stabilizer, PVP, was varied as 0.4, 0.8, 1.1 and 1.3 wt. % at the concentration of aniline hydrochloride was 0.1 mol L⁻¹.

Next, when the optimum amount of PVP was observed, the concentration of aniline hydrochloride was varied as 0.1, 0.2, 0.3 and 0.4 mol L⁻¹.

3.6 Corrosion Study

The corrosion study was carried out with a home-made equipment developed in laboratory. This device allowed program controlled cycles for immersion of metallic pieces in an aggressive solution medium, which consists of an aqueous solution of NaCl (3.5 wt. %) stored in a glass container. The operating conditions for one cycle were; immersion of recovered steel sheets for 15 min, wring out for 30 min, drying stage with bulbs 100 W for 10 min, and cooling time at room temperature for 5 min. The samples were tested in the solution medium during 30 days. The complete set up was maintained at room temperature.

3.7 Determination of Properties of Resins

There are four items of specification determined here namely; nonvolatile matter (NV), hydroxyl value (OHV), acid value (AV), and isocyanate group (NCO) content. Each of them will be described as follows.

3.7.1 Determination of Nonvolatile Matter (NV): ASTM D 2834-95

Place approximately 2 g of aqueous polyurethane dispersion into a flat-bottom dish and place in the oven maintained at $105.0 \pm 2.5^\circ\text{C}$. After heating for 24 h, weigh the dish.

$$\%NV = [(C - A)/S] \times 100$$

C	=	weight of dish and contents after heating (g)
A	=	weight of dish (g)
S	=	weight of sample used (g)

3.7.2 Determination of Hydroxyl Value (OHV): ASTM D 4274-05

This method for determination of hydroxyl value present in polyester polyol resin. The sample is acetylated using a known excess of acetic anhydride. The acid liberated by the acetylation is determined by back titrating with standard alkali.



Reagents

1. Methanolic potassium hydroxide, 1 M KOH
2. Pyridine/acetic anhydride solution
3. 1% phenolphthalein indicator solution

Procedure

Approximate 5 g polyester polyol into a 250 Erlenmeyer flask. Pipette 20 mL of the pyridine/acetic anhydride solution. Then fit a condenser to the flask and place on oil bath at 98 ± 2 °C for 2 h, swirling regularly. After that, cool flask in ice water and rinse condenser with 20 mL deionized water. Add 4-6 drops phenolphthalein indicator solution and titrate rapidly with methanolic KOH 1 M to the first faint pink end point. A blank titration is done following the same procedure as the sample. It is important that the blank and the sample be titrated at the same temperature.

$$\text{Hydroxyl value (mg KOH/ g sample)} = \frac{(B-S) \times M \times 56.1}{W}$$

B = Volume of KOH titrated in blank (mL)

S = Volume of KOH titrated in sample (mL)

M = Concentration of KOH (molarity)

W = Weight of sample (g)

3.7.3 Determination of Acid Value (AV): ASTM D 1639-90

For determination of free acid and/or the acidity of polyester polyol and prepolymer resin, which represents the number of milligrams of potassium hydroxide (KOH) required to neutralize the free acids in one gram of sample.

Reagents

1. Solvent/indicator solution, prepared from toluene/n-butanol; 3:1 volume ratio. Then add phenolphthalein indicator solution and neutralized by slowly add alcoholic KOH solution until first permanent pink colour before use.

2. Alcoholic potassium hydroxide (KOH) 0.1 N

Procedure

Approximate 5 g sample into a 250 Erlenmeyer flask. Add 25 mL of neutralized solvent/indicator solution to the sample and mix until dissolved. After that titrate sample with alcoholic KOH 0.1 N to pink end point, which will stay pink for 30 seconds.

$$\text{Acid value on solid} = \frac{V \times 5.61}{W \times N}$$

V = Volume of alcoholic KOH 0.1 N (mL)

W = Weight of sample (g)

$$N = \frac{\%NV}{100}$$

3.7.4 Determination of Isocyanate Groups (NCO) Content: ASTM 2572-97

This test method covers the determination of the isocyanate group (NCO) content of prepolymer.

Reagents

1. Di-*n*-butylamine in chlorobenzene 1.0 N
2. Hydrochloric acid (HCl) 1.0 N
3. Bromophenol blue 1% in ethanol
4. Methanol

Procedure

Weigh 1.0000 g of prepolymer in a 250 mL Erlenmeyer flask. Add 10 mL chlorobenzene. Add 20.0 mL of 1.0 N dibutylamine in chlorobenzene solution. Leave the solution stand for 1-1.5 h in the flask with the stopper. Add 40 mL of methanol. Add 4-6 drops of indicator solution. Titrate with 1.0 N HCl, a yellow end point. A blank titration is done using all reagents without the addition of the sample.

$$\% \text{ free } -\text{NCO} = \frac{(V1-V2) \times M \times 4.2}{W}$$

- V1 = The volume of 1.0 N HCl used in the blank titration
 V2 = The volume of 1.0 N HCl used in the sample titration
 M = Molarity of HCl
 W = Weight of sample (g)

3.8 Characterization

3.8.1 FTIR Analysis

Fourier transform infrared (FTIR) spectra of polyester polyol, aqueous polyurethane dispersion, PU/PMMA latexes, and PANI/PU/PMMA latexes were obtained using a Bruker Tensor 27 FTIR spectrometer in the range 400–4000 cm^{-1} at room temperature, employing the KBr disc technique.

3.8.2 Characterization of Molecular Weight Distribution by GPC

Molecular weight and molecular weight distribution of polyester polyol was determined using a Waters 150 CV gel permeation chromatography. One hundred microliters of a 0.5% solution of polyester polyol in TCB was injected at a flow rate of 1.0 mL/min onto a column set consisting of PLgel 10 μm mixed B 2 columns.

3.8.3 Particle Size and its Distribution

The particle size and its distribution of latexes were measured by laser light scattering method using MASTERSIZER 2000 (MALVERN). The sample of latexes were directly placed in the cell and adjust the solid content to around 1-2 wt. % with de-ionized water. The temperature of the cell was kept at around room temperature.

3.8.4 Morphology of Particles

The morphology of particles in PU/PMMA latexes, and PANI/PU/PMMA latexes was observed by transmission electron microscopy (TEM) JEM-200CX model. Samples for TEM observation were prepared by dropping highly diluted latex onto the formvar-coated copper grid, stained with phosphotungstic acid or osmium tetroxide, and dried in a desiccator at room temperature.

3.8.5 Morphology of the Coating Degradation

The morphology of metal surface coated with PANI/PU/PMMA latexes after immersion in the salt solution for 30 days was observed by scanning electron microscopy (SEM) JSM-6400 model. The SEM samples were sputter-coated with gold for 60 s.



CHAPTER IV

RESULTS AND DISCUSSION

4.1 Aqueous Polyurethane Dispersion

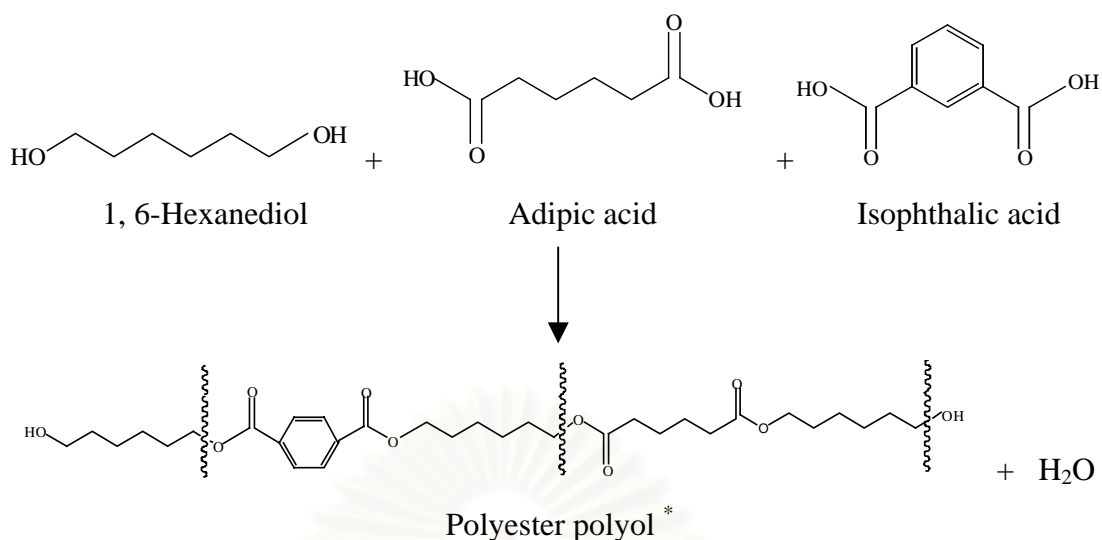
Polyurethanes (PU) are widely used in the coating and adhesive applications because of their excellent performance. Organic solvent based polyurethanes are increasingly restricted in their traditional applications because of the demands of environmental regulations, lower costs and safety. In contrast, aqueous polyurethane dispersions prepared with low levels of organic solvent seeing ever wider use.

In this research, aqueous polyurethane dispersion was synthesized from 2, 4-toluene diisocyanate and polyester polyol. The study was divided into 2 steps as following:

1. Synthesis and characterization of polyester polyol
2. Synthesis and characterization of aqueous polyurethane dispersion

4.1.1 Synthesis and Characterization of Polyester Polyol

Polyester polyol was synthesized from 1, 6-hexanediol, adipic acid, and isophthalic acid, at mole ratio 5:3:1 as shown in Scheme 4.1. The synthesis of polyester polyol is a condensation polymerization, which gives water as by product. With the excess amount of 1, 6-hexanediol in the reaction, the polyester polyol was obtained with hydroxyl (OH) end groups.



* From now on, the structure of polyester polyol will be represented as HO~~~~~OH

Scheme 4.1 Synthesis of polyester polyol

The reaction time was varied and the acid value of the mixture was studied by titrating directly with alcoholic KOH solution as shown in Table 4.1.

Table 4.1 The study of acid value of the synthesis of polyester polyol

Reaction time (h)	Acid value
4	32.0
5	27.0
6	18.4
7	7.2
8	4.3
9	3.7

It was found that the acid value decreased when the increase of reaction time. Finally, the acid value was found to be 3.7 at 9 h of the reaction time, this indicates that part of dicarboxylic acid was converted to polyester polyol.

Synthesis of polyester polyol was confirmed from functionality of polyols by analyzing it with FTIR spectroscopy. Figure 4.1 shows the absorption band at around wave number 3442 cm^{-1} which confirms free hydroxyl functional group in the synthesized polyester polyol. The absorption band at 1729 cm^{-1} is due to carbonyl stretching of ester linkage rather than the carboxylic acid of the starting materials. One reason is that no characteristic hydroxyl absorption of carboxylic acid appears in the absorption band around $3300\text{--}2500\text{ cm}^{-1}$. The other reason is that the acid value of the as prepared polyester polyol is very low, probably due to the trace amount of adipic acid and isophthalic acid left in the mixture. These absorption bands clearly confirmed the existence of polyester polyol. The other absorption band at 2936 and 2864 cm^{-1} are due to C-H stretching.

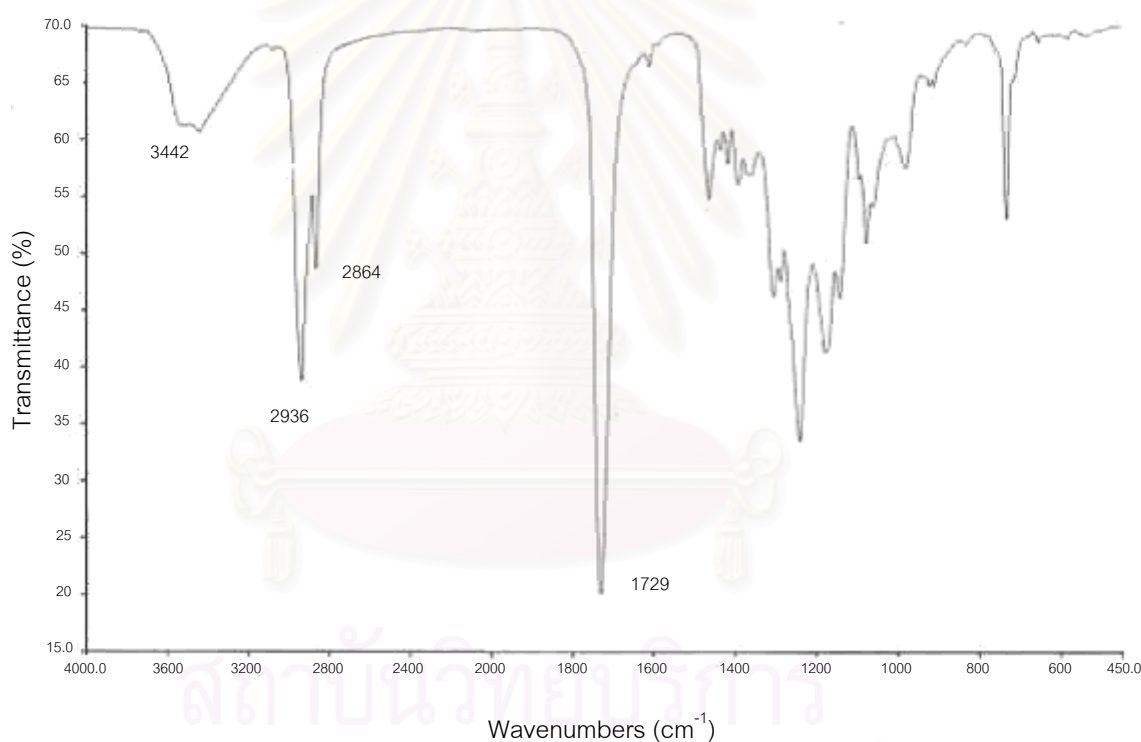


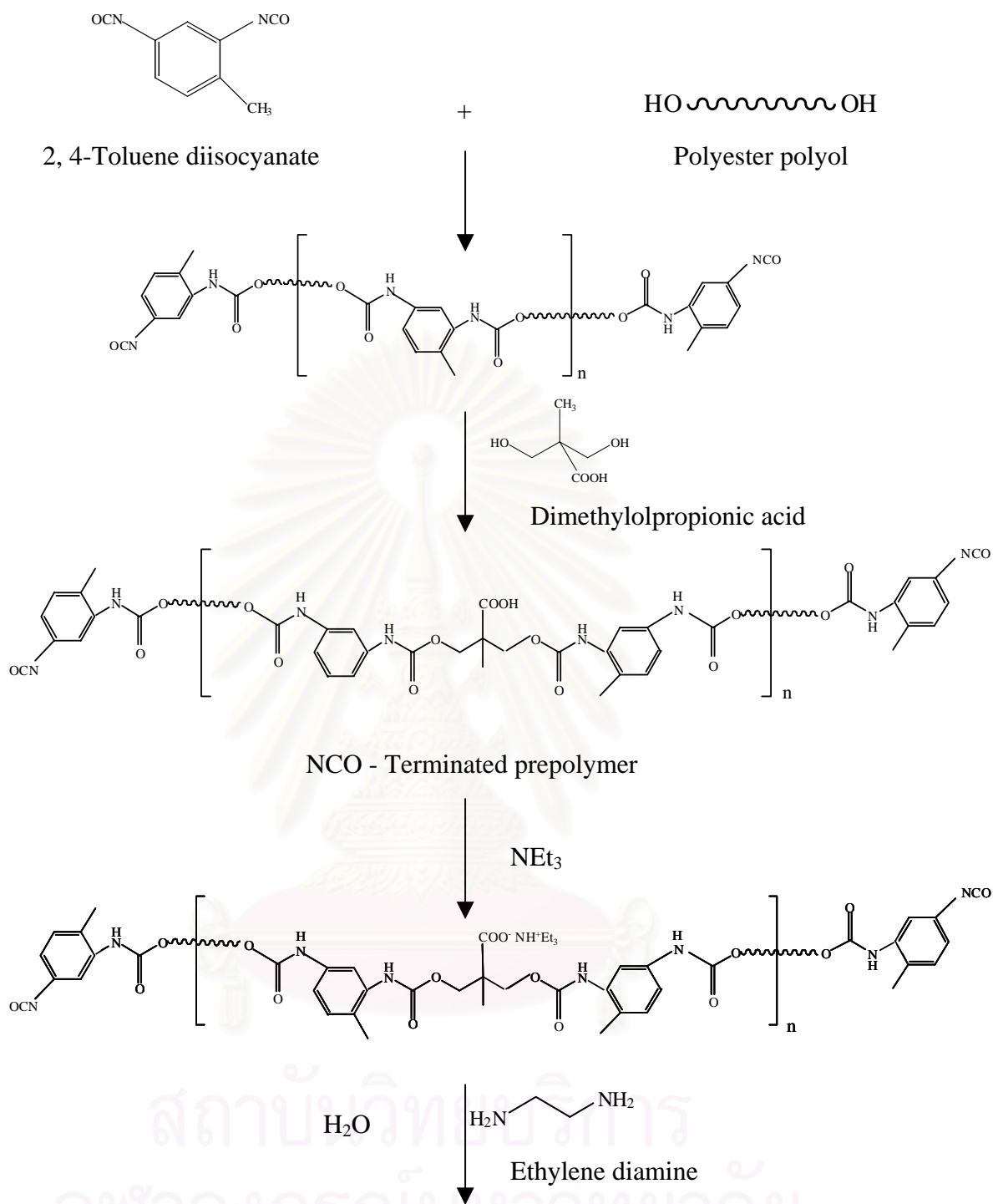
Figure 4.1 FTIR spectrum (neat) of polyester polyol.

The hydroxyl value of polyester polyol was determined by firstly acetylating with acetic anhydride and then titrating with alcoholic KOH solution. The hydroxyl value was found to be 140 mg KOH/g. The polyester polyol was waxy white viscous fluid at room temperature.

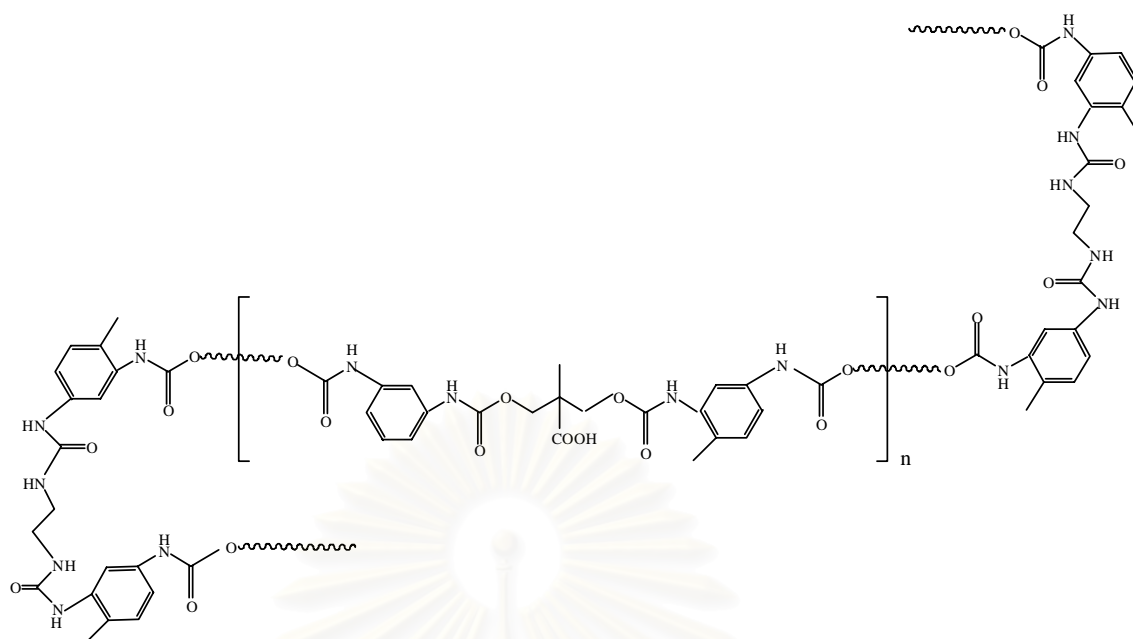
The molecular weight of polyester polyol was analyzed by gel permeation chromatography (GPC). It was found that the number average (\overline{M}_n) and weight average (\overline{M}_w) molecular weights of polyester polyol were 2,041 and 3,256, respectively.

4.1.2 Synthesis and Characterization of Aqueous Polyurethane Dispersion

The synthesis of the aqueous polyurethane dispersion is shown in Scheme 4.2. Aqueous-based polyurethane dispersion was prepared by prepolymer mixing process. Firstly, polyester polyol was reacted with 2, 4-toluene diisocyanate to form polyurethane prepolymer. Then dimethylolpropionic acid in *N*-methyl-2-pyrrolidone was added to the mixture. The reaction gave the prepolymer containing pendant acid group. It was then neutralized with triethylamine to form self ionic emulsifier, ammonium carboxylate [$-\text{COO}^-\text{HN}^+(\text{C}_2\text{H}_5)_3$], and disperse in the water. Afterwards, the chain extension step was accomplished by the addition of ethylene diamine to the aqueous prepolymer dispersion. Molecular weight of aqueous polyurethane dispersion was increased by the formation of urea linkage with NCO-terminated prepolymer and diamines. The increase of molecular weight affect to the mechanical properties of polyurethane.



Scheme 4.2 Synthesis of the aqueous polyurethane dispersion



Aqueous polyurethane dispersion

Scheme 4.2 (cont.) Synthesis of the aqueous polyurethane dispersion

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Figure 4.2 shows FTIR spectrum of synthesized aqueous polyurethane dispersion from polyester polyol. The absorption band at 1727 cm^{-1} is due to C=O stretching of polyester and also urethane linkage. The absorption at 3434 cm^{-1} is due to O-H stretching of water in latex and also N-H stretching of the amino group in polyurethane structure. The formation of urethane group -NHCOO- was confirmed, which supported the aqueous polyurethane dispersion structure.

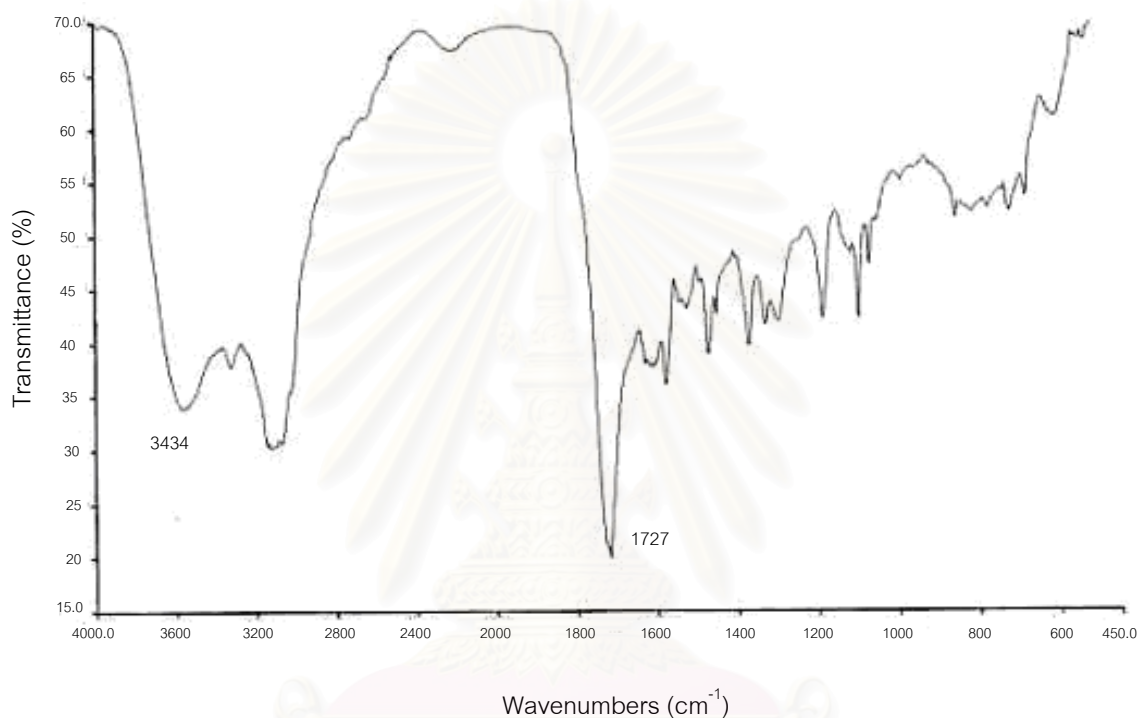


Figure 4.2 FTIR spectrum (neat) of aqueous polyurethane dispersion.

The obtained prepolymer had free isocyanate end group (%NCO) of 4.7%, which was measured by di-*n*-butylamine back titration method [30]. The aqueous polyurethane dispersion was a yellow milky latex. It had nonvolatile matter 37 % and pH 8-9.

The formation of polyurethane particle in the water phase is shown in Figure 4.3. The polyurethane particles were dispersed in the water by self anionic emulsifier, $\text{-COO}^-\text{HN}^+(\text{C}_2\text{H}_5)_3$.

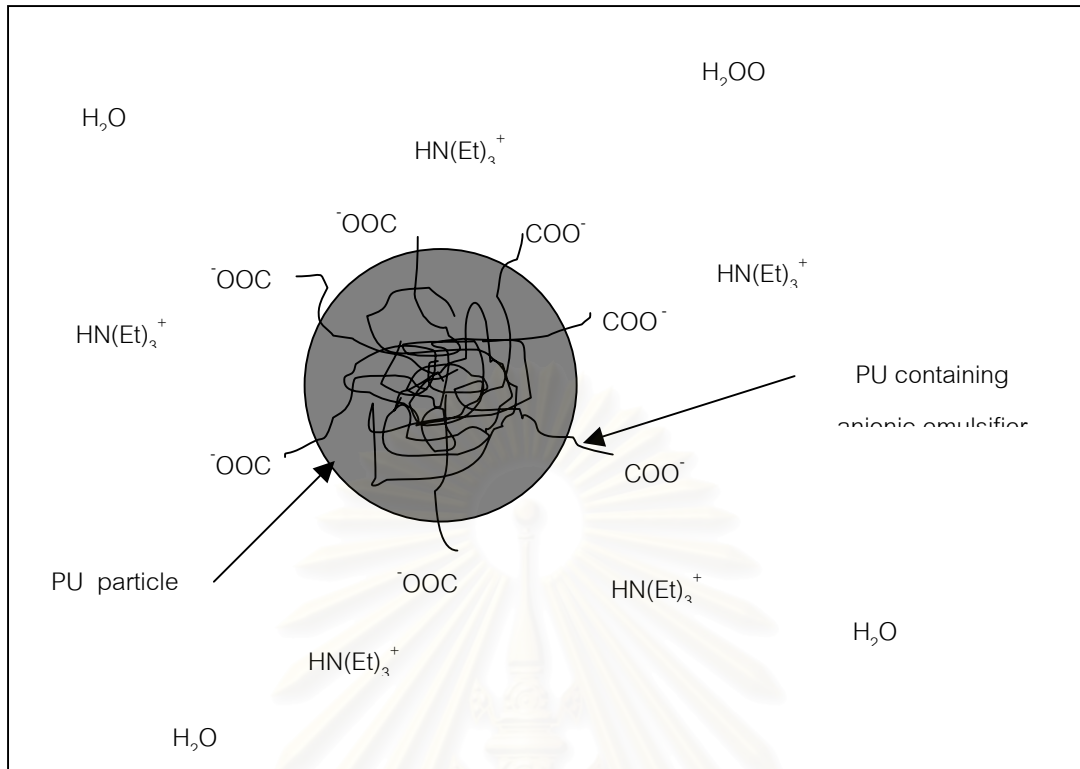


Figure 4.3 Diagrammatic formation of an aqueous polyurethane dispersion.

The particle size distribution of aqueous polyurethane dispersion was narrow as shown in Figure 4.4. The average particle size of polyurethane dispersion was found to be 182 nm.

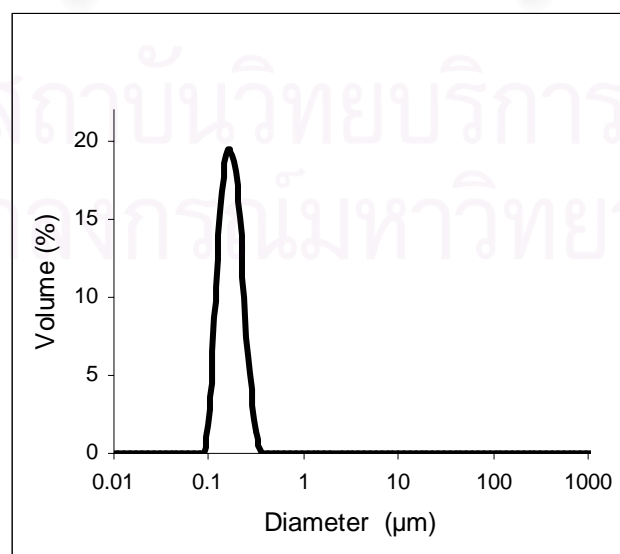


Figure 4.4 Particle size distribution of aqueous polyurethane dispersion.

4.2 PU/PMMA Latex

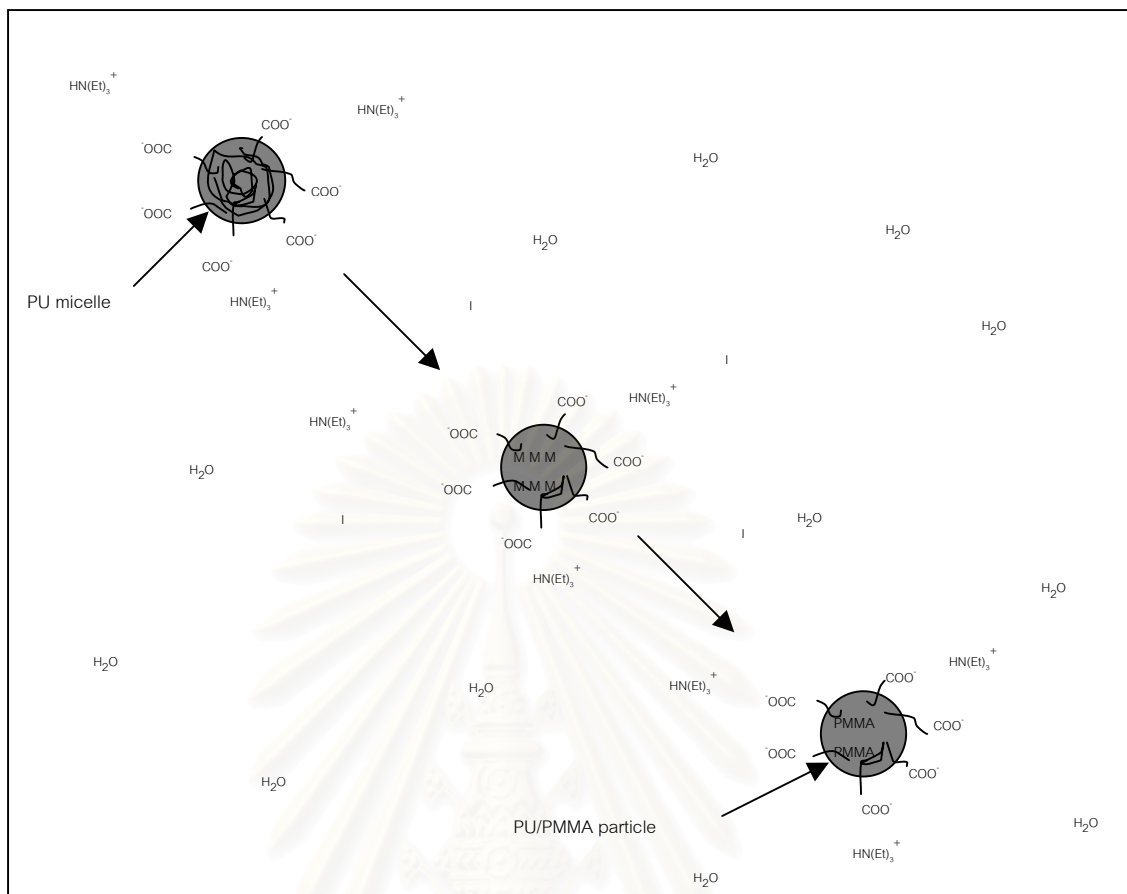
In the coatings industry there is a strong commercial need to optimize the performance of aqueous-based systems to replace solvent-based coatings as pressures to reduce volatile organic compounds (VOCs) increase. Aqueous polyurethane dispersions are known to offer high performance. The higher cost of aqueous polyurethane dispersions has led some resin suppliers to develop a range of polyurethane/polyacrylic latex which still maintains an excellent property balance [10].

4.2.1 Synthesis and Characterization of PU/PMMA Latex

In this research, the polyurethane (PU)/poly (methyl methacrylate) (PMMA) latex emulsion was prepared by soap free emulsion polymerization method as aqueous polyurethane dispersion can be emulsifier for the polymerization of hydrophobic MMA monomers.

The PU/PMMA latex was synthesized at different weight ratio of aqueous polyurethane dispersion and PMMA by changing the amount of the MMA monomers introduced while keeping the amount of PU constant.

Figure 4.5 shows the formation of PU/PMMA latex. PU/PMMA latex was synthesized by polymerization of MMA in aqueous polyurethane dispersion. Because MMA is not soluble in water, it diffused into PU micelle. After the mixture was heated, the initiator, tertiary butyl hydroperoxide, decomposed and entered into PU micelle. It then initiated the polymerization of MMA within PU micelle.



M = MMA monomers

PMMA = poly (methyl methacrylate)

I = Initiator

Figure 4.5 Schematic formation of PU/PMMA latex.

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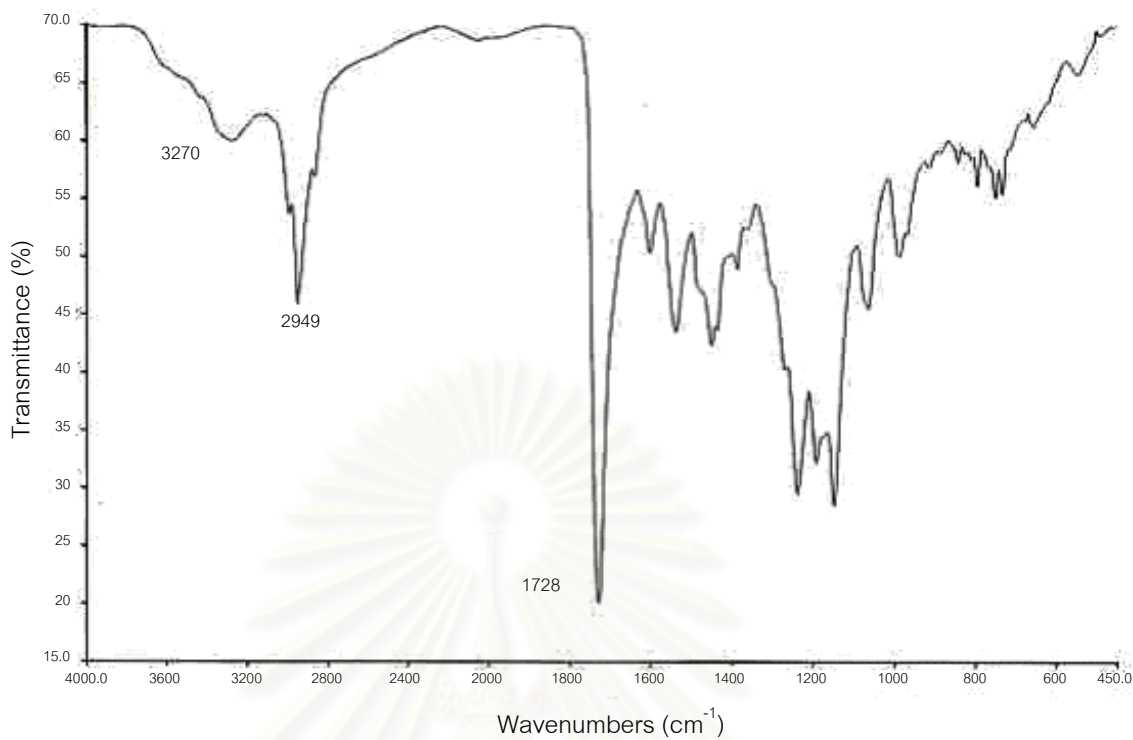


Figure 4.6 FTIR spectrum (neat) of PU/PMMA at 1:1 weight ratio.

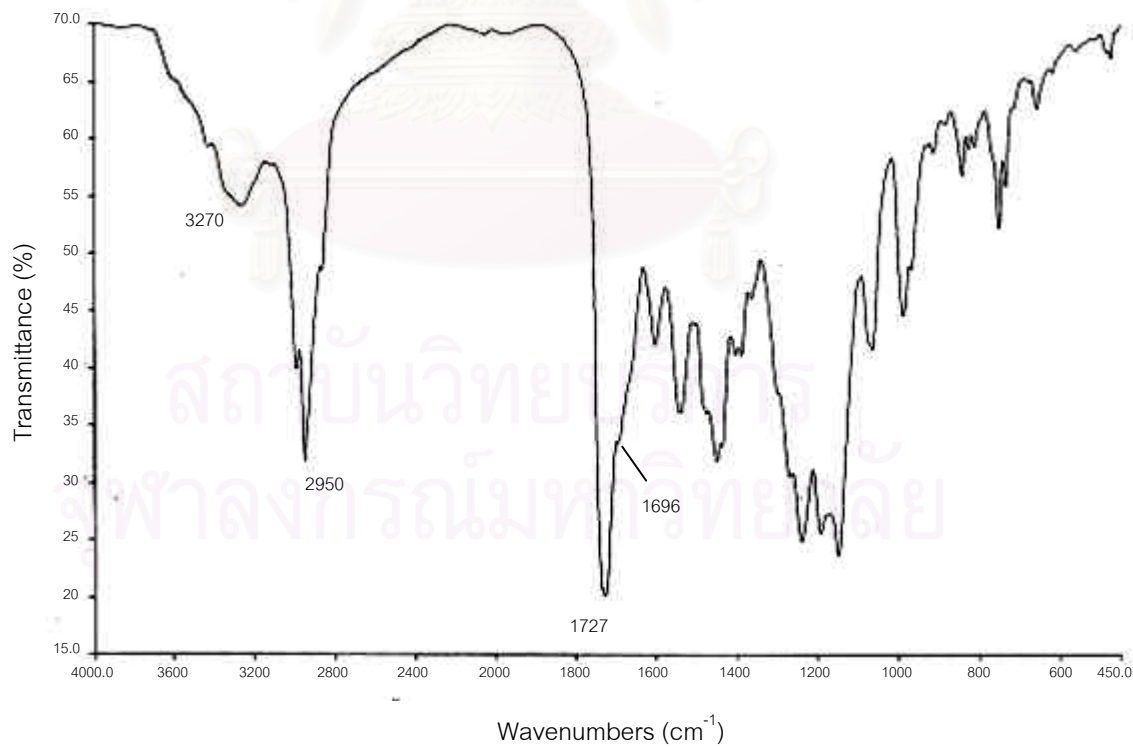


Figure 4.7 FTIR spectrum (neat) of PU/PMMA at 1:2 weight ratio.

Figure 4.6 and 4.7 exhibit the FTIR spectrum of PU/PMMA latex at 1:1 and 1:2, respectively. The absorption band at 3270 cm^{-1} is due to O-H stretching of water in latex and also N-H stretching of the amino group in PU structure. The sharp and intense absorption band at 1728 cm^{-1} is attributed to the C=O stretching of PMMA and PU, which they overlap in PU/PMMA 1:1 spectrum. When PMMA content was increased in PU/PMMA 1:2, it was obviously found the additional shoulder peak around 1696 cm^{-1} . It is plausibly attributed to the C=O stretching of PMMA. Accordingly, FTIR spectra clearly confirmed that PU/PMMA latex was obtained. In addition, this PU/PMMA FTIR pattern is similar to the work reported by M. Hirose et al. [6].

The PU/PMMA latex was obtained as a light yellow milky dispersion. Though it was similar to aqueous polyurethane dispersion but it was more viscous.

4.2.2 Size and Distribution of PU/PMMA Particle

The particle size distribution of PU/PMMA latex was determined by laser light scattering method. From Figure 4.8, it was found that the particle size distributions of all PU/PMMA latexes were narrow.

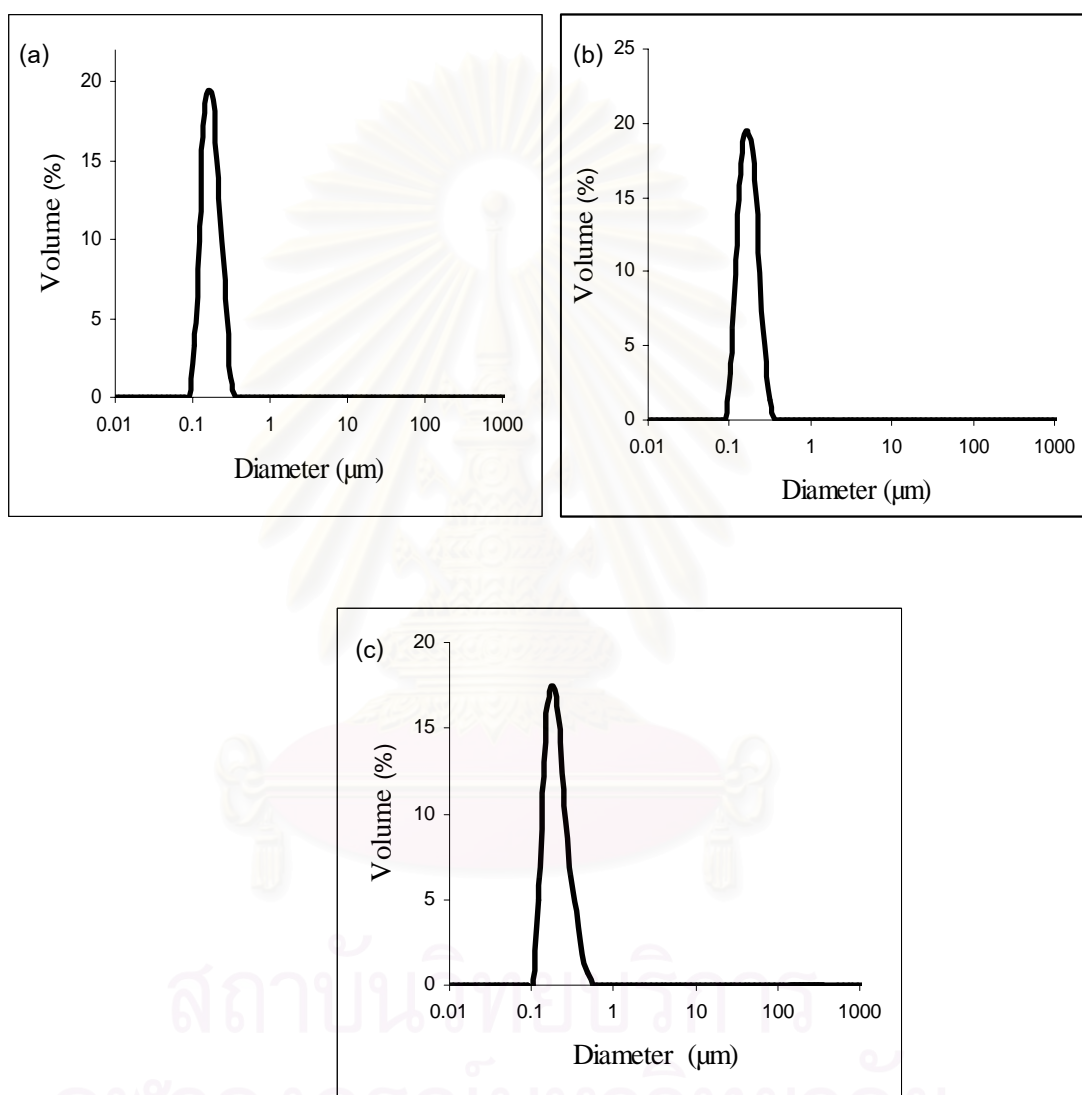


Figure 4.8 Particle size distributions of PU/PMMA latexes at 2:1(a), 1:1(b) and 1:2(c) weight ratios.

Analysis of the data in Figure 4.8 revealed that no population of MMA monomer droplets was observed in the particle size distribution, since monomer droplets were scarce, and MMA monomers were consumed to diffuse into polyurethane particle. In addition, the formation of a small population of aggregates was not detected in the particle size distribution. It represented good stability of the synthesized PU/PMMA latexes.

Table 4.2 shows the average particle size and polydispersity of PU/PMMA latex obtained from particle size distribution measurement.

Table 4.2 Diameter and polydispersity of PU/PMMA particles

PU/PMMA weight ratio	Diameter (nm)	Polydispersity
1:0	182	0.21
2:1	182	0.21
1:1	182	0.21
1:2	206	0.27

PU/PMMA latex prepared at ratios 2:1 and 1:1 had the same particle size as PU which was 182 nm. When the amount of PMMA was more than PU, the particle size of PU/PMMA, 206 nm, was larger than PU. The results clearly indicated that the particle size of PU/PMMA was enlarged by higher amount of PMMA with respect to PU. Since the PU particle in aqueous dispersion is an open or water-swollen structure [10], it can accommodate the acrylic emulsion particle up to a certain content without expansion as demonstrated in Figure 4.9(a) and (b). However, PU/PMMA at ratio 1:2, the PU over layer was swelled and thus larger particle was resulted as presented in Figure 4.9 (c).

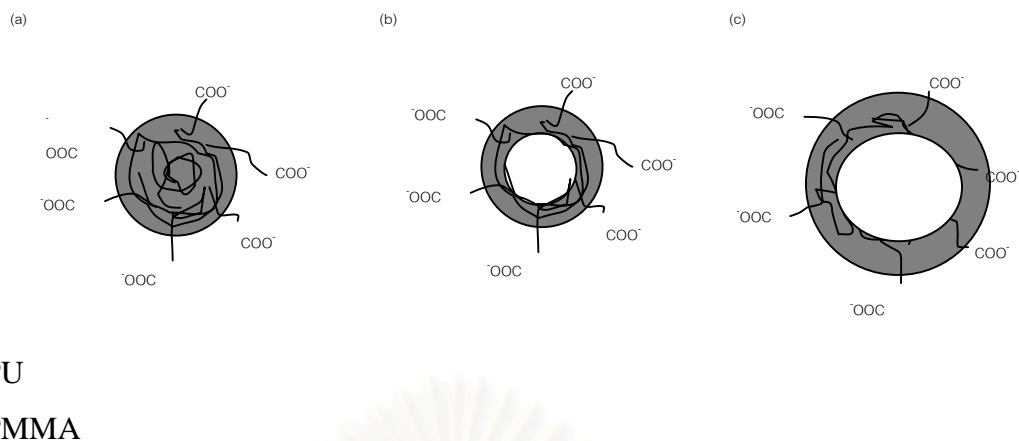


Figure 4.9 Schematic representation of the effect of MMA content on PU/PMMA particle size.

Figure 4.10 shows the TEM photographs of PU/PMMA latex. In these photographs, the bright isolated domain is PMMA and the dark continuous phase is PU, which is stained with phosphotungstic acid or osmium tetroxide. The inverted core (PMMA)-shell (PU) morphology is obvious, confirming that MMA monomers are polymerized in the core of the PU particles, similar results on this observation were reported by other research groups [6,7,18].

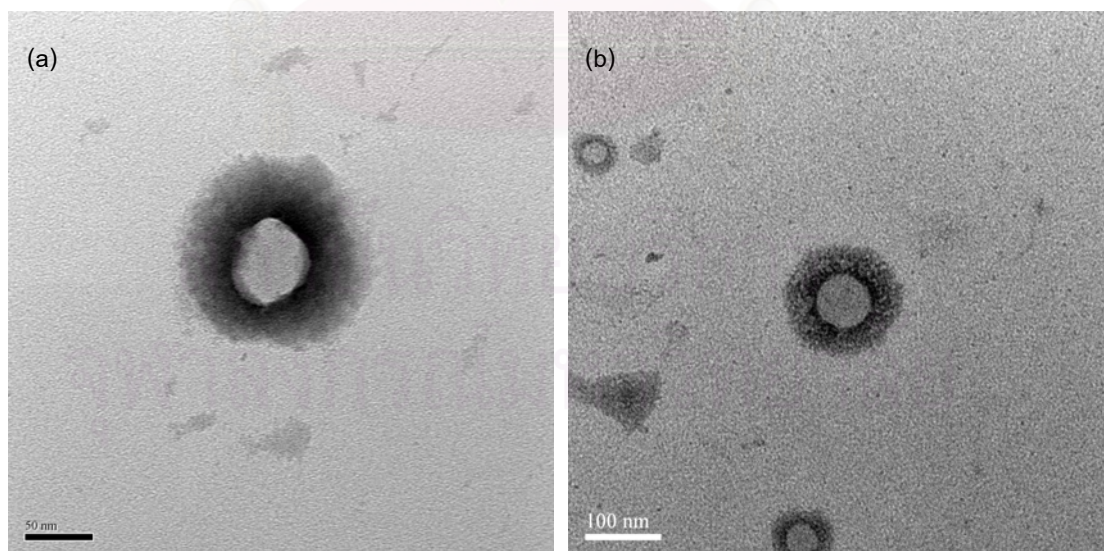


Figure 4.10 TEM photographs of PU/PMMA latex at 1:1 weight ratio was stained with phosphotungstic acid (a) and osmium tetroxide (b).

4.3 PANI/PU/PMMA Latex

Polyaniline (PANI) has been known to have good corrosion protective properties. Therefore, the combination of polyaniline with PU/PMMA latex would provide another application in marine environment. In this study, the synthesis of PANI/PU/PMMA latex was attempted.

4.3.1 Synthesis and Characterization of PANI/PU/PMMA Latex

The PANI/PU/PMMA latex was prepared by using PU/PMMA latex (1:1 ratio) as medium for polymerization of aniline hydrochloride. The reaction was the oxidative polymerization using ammonium peroxydisulphate as an oxidant. The PANI particle was stabilized with polymer steric stabilizer, Poly (*N*-vinylpyrrolidone) (PVP).

The synthesis of PANI/PU/PMMA latex was performed according to section 3.5.4. Therefore PANI/PU/PMMA latex was obtained and characterized by FTIR spectroscopy. Figure 4.11 exhibits the comparison of PANI, PU/PMMA, and PANIPU/PMMA latexes.

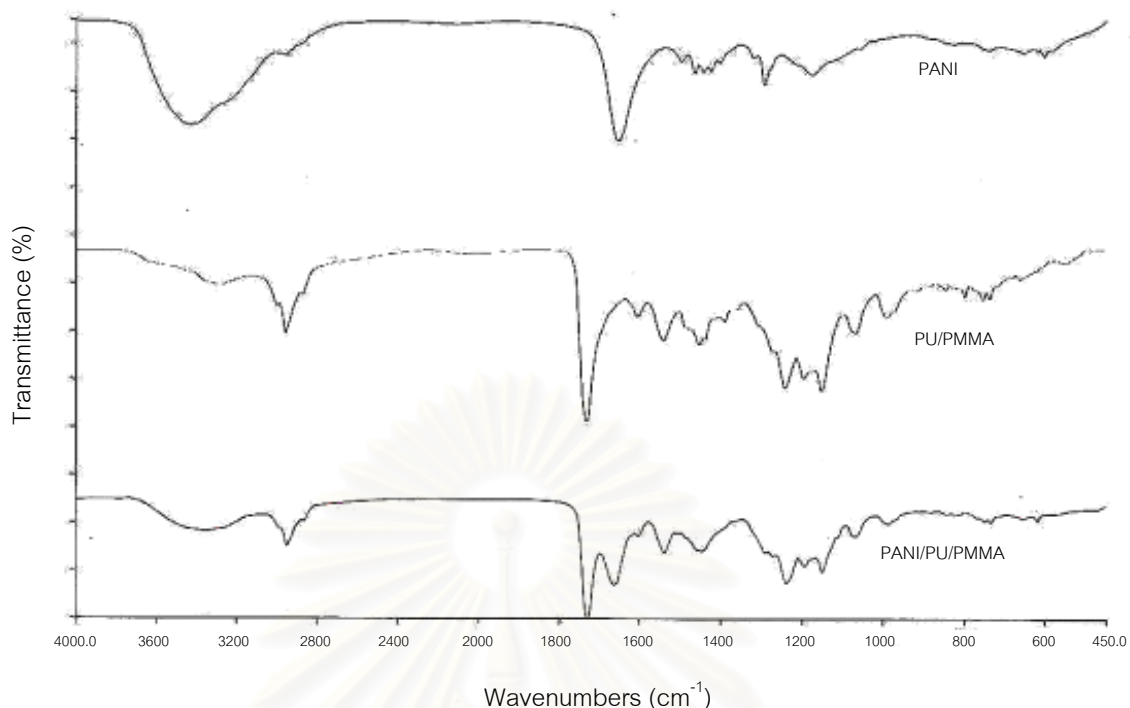


Figure 4.11 FTIR spectra (neat) of PANI, PU/PMMA, and PANI/PU/PMMA (0.1 mol L⁻¹ of aniline hydrochloride).

The pattern of the spectrum of the PANI/PU/PMMA latex is similar to both of the PANI and PU/PMMA latexes. The absorption band at 3354 cm⁻¹ appears for all three spectra. This is due to O-H stretching of water in latex and also N-H stretching of the amino group in polyaniline and polyurethane. The sharp and intense absorption band at 1729 cm⁻¹ is characteristic of C=O stretching of PU/PMMA and PANI/PU/PMMA. The sharp and intense absorption band of N-H bending at 1667 cm⁻¹ confirmed the structure of PANI and PANI/PU/PMMA. Accordingly, FTIR spectra prove that the synthesis of PANI/PU/PMMA latex was successful.

4.3.2 Size and Distribution of PANI/PU/PMMA Particle

In the synthesis of PANI/PU/PMMA latex, the concentration of PVP was varied from 0.4-1.3 wt. %. The results were shown in Table 4.3. It was found that at 0.4, 0.8, and 1.1 wt. % of PVP, the macroscopic precipitation was observed. At 1.3 wt. % of PVP, however, the dispersion latex was resulting with particle diameter of 188 nm and polydispersity of 0.23.

Table 4.3 The effect of PVP concentration on diameter and polydispersity of PANI/PU/PMMA particle (aniline hydrochloride 0.1 mol L^{-1})

Concentration of PVP (wt. %)	Diameter (nm)	Polydispersity
0.4	a	a
0.8	a	a
1.1	a	a
1.3	188	0.23

^a Macroscopic precipitate was present

This could be attributed to the insufficiency of PVP for entrapping the growing polyaniline particle in the reaction mixture which caused polyaniline partially formed to aggregate. This phenomenon had been described by J. Stejskal et al. as shown in Figure 4.12 [19, 20].

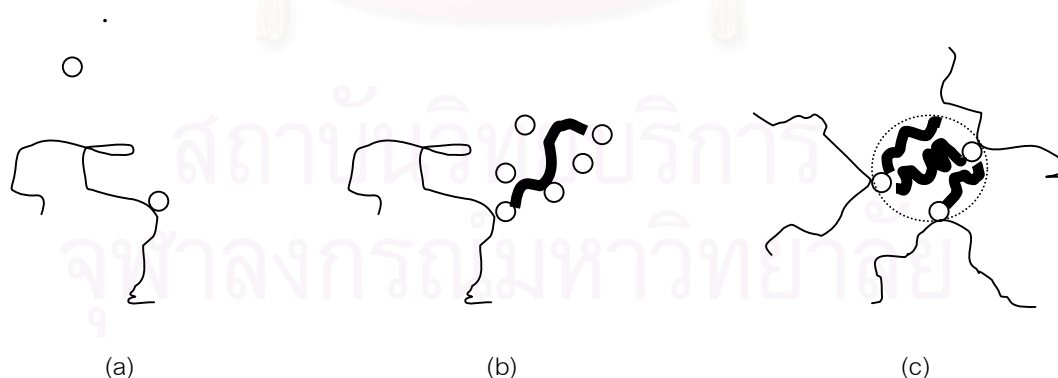


Figure 4.12 Polyaniline particle formation in aqueous phase [19, 20].

Aniline oligomers were produced in the early stages of aniline oxidation polymerization and adsorbed at stabilizer chains (Figure 4.12(a)), the growth of polyaniline started at the stabilizer chains (Figure 4.12(b)). The polyaniline particle was sequentially produced from these nuclei (Figure 4.12(c)) until monomer or oxidant or both were used up. Steric stabilizer, PVP, entrapped at the polyaniline particle surface would form a shell of colloidal particle and prevent their aggregation.

Consequently, the suitable concentration of PVP for this reaction was 1.3 wt.%. When the concentration of PVP was kept constant at 1.3 wt. % and the concentration of aniline hydrochloride was varied, PANI/PU/PMMA latexes were obtained with particle size and polydispersity as illustrated in Table 4.4. It can be seen that the particle size of PANI/PU/PMMA was slightly larger than PU/PMMA. The results indicated PANI plausibly heterocoagulated with PU/PMMA.

Besides it seemed that the particle size tended to increase with higher concentration of aniline hydrochloride. However, insignificant difference in size was observed as the concentration of aniline hydrochloride increased. This may be because the size of PANI particle was nearly in this range of concentration of aniline hydrochloride.

Polydispersity of all PANI/PU/PMMA latexes were about the same and approximately equal to PU/PMMA.

Table 4.4 The effect of concentration of aniline hydrochloride on diameter and polydispersity at PVP 1.3 wt. %

Concentration of aniline hydrochloride (mol L ⁻¹)	Dimeter (nm)	Polydispersity
0.0*	182	0.21
0.1	188	0.23
0.2	189	0.23
0.3	190	0.23
0.4	191	0.24

* PU/PMMA

While PU/PMMA latex was light yellow in color, the visual appearance of PANI/PU/PMMA latexes at all various concentration of aniline hydrochloride were milky gray, which the dark color represented PANI form [16, 21]. When the concentration of aniline hydrochloride was increased, the color of PANI/PU/PMMA latex became more intense.

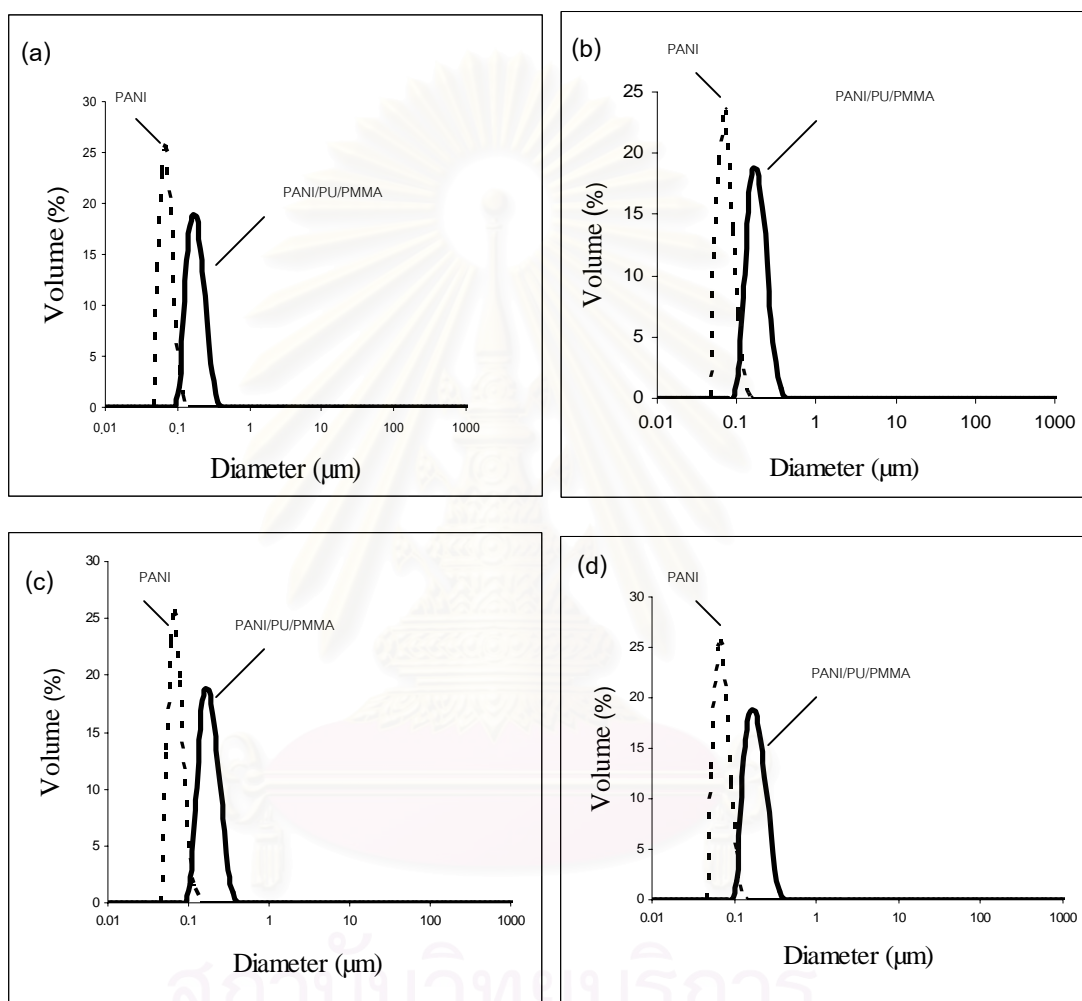


Figure 4.13 Particle size distribution of PANI (---) and PANI/PU/PMMA latex (—) prepared separately at various concentrations of aniline hydrochloride; 0.1 (a), 0.2 (b), 0.3 (c), and 0.4 (d) mol L⁻¹.

Analysis of the data in Figure 4.13 revealed that no other materials besides PANI/PU/PMMA were in the latex, particularly free PANI. This conclusion was confirmed by the polymerization of aniline hydrochloride was the same concentration and reaction condition as for the preparation of PANI/PU/PMMA. PANI was formed with the average particle in the range of 74-77 nm. Therefore, if free PANI could be formed during polymerization in PU/PMMA latex, the particle size distribution measurement should result more the one peak. According, it is possible that PANI was rather found on the surface of PU/PMMA.

Figure 4.14 illustrates the formation of PANI/PU/PMMA latex. In reaction mixture, the PU/PMMA particles and polyaniline particles were both dispersed in aqueous phase as shown in Figure 4.14(a). The larger particles represent PU/PMMA, with a negatively charged surface due to COO^- pendant groups in polyurethane chain while the small particle with a positive charge is PANI stabilized by PVP. Polyaniline was heterocoagulated on the PU/PMMA particle and the polymer steric stabilizer, PVP, continued to act as a stabilizer for the entire PANI/PU/PMMA particle as shown in Figure 4.14 (b).

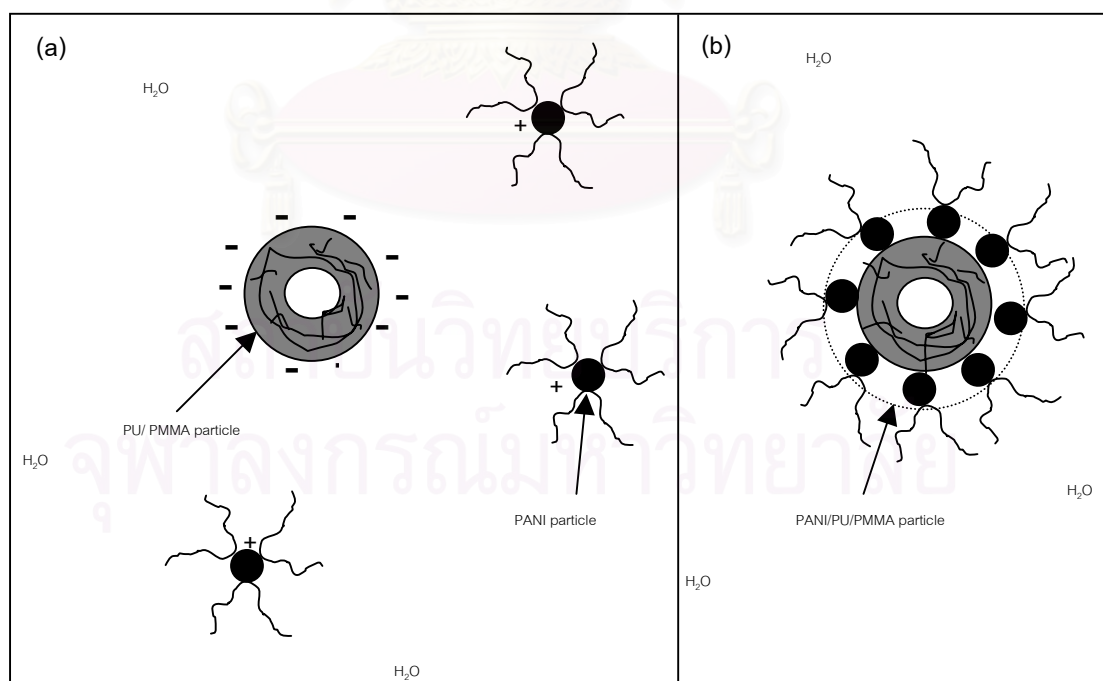


Figure 4.14 Diagrammatic representation of PANI/PU/PMMA particle.

Figure 4.15 shows the particle morphology of PANI/PU/PMMA, PU/PMMA, and PANI. PU/PMMA and PANI/PU/PMMA particles looked very much alike. It was plausible that PANI was only a thin overlayer on PU/PMMA particle. However, PANI/PU/PMMA particle size was measured to be 6-9 nm larger than PU/PMMA particle indicating the possible overlayer of PANI.

Furthermore, no free PANI particle, which was dark and opaque in a rice grain shape [21, 22, 23] as appeared in Figure 4.15(d), was obtained as shown in Figure 4.15(a) and 4.15(b). It can thus be assumed that PANI had been developed right on PU/PMMA particle.

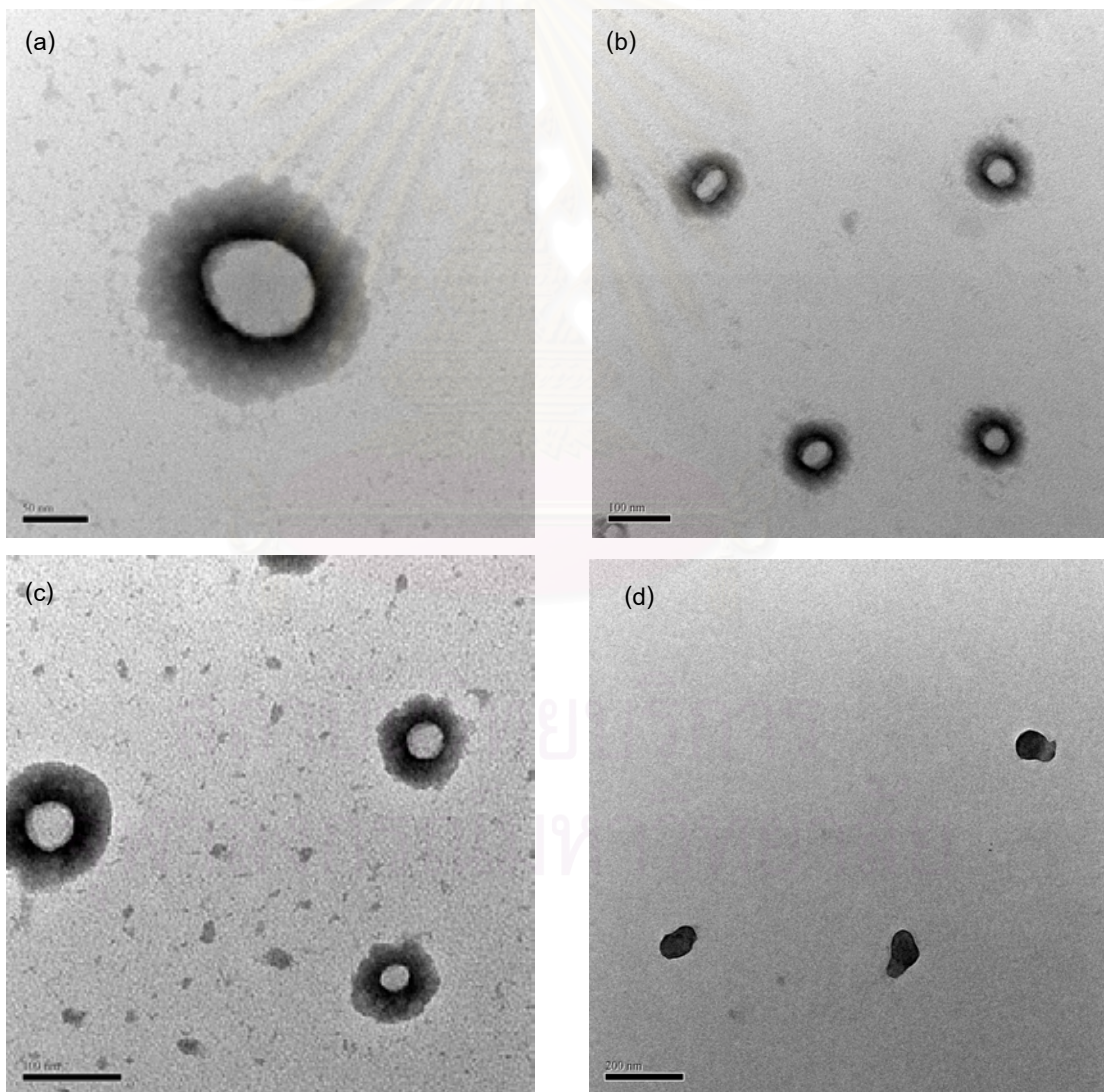


Figure 4.15 TEM photographs of latex particles; PANI/PU/PMMA $\times 50K$ (a) and $\times 25K$ (b), PU/PMMA (c), and PANI (d).

4.4 Corrosion Study

The contact of steel with water and oxygen produces corrosion, sooner or later, whatever paint is applied. Chloride ions from sea water or salt solution will speed up the process [14].

Finally, in this section described the corrosion performance of the panels coated with latexes specially indicated for steel and marine environment. The samples were tested in the NaCl solution (3.5 wt. %) 30 days. The degradations of films were characterized by FTIR and the coating surfaces were observed using digital camera and scanning electron microscope after immersed in the saline solution for 30 days. Results are compared between PU/PMMA and PANI/PU/PMMA coating.

4.4.1 FTIR Analysis

FTIR spectroscopic data indicated the degradation of the PU/PMMA film as shown in Figure 4.16. After 30 days in NaCl solution, the lower intensity of C=O absorption band was observed which was attributed to the disappearance of ester groups by hydrolysis and oxidation reactions. Changes produced in the 3000-3600 cm^{-1} frequency range are probably due to hydrogen bonding interaction between O-H groups of water.

The FTIR absorption spectra of the PANI/PU/PMMA film showed no signal of degradation being after 30 days. Because the FTIR pattern of the PANI/PU/PMMA film obtained after 30 days of exposure to saline solution (Figure 4.17(b)) was practically identical to that of the initial sample (Figure 4.17(a)), indicating that PANI improved the resistance against corrosion of latex, even when a very small concentration was used. This result agrees with the work previously reported [15, 16].

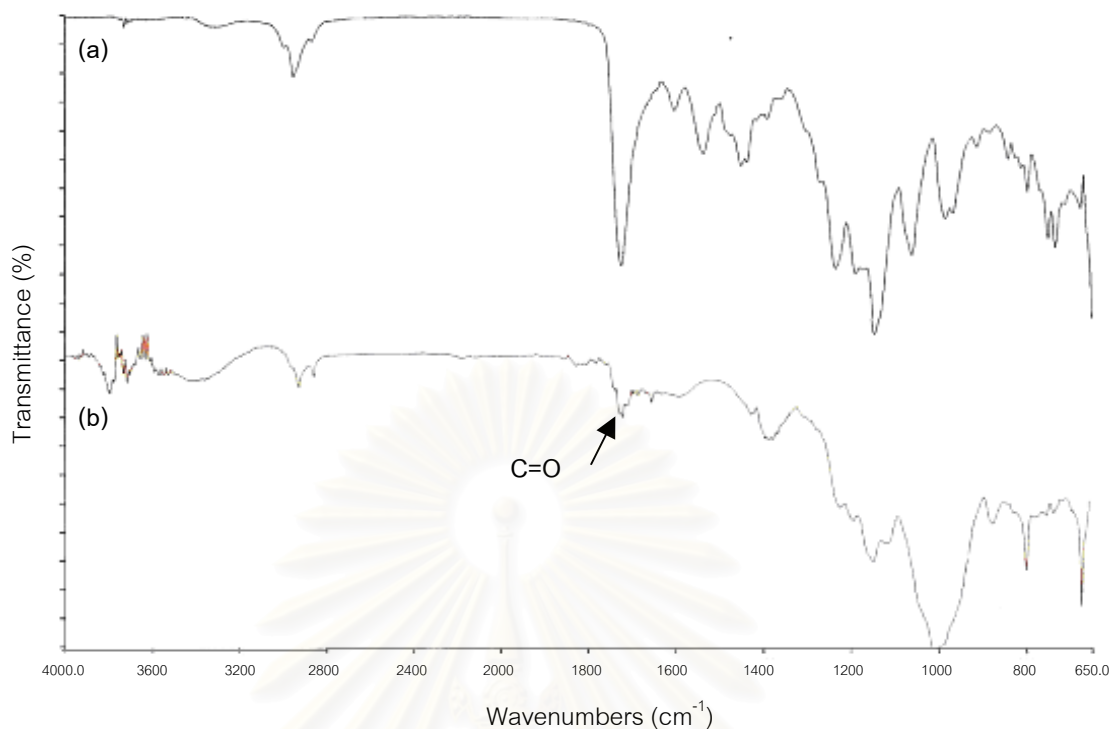


Figure 4.16 FTIR spectra of PU/PMMA film; initial sample (a), after 30 days of exposure in NaCl solution (3.5 wt. %) (b).

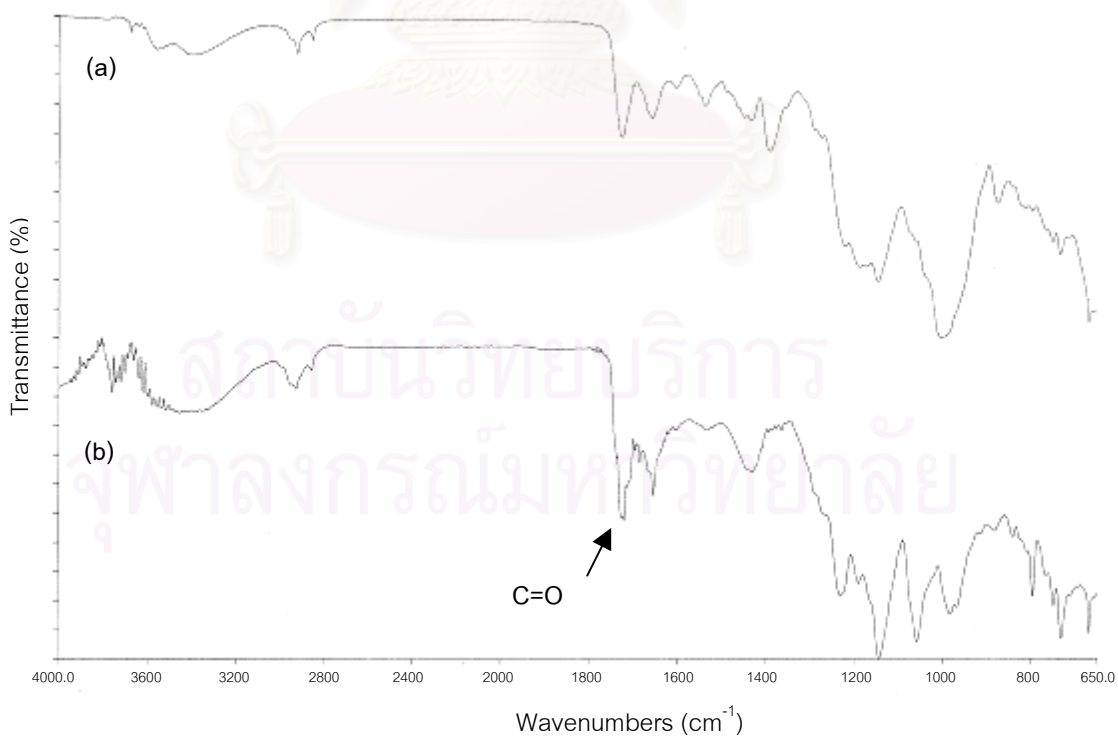


Figure 4.17 FTIR spectra of PANI/PU/PMMA film; initial sample (a), after 30 days of exposure in NaCl solution (3.5 wt. %) (b).

4.4.2 Morphology of the Coating Degradation

The morphology of metal surface coated with PU/PMMA and PANI/PU/PMMA latexes after immersion in the salt solution for 30 days were observed by digital camera and scanning electron microscopy (SEM).

Figure 4.18(c) shows the steel coated with PU/PMMA latex which had the rough superficial texture due to a lot of corrosion product, which was produced by the appearance of oxides in the steel. However, inspection to the PANI/PU/PMMA coating reveals that the initial smooth surface is almost intact, Figure 4.18(d). Thus, the degree of corrosion detected in its surface was noticeably lower than that found for the PU/PMMA films.

Figure 4.19 shows the steel coated with PANI/PU/PMMA latex at all various concentration of aniline hydrochloride, which all samples of PANI/PU/PMMA coating to perform slight degradation of steel surface, when compared with PU/PMMA coating in Figure 4.18(c). In summary, polyaniline can enhance corrosion protection property of PU/PMMA latex coating. Therefore, the PANI/PU/PMMA latexes had a corrosion resistance.

Photographs of the tested samples

SEM micrographs of the surface

(1 cm×1 cm)

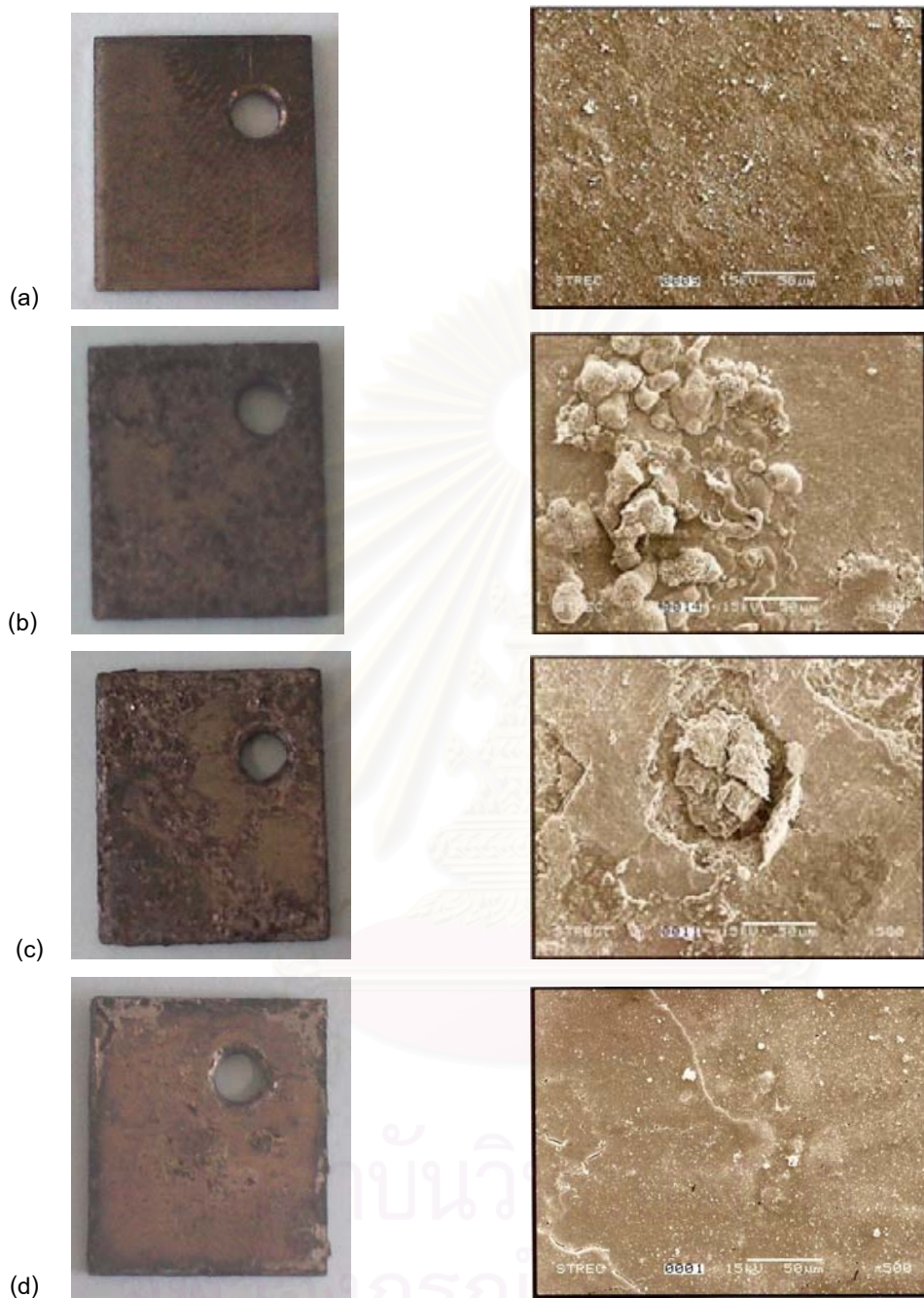


Figure 4.18 Photographs and SEM micrographs of the surface of tested samples; initial sample (a), no coating (b), coated with PU/PMMA latex (c) and PANI/PU/PMMA latex (d); (b), (c), and (d) immersed in NaCl solution (3.5 wt.%) for 30 days.

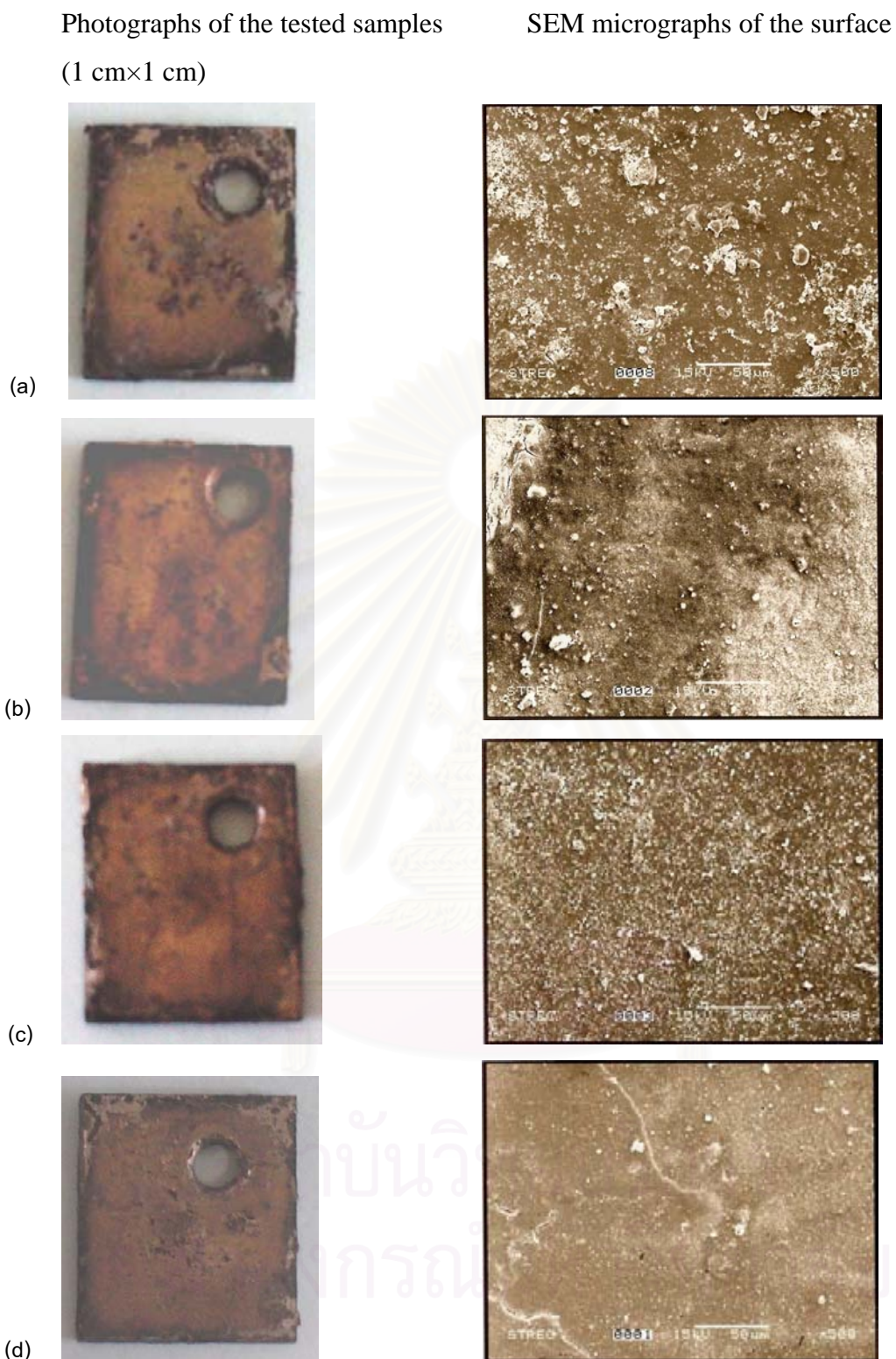


Figure 4.19 Photographs and SEM micrographs of the surface of tested samples coated with PANI/PU/PMMA latex at 0.1 (a), 0.2 (b), 0.3 (c), and 0.4 (d) mol L⁻¹ of aniline hydrochloride after immersed in NaCl solution (3.5 wt. %) for 30 days.

The role of polyaniline in active corrosion protection is due to its ability to intercept electrons at the metal surface [8]. Generally, the corrosion process of the metallic sheet dissolving as ions generates some electrons (anodic partial reaction), that are consumed by a secondary process (cathodic partial reaction), which is the reaction between oxygen and water giving hydroxide ions as their product. This hydroxide will react with iron (II) ion bringing Fe_3O_4 and Fe_2O as the corrosion products represented in Scheme 4.3. In fact, polyaniline is good conducting polymer that could retard the corrosive process by slowing cathodic partial reaction [24]. It can be explained that electrons from the anodic partial reaction are intercepted by polyaniline, and negative charge of metal surface invoked by electron transfer from polyaniline could prevent anodic iron dissolution near corrosion potential due to the cathodic protection effect.

Anodic partial reaction:



Cathodic partial reaction:



Corrosion product:



Scheme 4.3 Corrosion mechanism of steel when attacked by water and oxygen

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CHAPTER V

CONCLUSIONS AND SUGGESTIONS

A new kind of ternary PANI/PU/PMMA latex was successfully synthesized by using PU/PMMA latex as medium.

1. Polyester polyol was synthesized by condensation. It was obviously found that the acid value decreased when the reaction time was increased. This was because dicarboxylic acid could be converted to polyester polyol. The hydroxyl end group was obtained by adding the excess amount of diol in the reaction mixture.

2. Aqueous polyurethane dispersion was synthesized by prepolymer mixing process. The ionic group, $\text{COO}^-\text{HN}^+(\text{C}_2\text{H}_5)_3$, could assist the polyurethane to be dispersed in water phase.

3. PU/PMMA latexes were prepared by soap free emulsion polymerization methods using aqueous polyurethane dispersion as the emulsifier for the polymerization of hydrophobic MMA monomers. When a large amount of PMMA was introduced, the polyurethane over layer was swelled to form larger particle. Therefore, the PMMA content that grew in polyurethane particle affected to particle size of PU/PMMA. From TEM, PU/PMMA particle composed with PMMA acts as the core and PU acts as the shell.

4. PANI/PU/PMMA latex was synthesized by using PVP as steric stabilizer. The optimum concentration of PVP was 1.3 wt. %. The macroscopic precipitation was observed at lower concentration of PVP due to the insufficiency for entrapping polyaniline. The average particle size of PANI/PU/PMMA slightly increased around 6-9 nm from original PU/PMMA particle, but it seemed that the size tended to increase with higher concentration of aniline hydrochloride.

5. The corrosion protection performance was studied after immersion the tested sample in NaCl solution (3.5 wt. %) for 30 days. FTIR and SEM supported that PANI/PU/PMMA coating shown the better corrosion protection when compared to PU/PMMA coating. Therefore, PANI can enhance corrosion protection property of PU/PMMA latex. The reason is polyaniline intercepted electron from anodic reaction to slow cathodic reaction of water and oxygen, which reduced corrosion reaction.

5.1 Further Works

1. To improve the coating and corrosion protection properties of PANI/PU/PMMA latex.
2. To synthesize a new kind of latex for corrosion resistance coating by using polythiophene (PT) for the replacement of PANI, PT/PU/PMMA latex.



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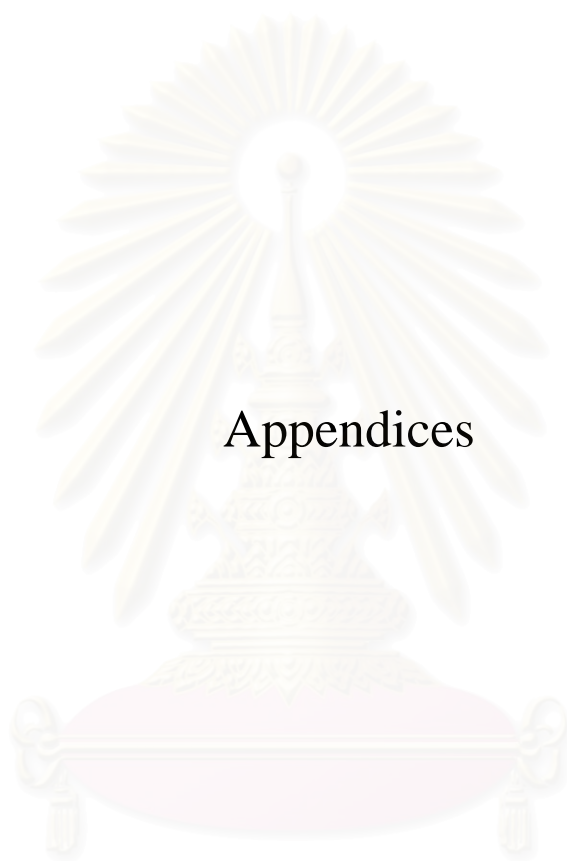
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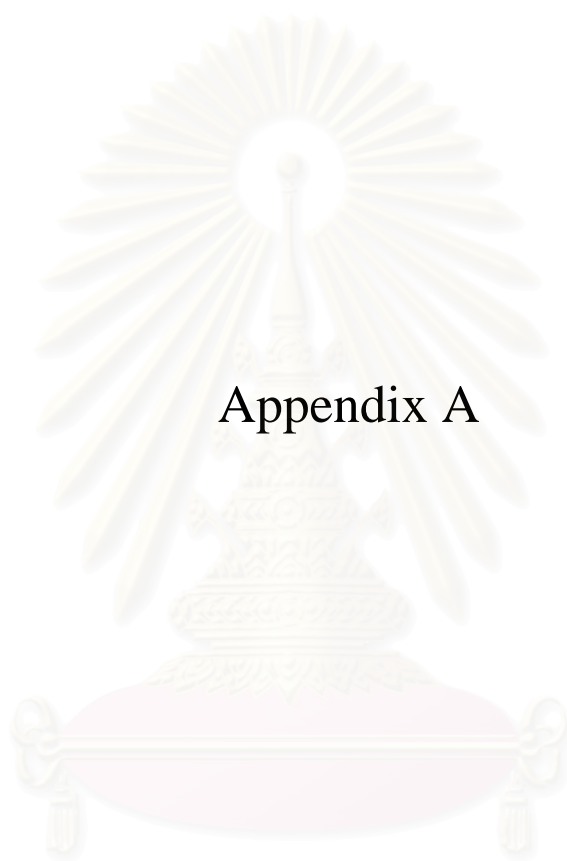


สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย



Appendices

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย



Appendix A

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

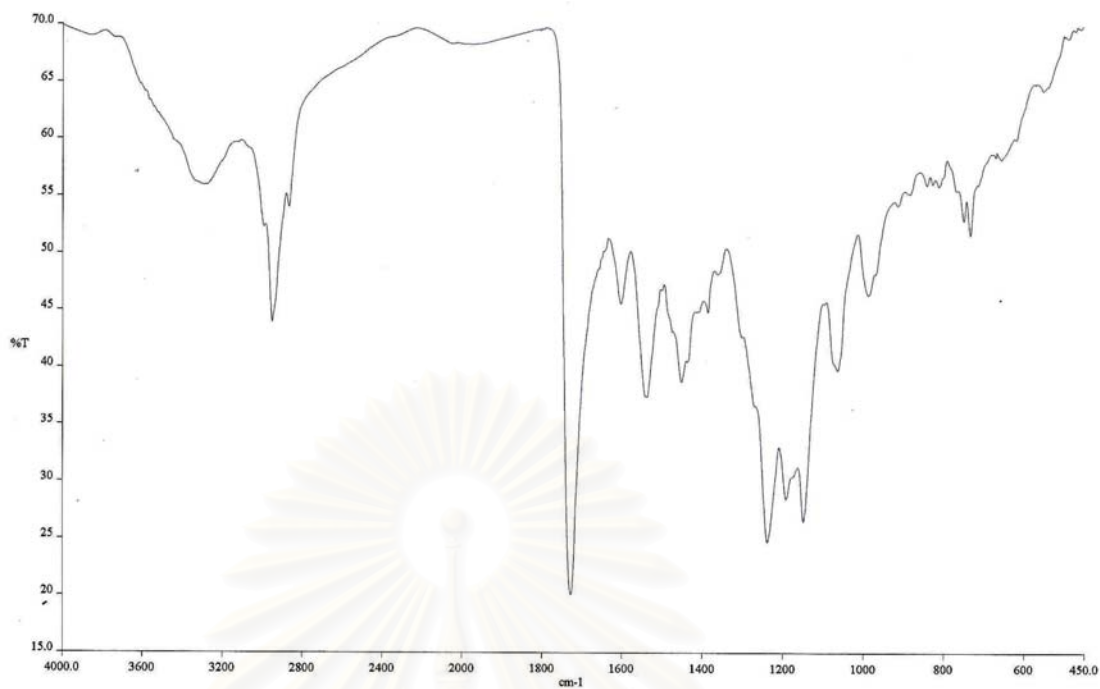


Figure A-1 FTIR spectrum (neat) of PU/PMMA latex at 2:1 weight ratio.



Figure A-2 FTIR spectrum (neat) of PU/PMMA latex at 1:1 weight ratio.

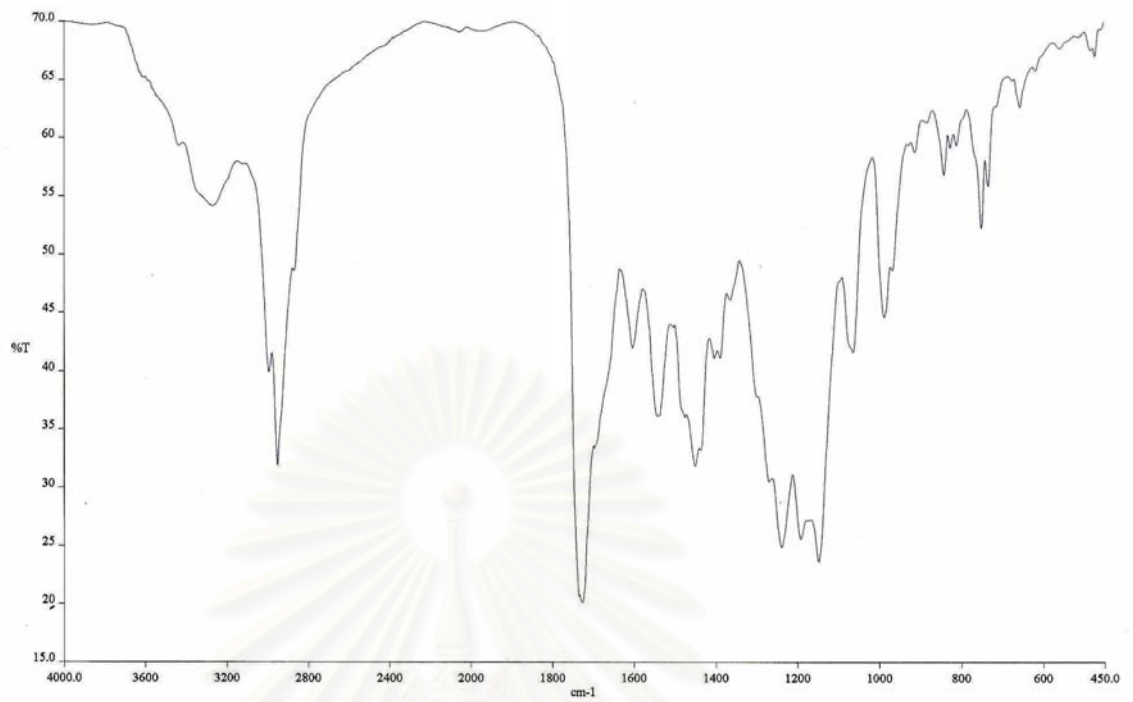


Figure A-3 FTIR spectrum (neat) of PU/PMMA latex at 1:2 weight ratio.

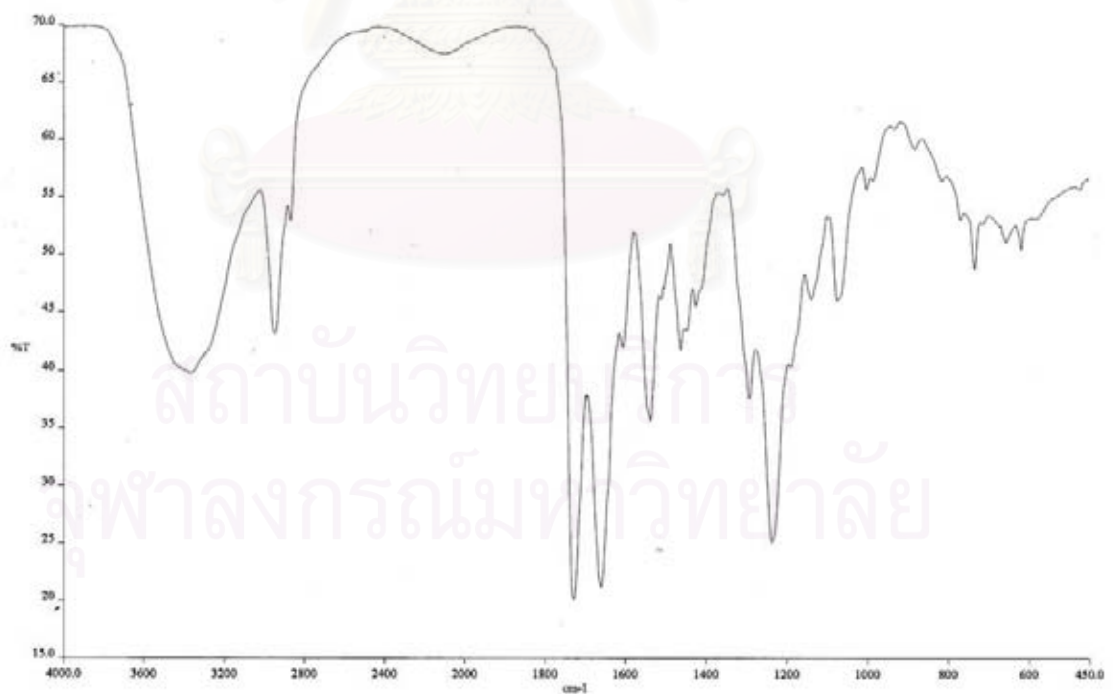


Figure A-4 FTIR spectrum (neat) of PANI/PU latex.

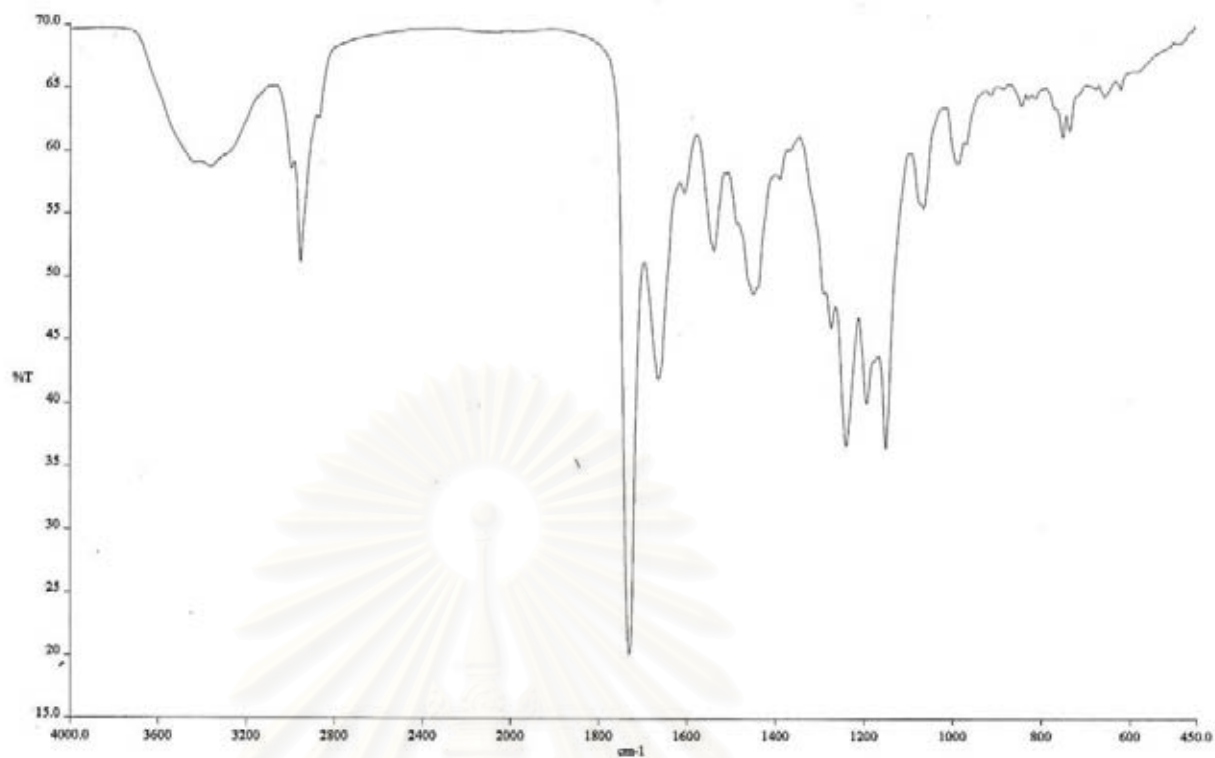


Figure A-5 FTIR spectrum (neat) of PANI/PU/PMMA latex; aniline hydrochloride 0.1 mol L^{-1} .



Figure A-6 FTIR spectrum (neat) of PANI/PU/PMMA latex; aniline hydrochloride 0.2 mol L^{-1} .

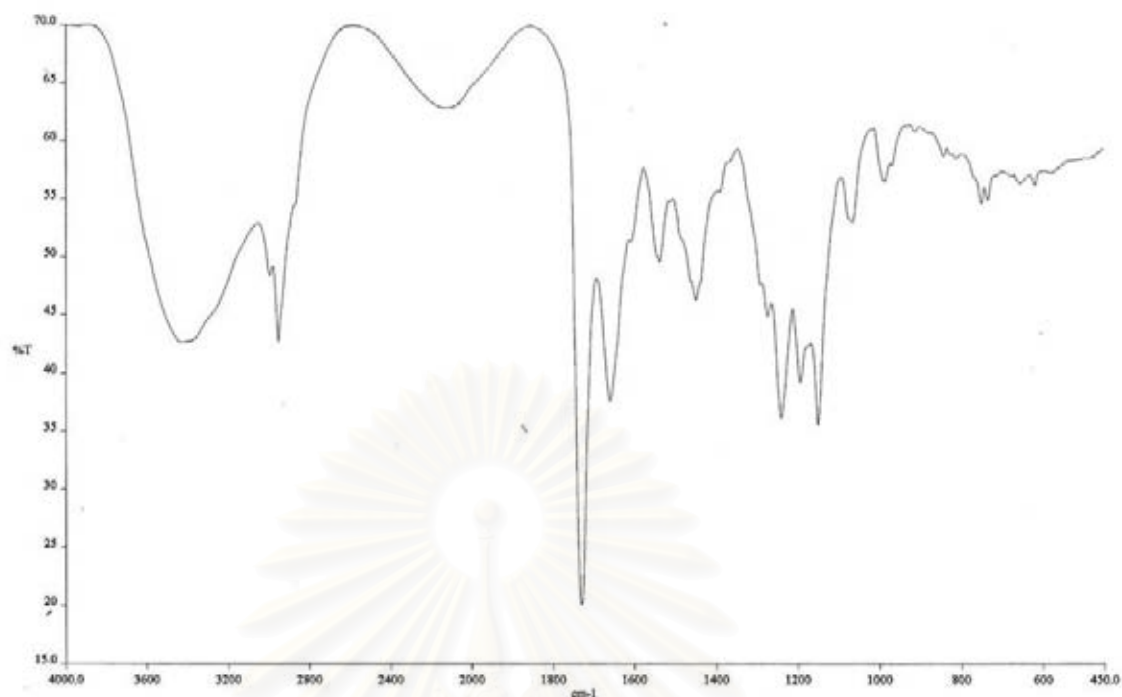


Figure A-7 FTIR spectrum (neat) of PANI/PU/PMMA latex; aniline hydrochloride 0.3 mol L^{-1} .

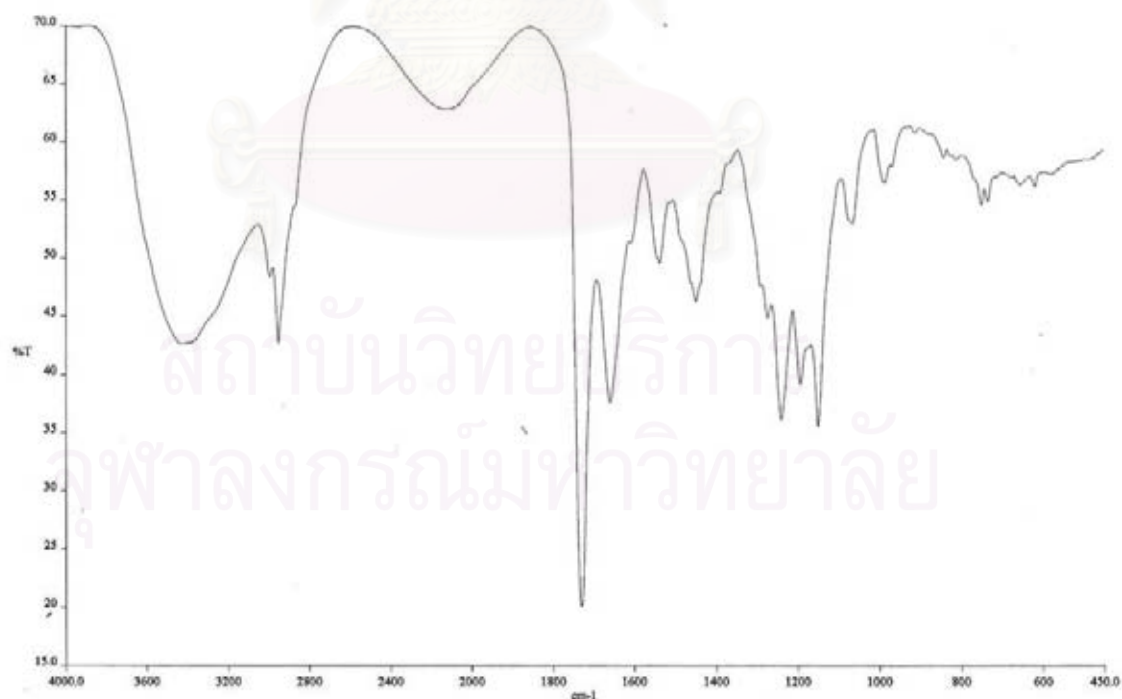
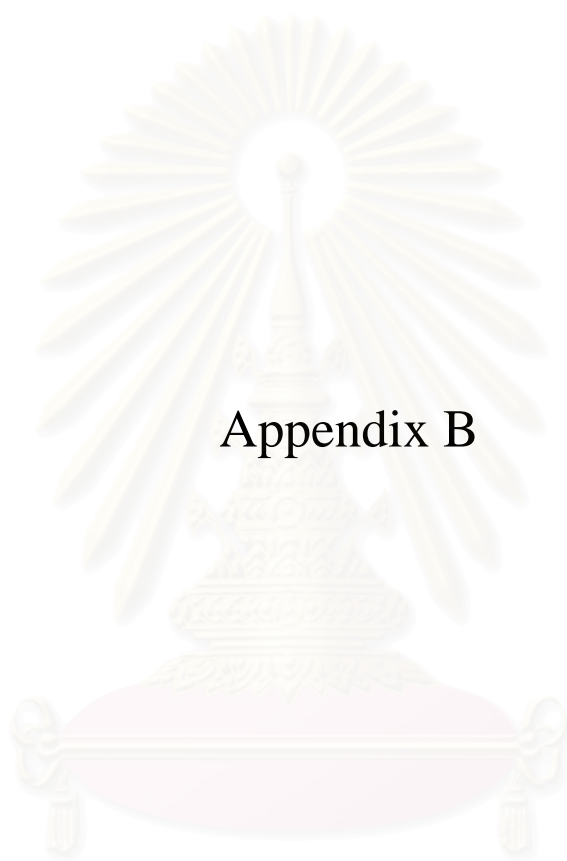


Figure A-8 FTIR spectrum (neat) of PANI/PU/PMMA latex; aniline hydrochloride 0.4 mol L^{-1} .



Appendix B

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

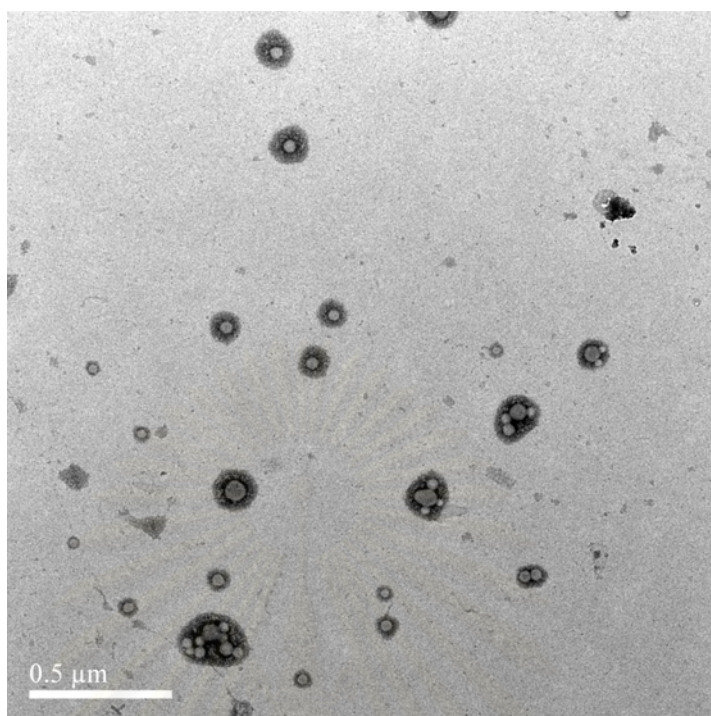


Figure B-1 TEM photograph of PU/PMMA particle stained with osmium tetroxide; $\times 10K$.

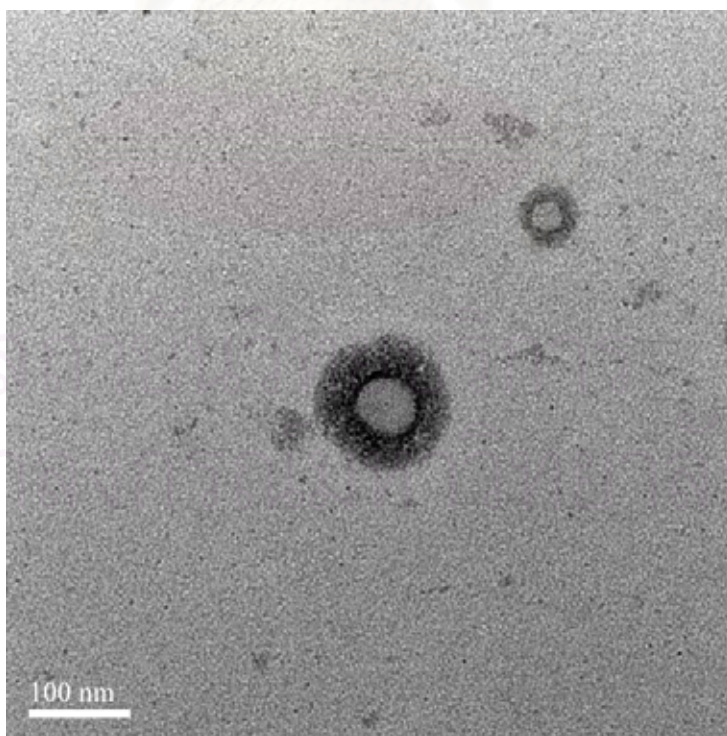


Figure B-2 TEM photograph of PU/PMMA particle stained with osmium tetroxide; $\times 30K$.

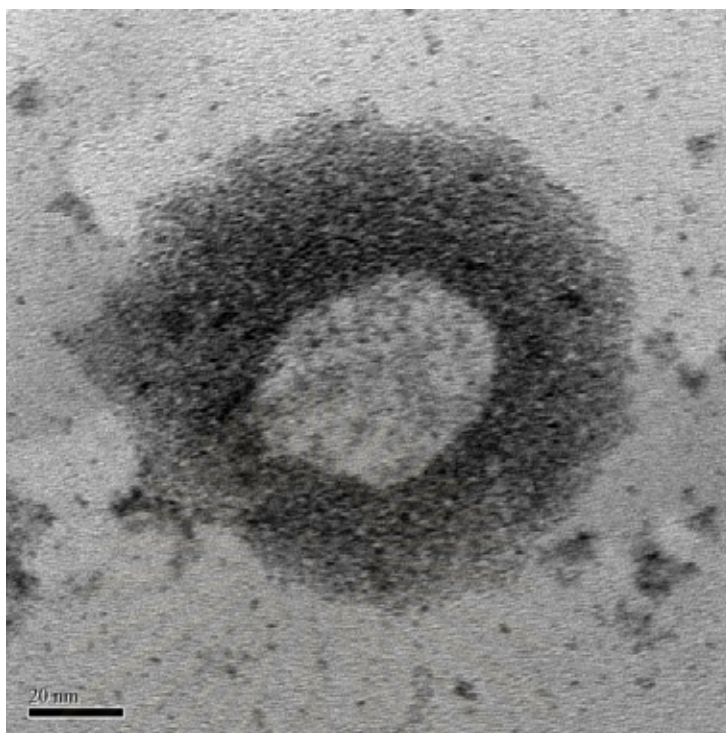


Figure B-3 TEM photograph of PANI/PU/PMMA particle stained with osmium tetroxide.

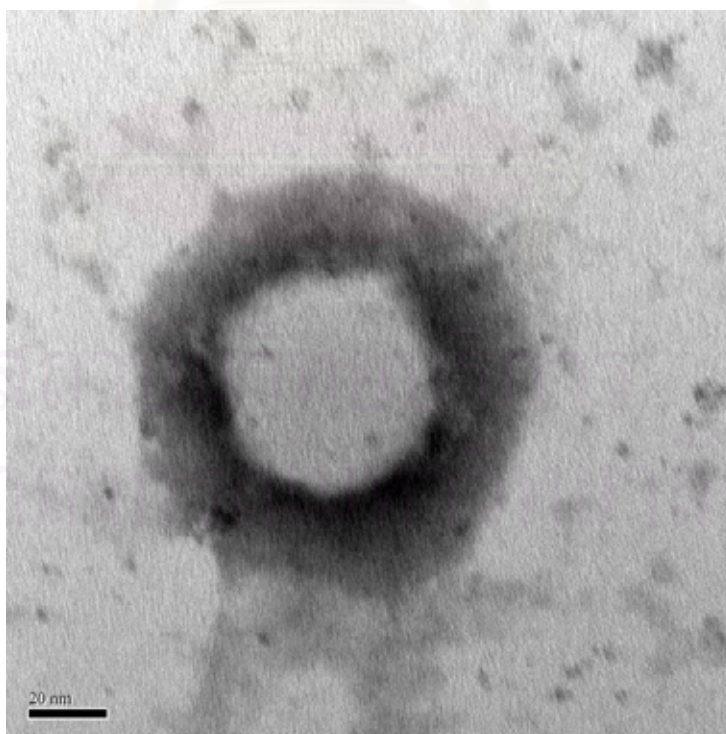


Figure B-4 TEM photograph of PANI/PU/PMMA particle stained with firstly osmium tetroxide and then phosphotungstic acid.

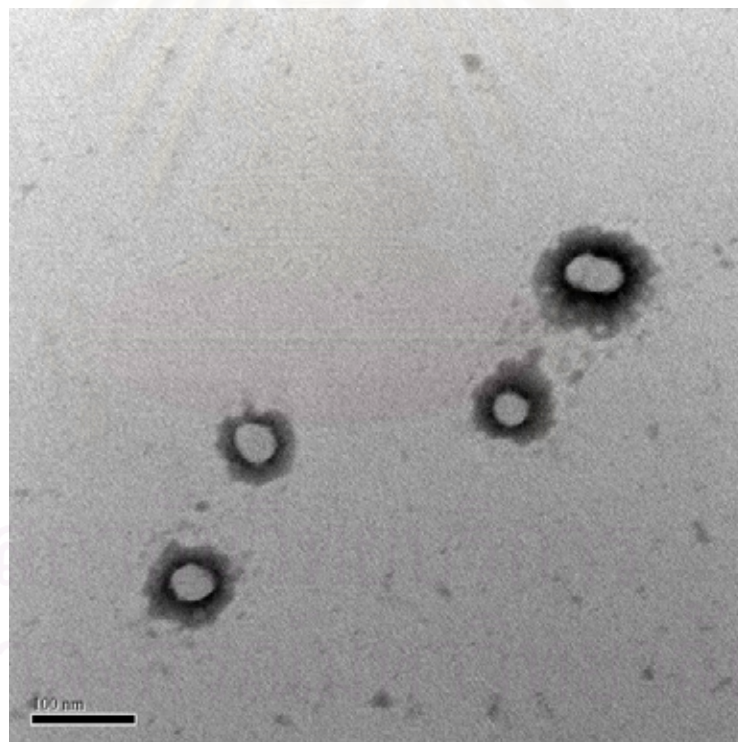
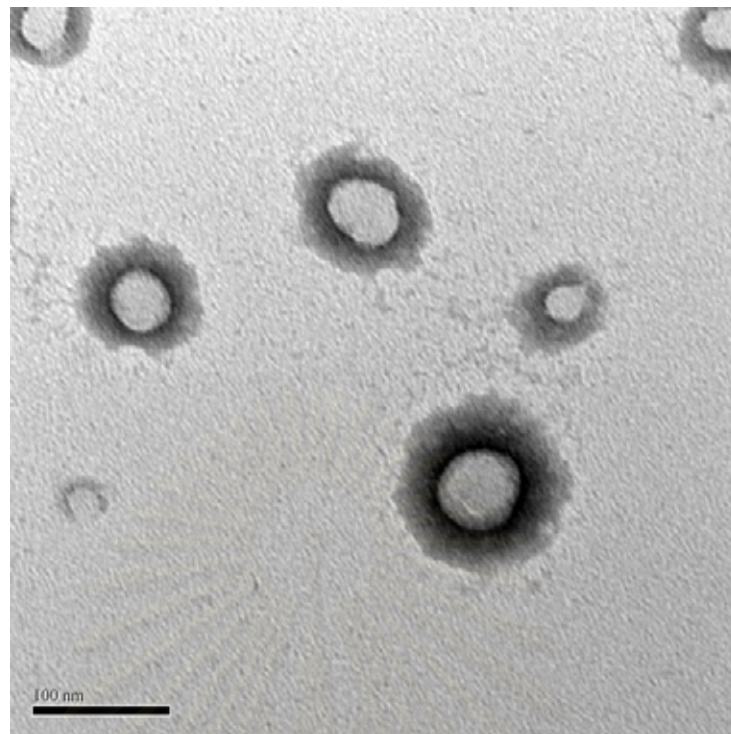


Figure B-5 TEM photograph of PANI/PU/PMMA particle stained with phosphotungstic acid at different area in the same sample.

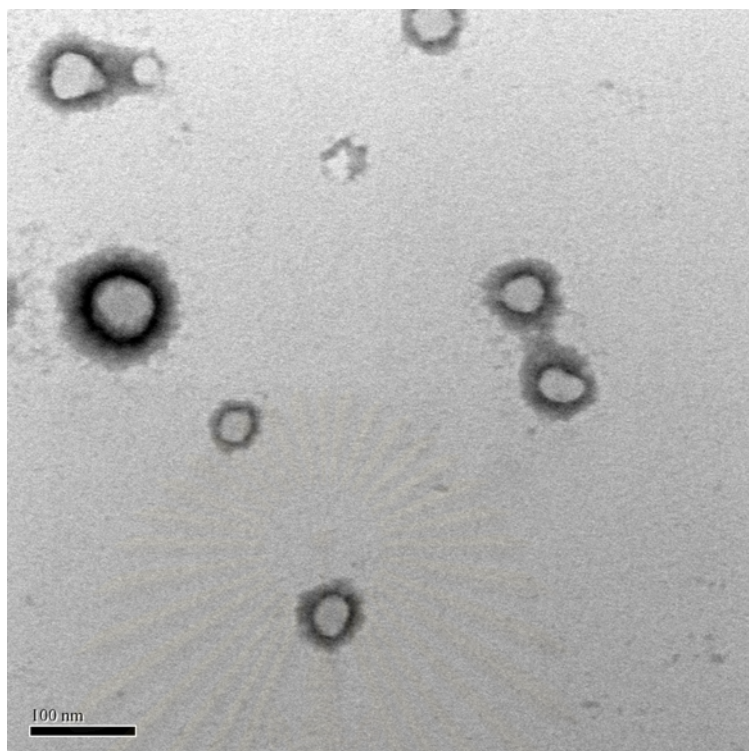


Figure B-5 (cont.) TEM photograph of PANI/PU/PMMA particle stained with phosphotungstic acid at different area in the same sample.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

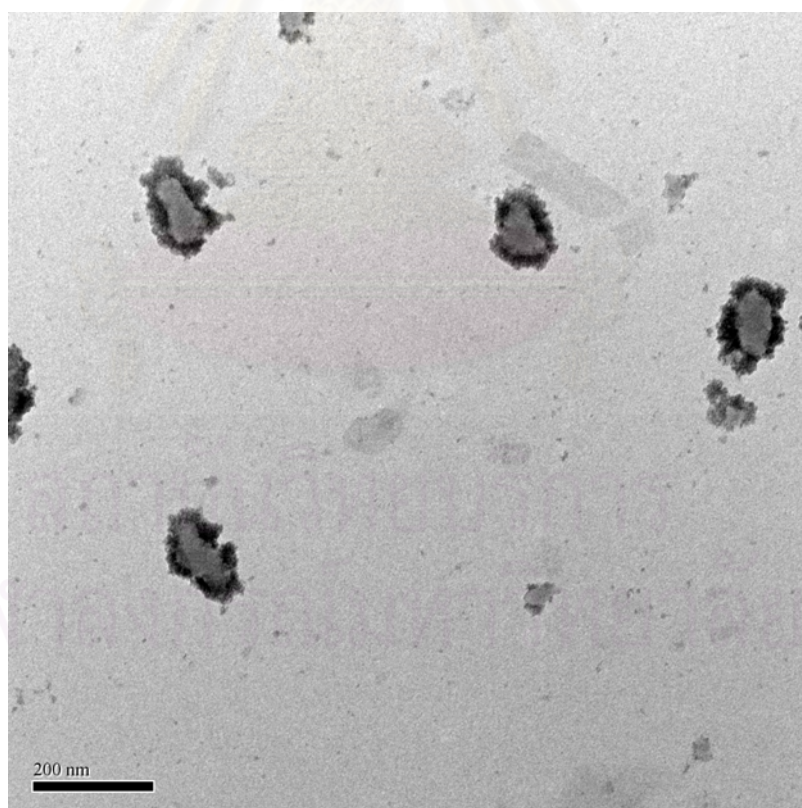
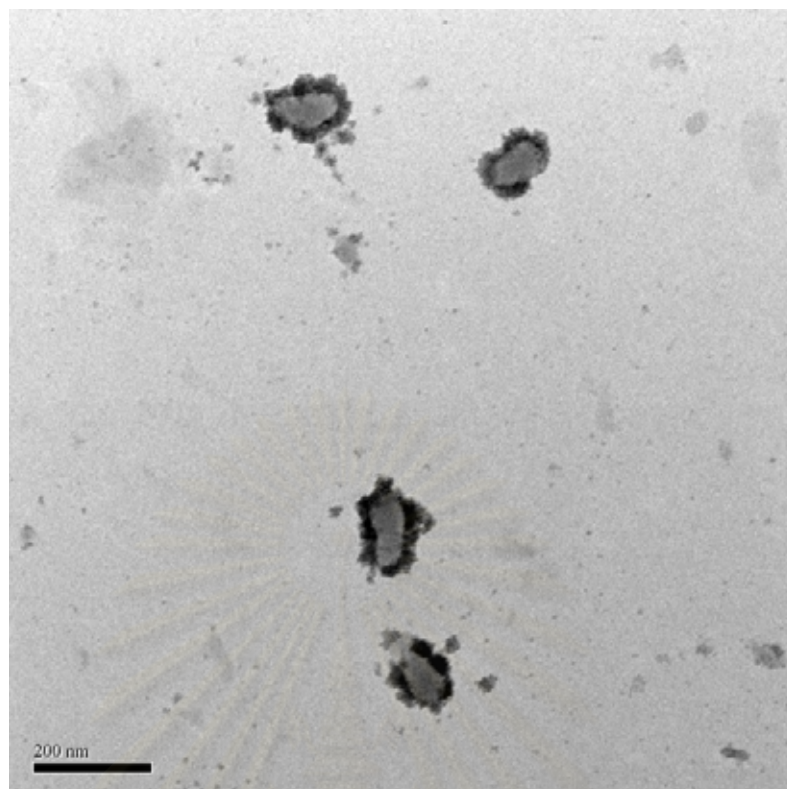


Figure B-6 TEM photograph of PANI particle stained with osmium tetroxide at different area in the same sample.

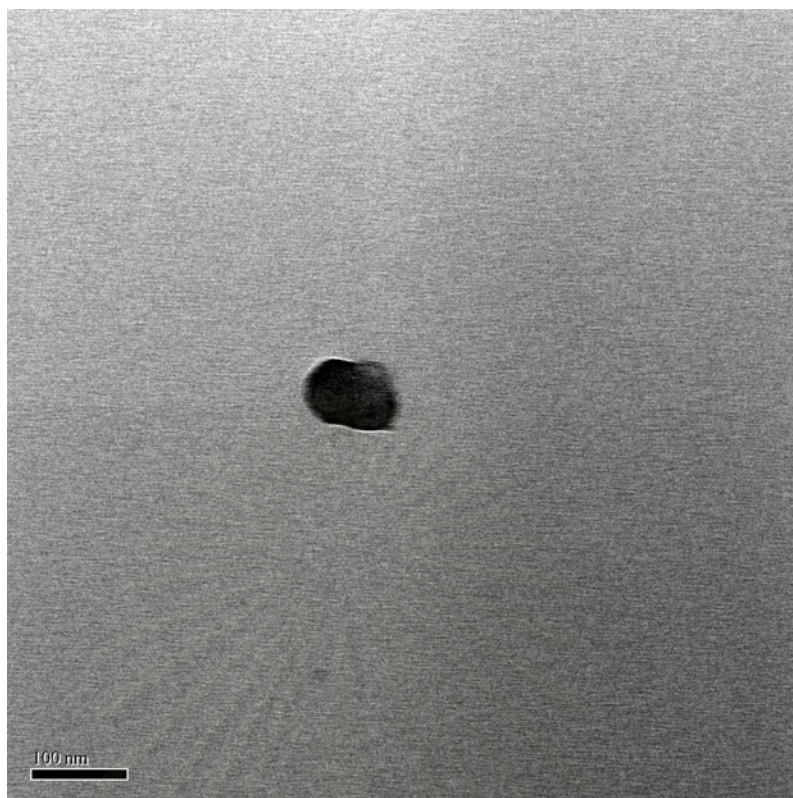


Figure B-7 TEM photograph of PANI particle stained with phosphotungstic acid; $\times 30K$.

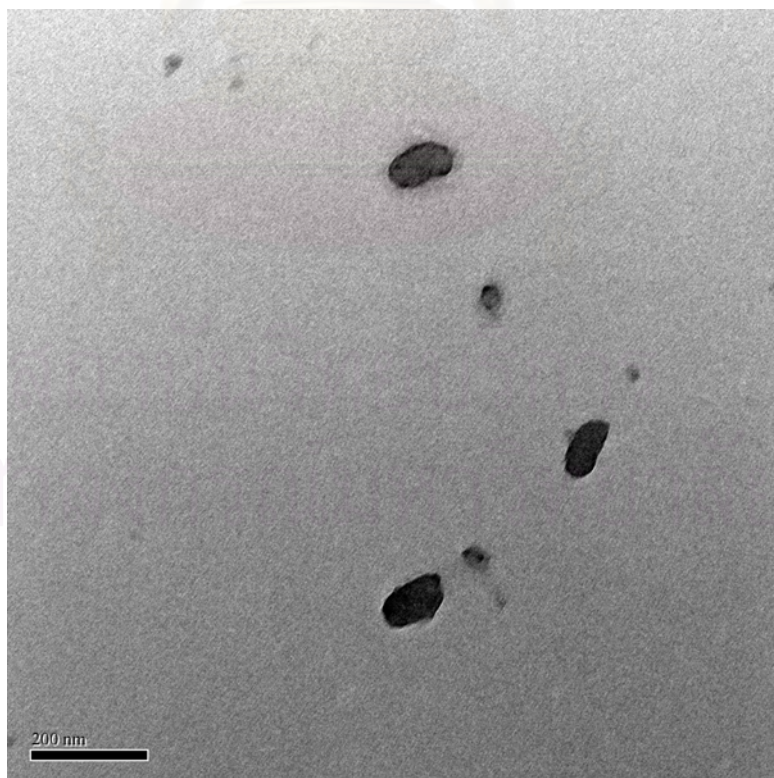


Figure B-8 TEM photograph of PANI particle stained with phosphotungstic acid; $\times 15K$.

VITAE

Miss Sakuntala Pomanee was born in Suphanburi, Thailand. She got a Bachelor's Degree of Science in Chemistry from Mahidol University in 2004. After that, she started her graduate study a Master's Degree in the Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University and completed the program in 2007.



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