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นางสาววรรณฤดี เต็มนิล

SYNTHESIS AND CHARACTERIZATION OF CORE-SHELL PPY/PU/PMMA LATEX

Miss Wanruedee Temnil

A Thesis Submitted in Partial Fulfillment of the Requirements

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พอลิพิวโรล/พอลิยูรีเทน/พอลิเมทิลเมทะคริเลต (พีพีวาย/พียู/พีเอ็มเอ็มเอ) แบบคอร์เชลล์ สามารถสังเคราะห์ได้ด้วยกระบวนการการเกิดพอลิเมอร์ 3 ขั้นตอน ขั้นแรกเกี่ยวข้องกับการเกิด พรีพอลิเมอร์ที่มีปลายสายโซ่เป็นหมู่ไอโซไซยาเนต โดยใช้ 2,4-โทลูอีนไดไอโซไซยาเนต และ พอลิเอสเทอร์พอลิออลซึ่งได้จากกระบวนการเกิดพอลิเมอร์แบบควบแน่นของ 1,6-เฮกเซนไดออล, อะดิพิกแอซิด และไอโซทาลิกแอซิด ใช้โครมาโทกราฟีแบบซึมผ่านเจลหาค่าการกระจายตัวของ น้ำหนักโมกุล พอลิยูรีเทนดิสเพอร์ชันในน้ำเตรียมจากกระบวนการการเกิดพอลิเมอร์แบบอิมัลชัน ด้วยตัวเอง โดยนำส่วนของวัฏภาคน้ำมันซึ่งประกอบด้วยพรีพอลิเมอร์ที่มีปลายสายโซ่เป็น หมู่ไอโซไซยาเนต, เอทิลีนไดแอมีนเป็นตัวขยายสายโซ่ และไทรเอทิลแอมีนสารทำให้เป็นกลางมา กระจายตัวในวัฏภาคน้ำ แล้วศึกษาผลของอัตราส่วนโดยโมลของหมู่ไอโซไซยาเนตต่อ หมู่ไฮดรอกซิล และไทรเอทิลแอมีนต่อไฮดรอกซีเมทิล โพรพิออนิกแอซิดต่อขนาดอนุภาค ขนาด อนุภาคโดยเฉลี่ยหาค่าโดยใช้เครื่องการกระเจิงแสงพลวัต ขั้นที่สองทำการเตรียมพียู/พีเอ็มเอ็มเอ แบบคอร์เชลล์จากกระบวนการเกิดพอลิเมอร์แบบสบู่ โดยใช้เทอร์เทียรีบิวทิลไฮโครเปอร์ออกไซด์ (ทีบีเฮชพี) เป็นสารริเริ่มปฏิกิริยา และศึกษาผลของอัตราส่วนโดยน้ำหนักของ พียู/พีเอ็มเอ็มเอต่อ ขนาดอนุภาค ขั้นที่สามสังเคราะห์พอลิพิวโรลเป็นเชลล์เหนือพื้นผิวของคอร์ ในกระบวนการการ เกิดพอลิเมอร์แบบออกซิเดทีฟจะใช้เฟอร์ริกคลอไรด์และพอลิ(เอ็น-ไวนิลไพโรลิโดน)(พีวีพี) เป็น ตัวออกซิแดนซ์และตัวทำให้เสถียรตามลำดับ ที่ความเข้มข้นของพิวโรลแตกต่างกันส่งผลให้ขนาด อนุภาคของ พีพีวาย/พียู/พีเอ็มเอ็มเอ มีค่าต่างกัน การปกคลุมของพิวโรลบนผิวของคอร์แสดงโดย ใช้กล้องจุลทรรศน์อิเล็กตรอนแบบส่องผ่าน และใช้เอฟทีไออาร์ในการพิสูจน์เอกลักษณ์ ได้ใช้วิธี เคมีไฟฟ้าในการตรวจสอบการกัดกร่อน แล้ววิเคราะห์ด้วยกล้องจุลทรรศน์อิเล็กตรอนแบบส่อง กราด พบว่าฟิล์มต้านทานการกัดกร่อนได้

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> WANRUEDEE TEMNIL: SYNTHESIS AND CHARACTERIZATION OF CORE-SHELL PPY/PU/PMMA LATEX. THESIS ADVISOR: ASSOC.PROF. SUPAWAN TANTAYANON, Ph.D., 84 pp.

Polypyrrole/polyurethane/poly(methyl methacrylate) (PPy/PU/PMMA) core-shell particles were successfully synthesized by a three-stage polymerization process. The first stage involved the formation of NCO-terminated prepolymer based on 2,4-toluene diisocyanate and polyester polyol which was synthesized by condensation polymerization based on 1,6-hexanediol, adipic acid, and isophthalic acid. The molecular weight distribution was measured through gel permeation chromatography. Aqueous PU dispersion was then produced by self-emulsification method in which an oil phase containing NCO-terminated prepolymer, the chain extender ethylene diamine (EDA), and the neutralizing agent triethyl amine (TEA), was dispersed in the water phase. The influence of NCO/OH and TEA/DMPA molar ratios on the particle size of PU was investigated. The average particle size of some selected products was measured through dynamic light scattering. The second stage was to produce a core of PU/PMMA via soap free emulsion polymerization technique using tertiary butyl hydroperoxide (TBHP) as the initiator. The effect of the weight ratio of PU/PMMA on its particle size was also studied. The third stage was to synthesize the shell of polypyrrole over the surface of core particles. Ferric chloride and poly (*N*-vinylpyrrolidone) (PVP) were used as the oxidant and stabilizer, respectively, in the oxidative polymerization of pyrrole. The coverage of PPy onto the core surface was viewed by transmission electron microscopy. All the resulted products were characterized by FTIR spectroscopy. Finally, the electrochemical corrosion tests of iron disks coated with PPy/PU/PMMA films were performed. By using scanning electron microscopy, it was observed that these latex films have good corrosion resistance.

Field of Student ...Petrochemistry and Polymer Science...Student's Signature…………….……

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LIST OF ABBREVIATIONS

cm	Centimeter
°C	Degree Celsius
g	Gram
h	Hour
mg	Milligram
mL	Milliliter
min	Minute
m	Molarity
mol L^{-1}	Mol per Litre
nm	Nanometer
N	Normal
$\overline{M}$n	Number average molecular weight
$\overline{M}$w	Weight average molecular weight
cm^{-1}	Wave number
wt.%	Weight Percentage

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. The evaporation of volatile organic compounds (VOCs) during the formulations of coatings, inks, and paints cause a wide variety of air quality problems. Consequently, governmental organizations such as the Environmental Protection Agency (EPA) in the United States and Local Air Quality Regulators have stepped up their efforts to limit the amounts of VOCs released to the atmosphere. These regulations and consumer demands are forcing industries to develop environmentally friendly products [1]. Among several options to develop technology, water is the best choice to use as a medium in formulating coating systems. To reduce or eliminate organic solvents from the formulations, solvents should be partially or completely replaced with environmentally benign solvents (e.g., water), in the coating formulations to achieve little or no VOC content [2,3,4,5].

Waterborne polymer emulsions are an important class of materials, especially in the paint and coating industry. Increasing concern for health, safety, and the environment has driven many researchers to prepare waterborne polymers with sophisticated composition and architecture, which are expect to exhibit almost the same performances as conventional solvent-borne systems. 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 emulsions and polyurethane aqueous dispersions have been used extensively in coatings applications. Both systems have some disadvantages such as reduced film formation, lower chemical resistance, coarse mechanical properties of acrylic, a high cost, low pH stability, and limited outdoor durability of polyurethane [6]. To improve the properties of an individual polymer system it is common to mix them. Better mechanical stability, solvent and chemical resistance, and toughness are obtained from the polyurethane portion. Outdoor resistance, pigment ability, and lower cost are due to the acrylic component. Therefore it is of great interest to produce emulsions in which each particle is composed of acrylic polymer and polyurethane components.

There is an increasing interest on the use of conducting polymer to protect reactive metals against corrosion [7]. Particularly, polypyrrole was the most frequent candidate because of its stability in air, high electrical conductivity and easy synthesis and polymerization.

Accordingly, it will be useful if polyurethane, poly (methyl methacrylate) and polypyrrole 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.

OBJECTIVES

The objectives of this research work are:
1. To synthesize core-shell PPy/PU/PMMA latex.
2. To improve corrosion prevention property of polyurethane.

SCOPE OF RESEARCH WORK

The scope of this research work will cover:

1. The preparation of polyester polyol by condensation polymerization method.

2. The preparation of aqueous polyurethane dispersion by prepolymer mixing process.

3. The preparation of two-layer 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. The preparation of three-layer PPy/PU/PMMA latex by oxidative polymerization of pyrrole in the presence of PU/PMMA latex. Pyrrole was varied from 1.2-1.5 mol L^{-1}, respectively.

5. To investigate the protection performance of PPy/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

The formation of a urethane group from the reaction between isocyanate and hydroxyl compounds was originally identified in the 19th Century. However, it was only in the late 1930s that Otto Bayer discovered the chemistry of the polyaddition reaction between diisocyanates and diols developing urethane polymer, initially producing a range of elastomers and rigid foams.

Polyurethane formulations are generally designed to exploit several different isocyante reactions simultaneously. Almost all the reactions are exothermic which usually provides sufficient energy to cure the polymer and to drive processing operations such as mould filling and foaming. Catalysts are used to balance the rates of the various reactions and to control the overall rate of cure during processing.

Linear polyurethanes (PU) are polymers in which the principal chain structure is composed of aliphatic or aromatic sections R and R_1 fixed together with polar urethane groups (formula 1):

$$\sim R-NH-\overset{\overset{\displaystyle O}{\|}}{C}-O-R_1\sim \qquad (1)$$

Wherein R makes an aliphatic, aromatic or alicyclic radical derived from the isocyanate monomer, and R_1 is a more complex group derived from the polyol component (polyether or polyester). The commercial manufacture of polyurethanes is nearly solely based on the polyaddition process which involves diisocyanates and bi-functional or multi-functional polyols with hydroxyl terminal groups (Eq. (2)):

$$n\text{OCN–R}_1\text{–NCO} + n\text{HO–R}_2\text{–OH} \rightarrow \text{...} \text{–(–O–R}_2\text{–O–OC–NH–R}_1\text{–NH–CO–)}_n \qquad (2)$$
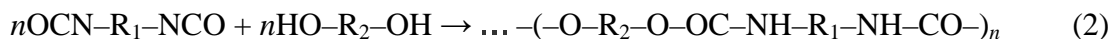
The possible presence of multi-functional components, e.g., triisocyanates obtained from the trimerisation process of isocyanate monomers, or the use of branched hydroxyl polyols, will yield polyurethanes with three-dimensional cross-linking.

The structure of PU chains can be additionally diversified by the polyaddition process regime, and in particular by the relative sequence of charging individual feeds. It is a frequent practice that a prepolymer is synthesised initially and an excess amount of one component is used, e.g., too much diisocyanate (B) in relation to polyol (A). When the polyol component is added to diisocyanate, the molar ratio of the reacting substances is decisive for the obtained size of the isocyanate prepolymer macro-molecule (Eq. (3)):
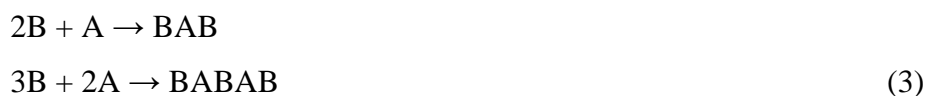
$$2\text{B} + \text{A} \rightarrow \text{BAB}$$
$$3\text{B} + 2\text{A} \rightarrow \text{BABAB} \qquad (3)$$

The synthesised urethane–isocyanate prepolymer BAB or BABAB can be further extended at the next reaction step by means of a low-molecular weight diol, e.g., 1,4-butanedion (BD) or other compound which has active hydrogen atom(s) in its structure. High-molecular weight polyurethanes are produced in this way, and the size of the final macro-molecule – when there are no diffusion constraints – is controlled by the molar ratio of the reacting functional groups (Eq. (4)):

$$n\text{OCN–BABAB–NCO} + n\text{HO–CH}_2\text{–CH}_2\text{–CH}_2\text{–CH}_2\text{–OH} \rightarrow$$
$$\text{–(O–CO–NH–BABAB–NH–CO–O–CH}_2\text{–CH}_2\text{–CH}_2\text{–CH}_2\text{)}_n \qquad (4)$$
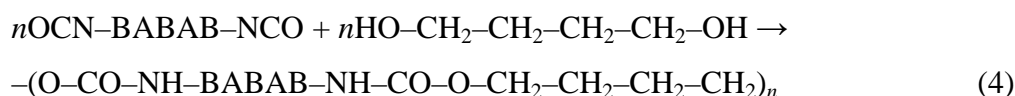
It is also possible to synthesize polyurethanes in a single-stage process. The molar ratios for diisocyanate, polyol and extender should be carefully selected then, yet the chain structure will not be so precisely defined in that case.

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 [8].

2.1.1.2 Definitions

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

$$OH \sim\!\!\sim OH \quad + \quad OCN \sim\!\!\sim NCO \longrightarrow \sim\!\!\sim NH\text{-}CO\text{-}O \sim\!\!\sim$$

Polyol   Diisocyanate   Polyurethane
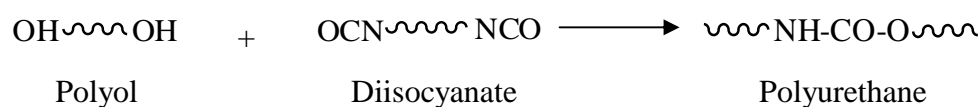
Scheme 2.1 Polyurethane reaction

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 [9].

2.1.1.3.1 Isocyanate reactions with hydroxyl

The most important reaction in the manufacture of polyurethane is between isocyante and hydroxyl groups. The reaction product is a carbamate, which is called a urethane in the case of high molecular weight polymers. The reaction is exothermic and reversible going back to the isocyanate and alcohol.

Reaction with an alcohol yields urethane:

RNCO   +   R'OH $\longrightarrow$ RNHCOOR'   (urethane)
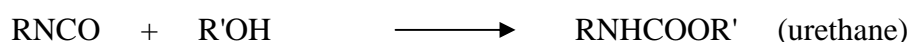
2.1.1.3.2 Isocyanate reaction with water

The reaction of isocyanates with water to produce an amine and carbon dioxide is highly exothermic. The initial reaction product is carbamic acid, which breaks down into carbon dioxide and a primary amine. The amine will then react immediately with another isocyanate to form a symmetric urea. Due to the formation of carbon dioxide the water reaction is often used as a blowing agent as the level of blow can be tailored, simply by adjusting the amount of water in the formation.

Reaction with water produces a carbamic acid:

RNCO   + H_2O $\longrightarrow$ RNHCOOH (carbamic acid)

RNHCOOH $\longrightarrow$ RNH_2 (amine)   + CO_2

RNCO   +   R'NH$_2$ $\longrightarrow$ RNHCONHR' (urea)

2.1.1.3.3 Isocyanate reaction with amines

Isocyanate react with primary and secondary amines to produce di- and tri-substituted urea respectively whilst tertiary amines from labile 1:1 adducts, but generally do not react with isocyanates.

Reaction with an amine yields a urea:

RNCO   +   R'NH$_2$ $\longrightarrow$ RNHCONHR' (urea)

RNCO   +   R'NHR″ $\longrightarrow$ **RNHCON—R'**(urea)
                                         |
                                        R''

2.1.1.3.4 Isocyanate reaction with urea

Biurets are formed from the exothermic reaction of an isocyanate with a urea. With di-substituted urea, mostly formed by the water reaction a biuret is formed through the active hydrogen.

Reaction with an urea yields a biuret:

RNCO   +   R′NHCONHR″ $\longrightarrow$ R′NCONHR″ (biuret)
                                            |
                                           O=C —NHR

2.1.1.3.5 Isocyanate reaction with urethane

An allophonate group is the result of exothermic reaction of isocyanate with the active hydrogen on a urethane group.

Reaction with an urethane yields an allophonate:

RNCO   +   R′NHCOOR″ $\longrightarrow$ R′NCOOR″ (allophonate)
                                           |
                                          O=C —NHR

Scheme 2.2 Reactions of isocyanate

2.1.2 Polyurethane coating

Polyurethane coatings were originally defined as products made from polyisocyanates and polyols but now a broader definition is used that includes all system based on a polyisocyanate whether the reaction is with a polyol, apolyamine or with water. Consequently a polyurethane coating may contain urethane, urea, allophanate and biuret linkages. Polyurethane coatings have grown rapidly because of the highly versatile chemistry and the excellent properties including toughness and abrasion.

There are four broad types of polyurethane technology used in the coating industry, the first three of which are reactive systems with the fourth category covering all systems with no isocyanate reaction during final application:

- Two-component systems consisting of polyisocyanate and a polyol or polyamine that are mixed just prior to application with cure generally taking place at ambient temperature.

- Oven-curing polyurethanes use similar materials to the first category except that a blocked isocyanate is use to provide a storage stable one-pack mix with the polyol or polyamine.

- Moisture-cure polyurethanes are one-component, high molecular weight, low free isocyanate content prepolymers that cure by the reaction with moisture from the environment to form urea linkage.

- Non-isocyante reactive systems, such as thermoplastic polyurethane-based lacquers, aqueous polyurethane dispersion, urethane oils and alkyds, and radiation-cures polyurethanes already containing urethane or urea linkages and where there are no further isocyanate reactions during application.

2.1.2.1 Diisocyanate

When analyzing the changes which took place over the last decade in the diisocyanate production process, a clear qualitative revaluation can be noticed. The group of regular products, like aliphatic and aromatic diisocyanates [10].

2.1.2.1.1 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.

Hexamethylene diisocyanate (HDI)

Isophorone diisocyanate (IPDI)

Norbornane diisocyanate (NBDI)
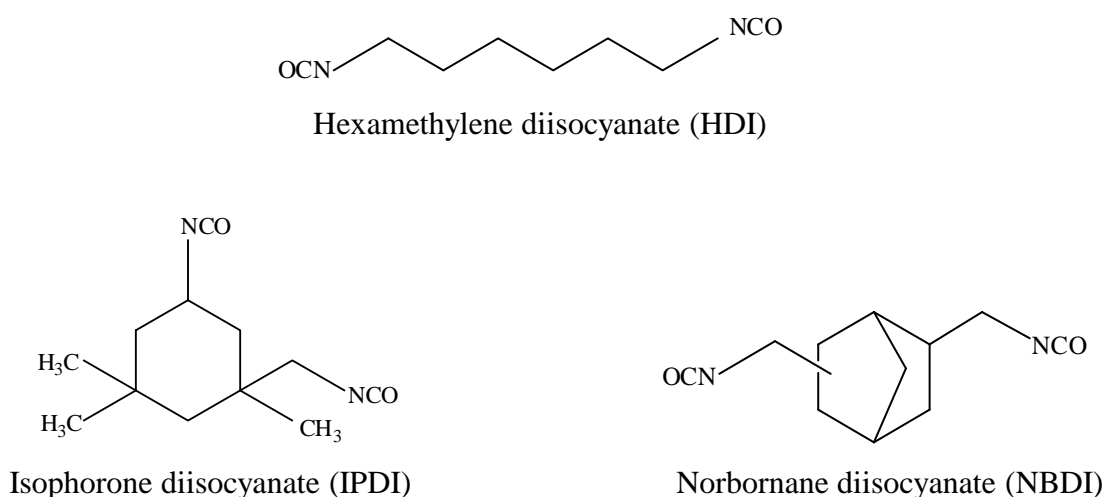
Figure 2.1 Types of aliphatic diisocyanate**.**

2.1.2.1.2 Aromatic diiscyanates

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).
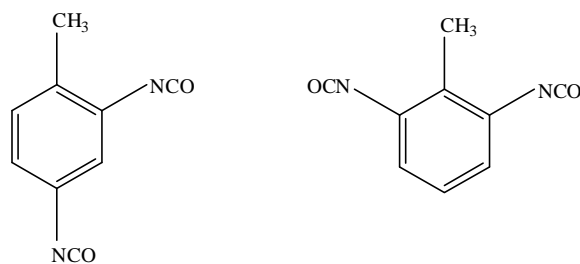
2,4 and 2,6-toluene diisocyanate (TDI)
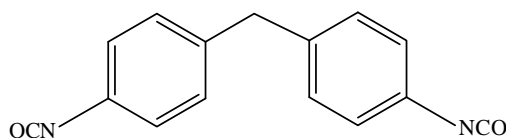
4,4'-methylene diphenyldiisocyanate (MDI)

Figure 2.2 Types of aromatic diisocyanate.

2.1.2.2 Polyols

2.1.2.2.1 Aliphatic linear polyether

The basic polyether polyols applicable for the production of linear PUs can be obtained by the addition reaction (following the anionic mechanism principle) of ethylene or propylene oxide to suitable glycols, produced beforehand in the water addition process to corresponding oxiranes in the catalytic presence of NaOH.

2.1.2.2.2 Aromatic polyethers

Within the group of aromatic polyethers which are important for the polyurethane processes, dianoles are worthy of notice. They are polyethers (e.g., Dianole 24) obtained in the reaction of 2,2-bis(4-hydroxyphenyl)propane (bisphenol-A) with oxiranes.

2.1.2.2.3 Aliphatic saturated polyester

The polycondensation process of dicarboxylic acids and glycols makes the most frequently used method for the synthesis of linear polyestrols. Polyadipates of

ethylene glycol, diethylene glycol or propylene glycol are usually utilised as linear polyesters in the polyurethane elastomers production processes.

Table 2.1 Coating performance versus polyol type

	Acrylic	**Polyester**	**Polyeter**
Application conditions	Equal	Equal	Equal
Viscosity	Medium	High	Low
Appearance	Excellent	Very good	Good
Hardness	Hard	Medium	Soft
Brittleness	Fair	Excellent	Excellent
Gloss retention	Excellent	Fair	Poor
Solvent resistance	Excellent	Fair	Fair
Salt water spray resistance	Excellent	Very good	Good

2.1.2.3 Difunctional chain extenders

Diols make the group of difunctional chain extenders for urethane–isocyanate prepolymers, which is most widely employed in the production of PU elastomers. That group comprises ethylene glycol, diethylene glycol, 1,4-butanediol and 1,6-hexanediol. Diamines, like 1,2-ethylenediamine and 1,6-hexamethylene-diamine, can also be used as chain extenders, but in this case urethane chains are extended through urea groups. Aliphatic amines are used frequently to extend chains of urethane ionomers.

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 processed 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 melecular 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 salvation 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. [11], 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 salvation 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 [11].
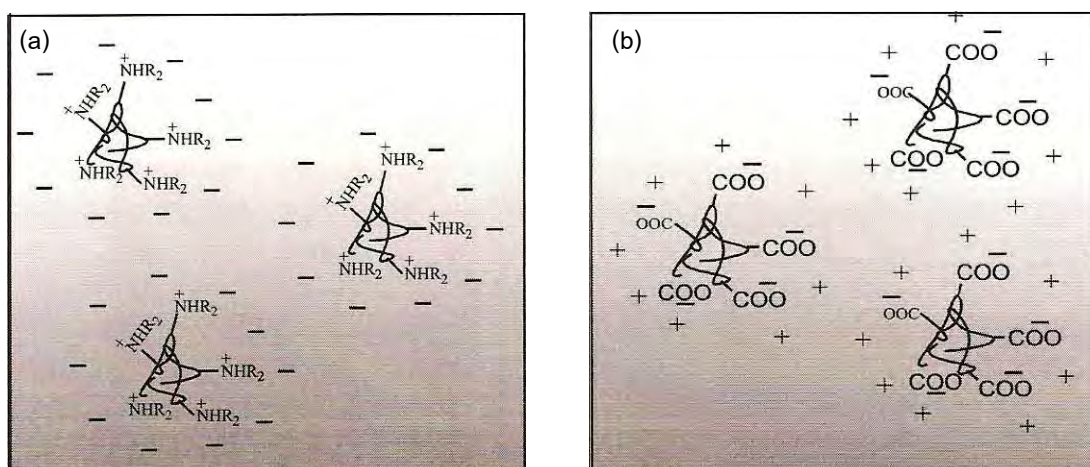
Figure 2.3 Schematic of micelles formed by (a) cationic and (b) anionic polyurethane ionomers in water [11].

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 is 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, ~10^{17-18} /cm^3), monomer droplets (1-10 µm, 10^{8-9}/ cm^3) stabilized by an emulsifier, and an aqueous phase where free emulsifier molecules (~10^{18}/ cm^3) and a small part o 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 [12].

2.1.5 Polypyrrole

Corrosion of metals is an enormous problem throughout the world. Several techniques have been used to protect metals from corrosion. Among them, polymer coatings may be the most widely used technique. In general, good corrosion protection requires that the coatings have good adhesion to the metal substrates.

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 [7].

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 polyminyl 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.

Polypyrrole (PPy) consisting of five-membered heterocyclic rings is one of the most promising conducting polymers. PPy has been extensively explored because of their easy synthesis, tunable conductivity, reversible redox property, and environmental stability. PPycan be easily prepared by chemical or electrochemical polymerization via the oxidation of pyrrole monomers. In general, chemical polymerization leads to intractable powder, whereas electrochemical polymerization results in film deposited on the electrode [13].
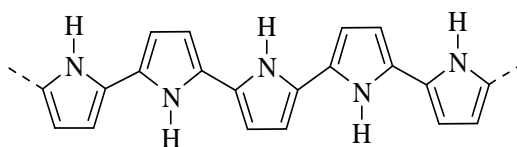
Figure 2.4 Molecular structure of PPy in neutral state.

2.2 Literature reviews

In 1993, Dearmitt *et al*. [14], describe for the first time the preparation of colloidal dispersions of surfactant-stabilized polypyrrole particles in aqueous media using an anionic surfactant, sodium dodecylbenzenesulfonate. The particles are submicrometer-sized and have nonspherical, irregular morphology quite unlike the uniform spherical particles obtained using polymeric stabilizers. They investigated the effect of the initial surfactant concentration on the colloidal stability of the polypyrrole particles and found that precipitation occurred at surfactant concentration below approximately 3.0% w/v.

In 1995, Wiersma *et al*. [15], found the route to obtain waterborne colloidal dispersions of intrinsically conducting polymers. Use is made of commercial aqueous resin dispersion, stabilized by non-ionic surfactants, to which aqueous solutions of oxidant and pyrrole are added. Core-shell particles were shown in Figure 2.5 to exist in polypyrrole/polyurethane and polypyrroleialkyd dispersions by TEM, dielectric measurements and microelectroforesis. Coatings from these dispersions have good conductivity and stability.
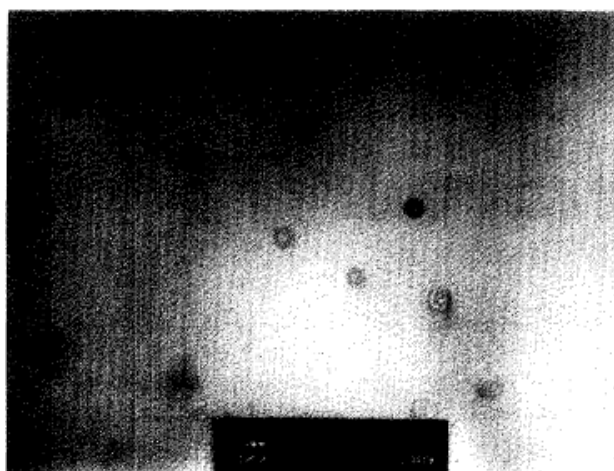
Figure 2.5 TEM picture of a freeze-dried core-shell dispersion. Magnification 315000x.

In 1998, Son *et al*. [16], prepared aqueous polyurethane (PU) dispersion by pre-polymer mixing and neutralization emulsification method. The particle sizes were sensitive to the molecular weights of PU pre-polymer, the degree of neutralization, and the dielectric constant of the dispersion medium. The lower the concentration of carboxyl groups per unit chain length, the larger the particle size of the PU dispersion. The PU particle sizes decreased as the degree of neutralization increased were shown in Figure 2.6, because the dissociated carboxyl groups were capable of stabilization. As the dielectric constant of the carboxyl groups decreased.
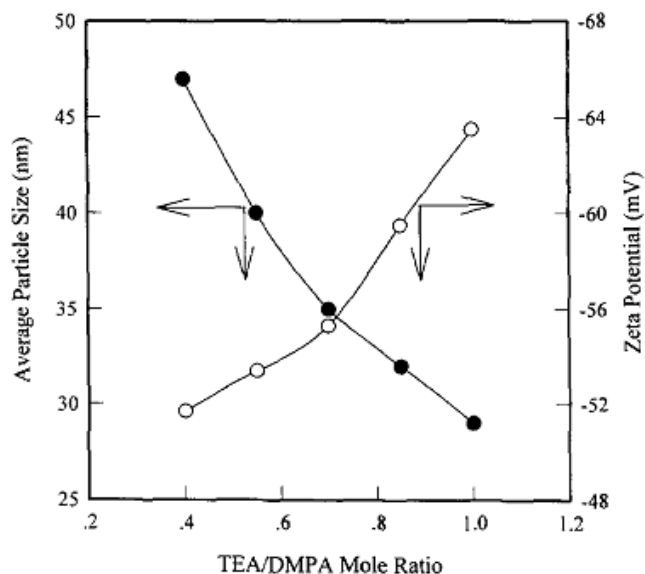
Figure 2.6 The effect of TEA/DMPA mole ratio on zeta potentials and average particle sizes of PU dispersion (polyol Mw = 2000).

In 1999, Huijs *et al.* [17], prepared core-shell latex with a conductive shell. They have focussed on the relation between the conducting polymer content and the shell morphology and on its influence on conductivity. In Figure 2.7 it can be seen that at higher polypyrrole (PPy) content, different shell structures are formed and finally even separate polypyrrole particles appear.
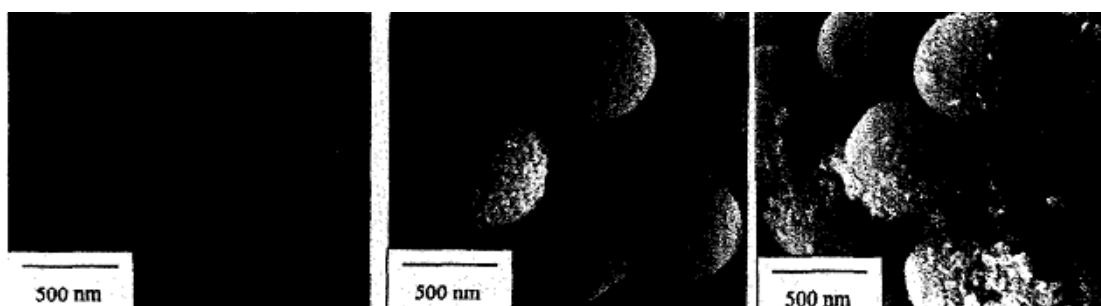
Figure 2.7 SEM micrograps of a PBMA-latex coated with 1 wt.% (a), 4 wt.% (b), 8 wt.% (c) polypyrrole.

The conducting shell around the transparent PBMA latex can be made visible with TEM, as shown in Figure 2.8. TEM micrograph of sections of the dried conductive latex embedded in epoxy give the conclusive evidence for the core-shell structure.
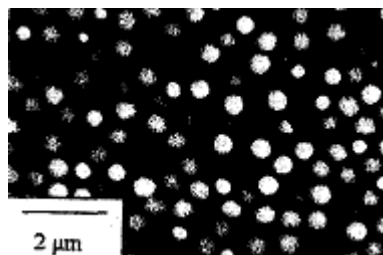
Figure 2.8 TEM micrograph of section (±60 nm) of a PBMA latex with 16 wt.% PPy embedded in epoxy.

In 1999, Dong *et al*. [18], prepared waterborne polyacrylate-polyurethane microspheres, which polyurethane acts as the shell and acrylic polymer as the core. From transmission electron microscopy (TEM) (Figure 2.9), it was shown that the PU layer was stained by osmium tetraoxide 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.
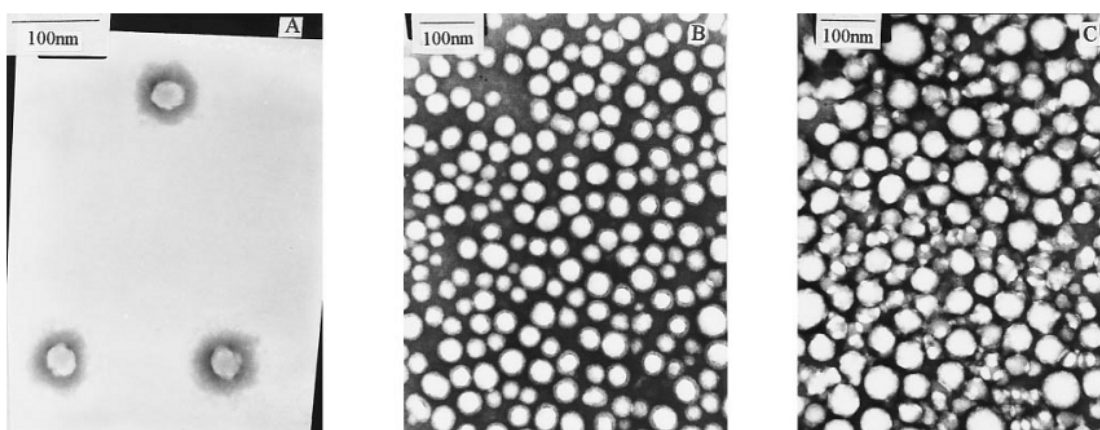
Figure 2.9 Transmission electron micrographs of the PAC-PU microspheres: (A) F2, (B) F5, (C) F7.

In 2001, Lee *et al*. [19], 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. In Figure 2.10, 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.
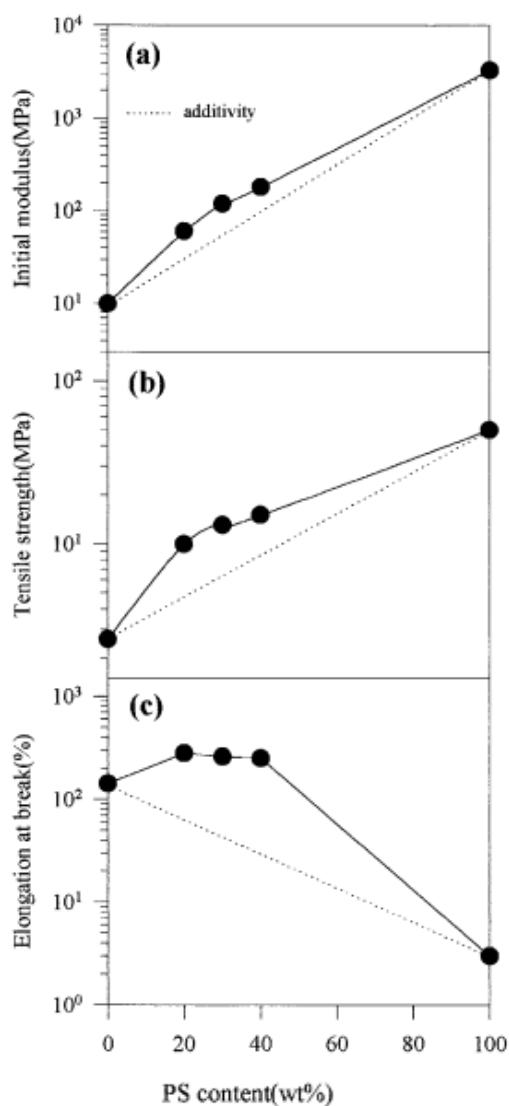
Figure 2.10 Additivity of mechanical properties for PU/PS latex cast film; (a) initial modulus, (b) tensile strength, (c) elongation at break.

In 2000, Delpech *et al*. [20], synthesized waterborne anionic polyurethane and poly(urethane-urea) by using 4,4-dicyclohexylmethane diisocyanate ($H_{12}MDI$), poly(propylene glycol) (PPG) and dimethylolpropionic acid (DMPA). Three types of chain extenders were used, hydrazine (HYD), ethylenediamine (EDA) and ethylene glycol (EG), producing poly(urethane-urea) and polyurethane. The mechanical properties of the cast films and the adhesive properties of the coatings studied in this work were dependent on the combination of the constituents of polymer chains (length of soft segment, NCO/OH ratio, type of chain extender and presence or not of solvent in the synthesis). The mechanical resistance, i.e. increasing values of stress with strain and modulus of elasticity, was favored, in general, by increasing NCO/OH ratio and decreasing length of soft segment. The aqueous dispersions in which acetone was added during the synthesis resulted in films with lower mechanical resistance in comparison with the dispersions cast films produced without addition of acetone (PD). Figure 2.11 shows the stress–strain curves of films obtained from casting of aqueous dispersions based on PPG, with the addition of acetone and chain-extended with HYD. It can be observed that the increase in NCO/OH ratio increased the mechanical resistance of the material because there is an increase in the degree of interchange hydrogen bonding, which leads to the formation of more rigid films.
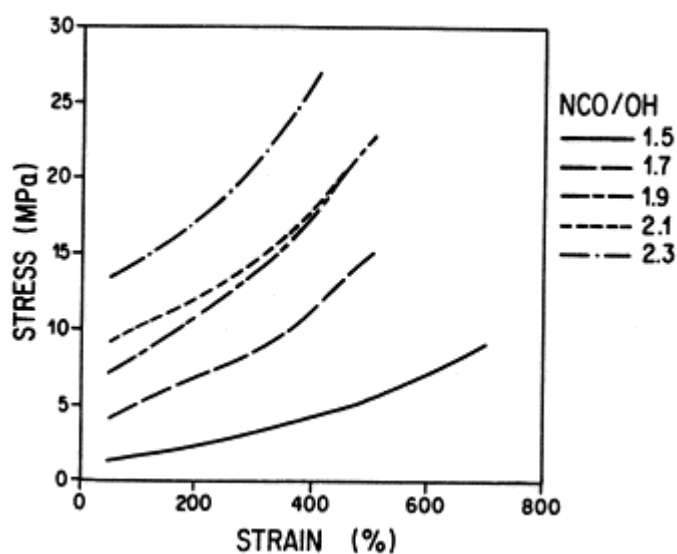
Figure 2.11 Stress–strain curves of cast films obtained from aqueous dispersions synthesized with PPG, HYD as chain extender, in the presence of acetone (AR).

Poly(urethane-urea)s cast films obtained from aqueous dispersions chain-extended with EDA showed higher mechanical resistance than those in which HYD was the chain extender. On the other hand, polyurethanes cast films, based on EG as chain extender, showed higher elastomeric character.

In 2000, Omastova *et al*. [21], synthesized poly(methyl methacrylate) and polypyrrole (PMMA/PPy) by a chemical oxidation of pyrrole in a PMMA latex medium. The obtaining of composites with conductivity in the range of 10^{-9} to 0.1 S/cm, depending on the PPy content. The advantage of the presented method is possibility of using water as a solvent. The results of XPS analysis of PMMA/PPy powder composites (Figure 2.12) showed that the PPy content at the surfaceof the particles is smaller than the overall PPy content determined by elemental analysis. This indicates that pyrrole is polymerized also interior of the PMMA particles.
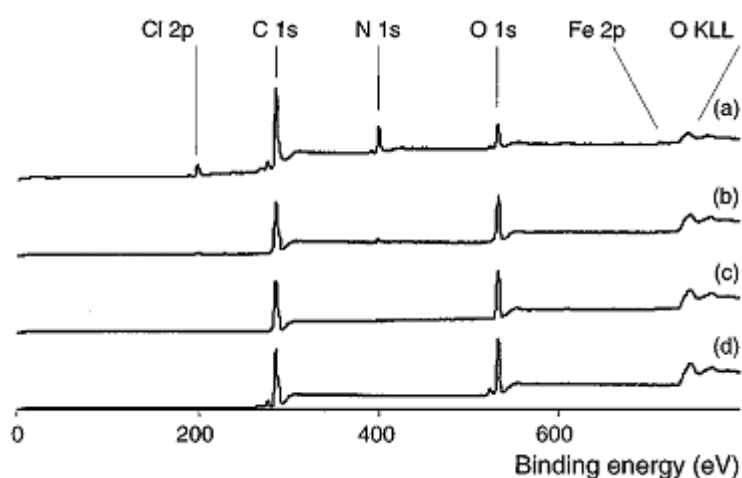
Figure 2.12 Survey XPS spectra of (a) chemically synthesized PPy, (b) powder PMMA/PPy composite containing 9.89 wt.% PPy, (c) PMMA/PPy composite containing 1.12 wt.% PPy, and (d) PMMA.

In 2004, Chen *et al*. [22], 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

$(0.03\% K_2S_2O_8)$ 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 Figure 2.13, shows that PU/PA/EP LIPN improved the water resistance of film due to the excellent hydrophobicity of EP. When EP content increased from 0 to 10%, the water absorption of the films decreased sharply from 96.6 to 12.6%. However, when EP content exceeds 10%, the water absorption of the films increased to certain extent.
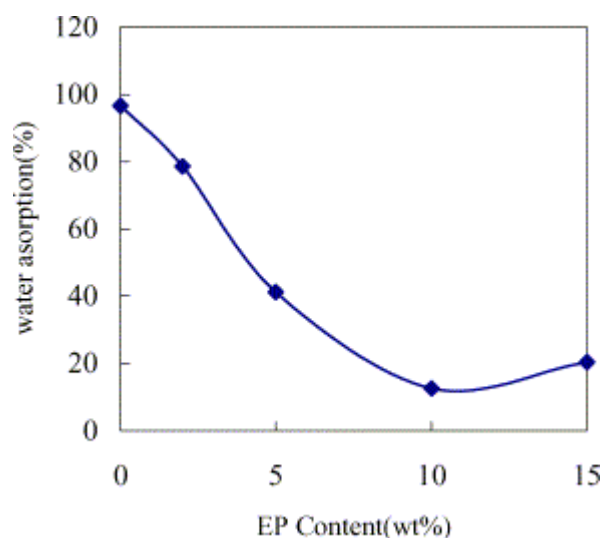
Figure 2.13 The influence of EP content on water resistance of the films.

In 2005, Brown *et al.* [23], 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. Table 2.2 shows 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.

Table 2.2 The effect of particle size: tensile data for PUR, hybrids, acrylics and blends

Sample	Particle size (nm)[a]	Elongation (%)	Ultimate tensile modulus (psi)	100% Modulus (psi)
Polyurethane				
PUR	96	657	4303	880
U/A Hybrids				
UASoft	114	940	4407	895
UAHard	113	400	5186	2326
Acrylics				
AcSoft2	77	367	611	235
AcHard2	85	ND	ND	ND
PUR/low T_g acrylic blends				
BI (AcSoft1)	58	430	1152	398
BI (AcSoft2)	77	476	2096	555
BI (AcSoft3)	203	440	1393	450
PUR/high T_g acrylic blends				
BI (AcHard1)	60	157	2058	1780
BI (AcHard2)	85	174	2571	2320
BI (AcHard3)	201	16	2003	0

In 2005, Ocampo *et al.* [24], 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. Figure 2.14 shows the photographs of Hempadur 45182 films in NaCl solution. Scanning electron microscopy and elemental analysis were also techniques used to follow the degradation process of the films. The regular surface of the initial samples (Figure 2.14 (a)) changed to a rough superficial texture (Figure 2.14 (b)), which was produced by the appearance of oxides in the polymer matrix.
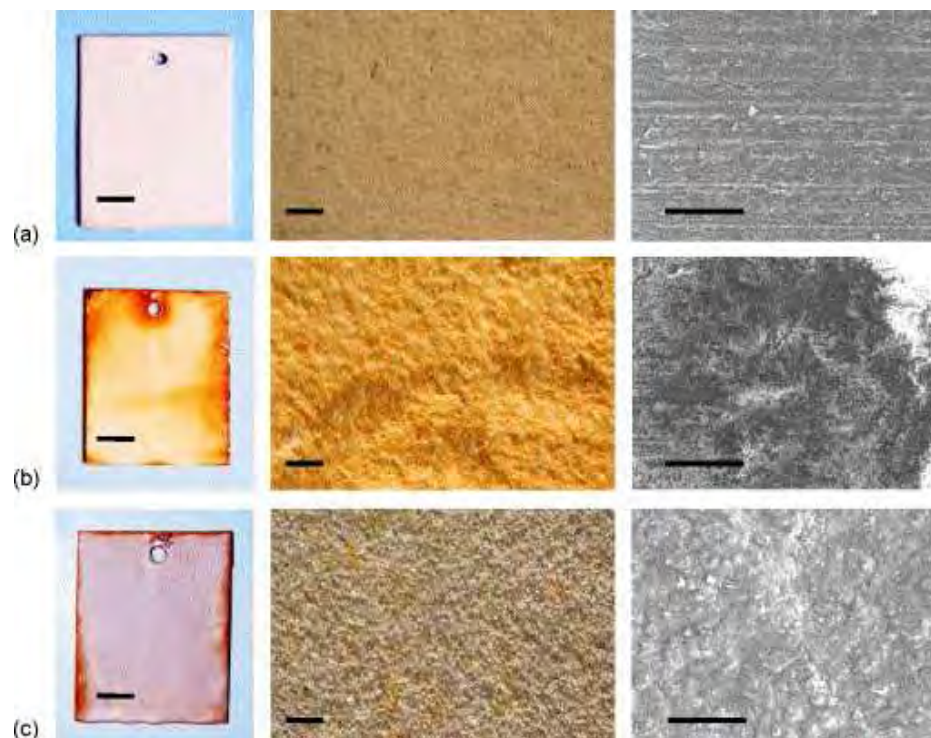
Figure 2.14 On the left, photographs of the painted rectangular test pieces (scale bar: 1 cm): (a) initial sample, (b) and (c) samples without and with conducting polymer, respectively. In the middle, optical micrographs from the polymeric films (scale bar: 200 μm) and scanning electron micrographs on the right (scale bar: 100 μm).

In 2006, Bao *et al*. [25], studied the effect of NCO/OH molar ratio on the dispersion characteristics and properties of dispersion casting films. They described a new series of water-borne polyurethane dispersions where the ionic groups are incorporated in both soft and hard segments using modified castor oil, polyether glycol, and isophorone diisocyanate (IPDI) as main materials according to prepolymer mixing process. The average particle diameter increases with increasing NCO/OH molar ratio. The tensile strength and hardness of the PU fimls increase and solvent absorptivity of films decreases with increase in NCO/OH molar ratio.

In 2007, Hosseini *et al*. [26], synthesized compact hybrid polypyrrole phosphate (PPy–P) composite film on mild steel via electrochemical and using electrochemical impedance spectroscopy (EIS) in 3.5% NaCl solution to evaluate the protective performance against corrosion of these coatings. Figure 2.15 a and b shows

SEM micrographs of PPy films and their composite on mild steel fabricated by CV technique. As observed, the surface morphology of PPy changed in the presence of sodium phosphate additives. By the comparison of Figure 2.15 (a and b), it can be seen that the pure PPy film exhibits a rougher surface morphology than the PPy–P composite. Also, a SEM micrograph of the PPy–P composite (Figure 2.15b) proves that the coating structure is compact, and the spatial distribution of phosphate particles in the composite is quite uniform. The PPy layers are porous, and the protection depends on the quality of the oxide film.
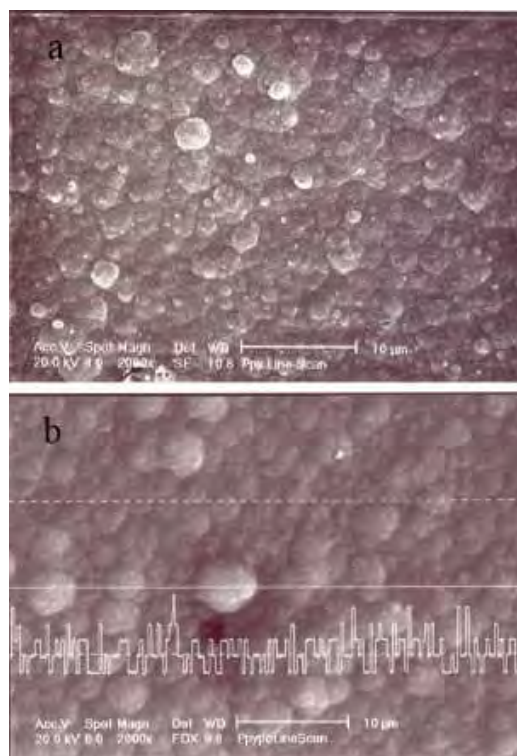
Figure 2.15 SEM images obtained from PPy films grown potentiodynamically: (a) in 0.1 M oxalic acid + 0.1 M pyrrole, (b) in 0.1 M oxalic acid + 0.1 M pyrrole + 0.001 M sodium phosphate after one CV scan between −0.6 and 1 V (SCE).

The corrosion behavior of mild steel covered by the electrodeposited PPy and PPy–P film in corrosive medium NaCl 3.5% is investigated. PPy and PPy–P layers, and PPy–P layer proved to offer better protection, i.e., OCP is established in the passive region for a longer period of time under the given experimental conditions.

In 2008, Chai *et al*. [27], prepared aqueous polyurethane dispersion by using carboxyl acid group to make the polyurethane dispersible, and then nanograde core-shell and crosslinked IPN structure polyurethane/polyacrylate composite latex (PUA) were synthesized by soap-free emulsion polymerization method with polyurethane dispersion as seed. The particle morphology of PUA composite emulsion is inverted core-shell structure with PA as core, with PU as shell. Figure 2.16 show the morphology of the crosslinked PUA emulsion is multi-core structure.
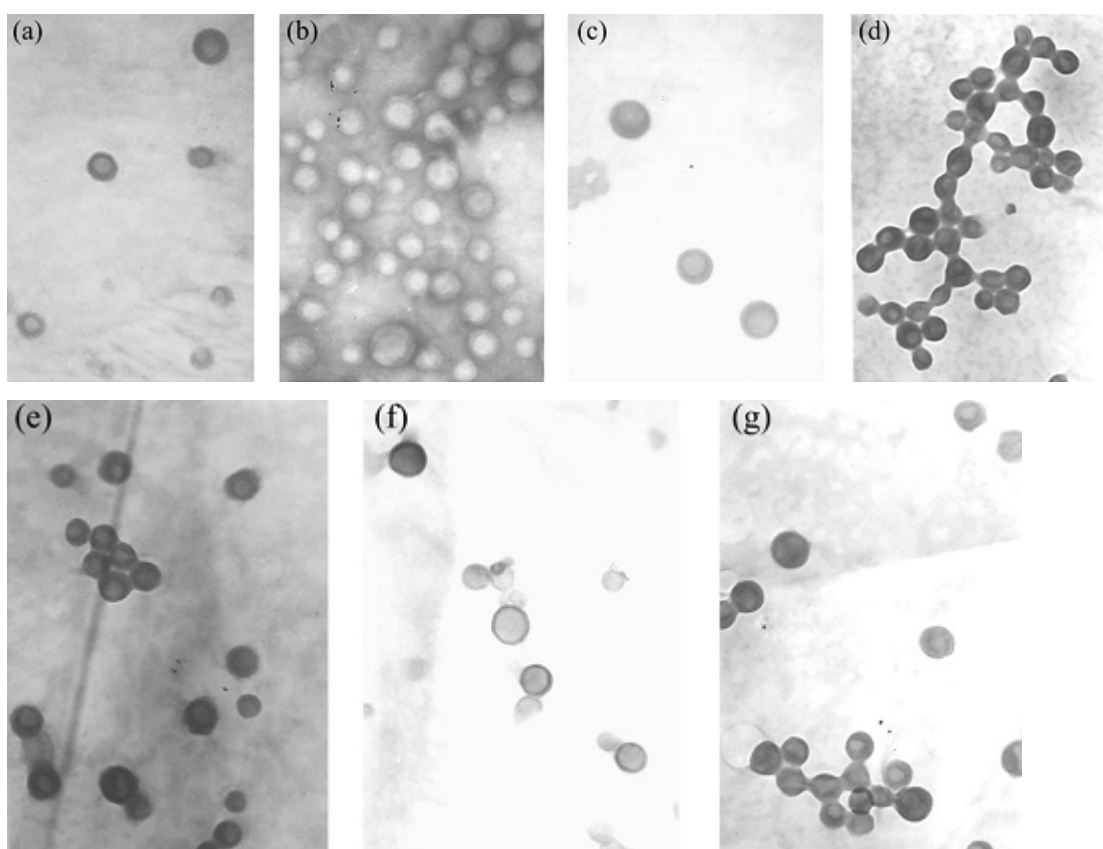
Figure 2.16 TEM photographs of (a) PUA1, (b) PUA3, (c) PUA5, (d) PUA6, (e) PUA7, (f) PUA8, and (g) PUA9.

In 2008, Lu *et al*. [28], prepared core-shell particles consisting of polystyrene–poly(ethylene glycol) monomethacrylate (PS–PEGMA) core covered with polypyrrole (PPy). Monodisperse PS–PEGMA particles have been used as a template for deposition of polypyrrole (PPy). The SEM images presented in Figure 2.17

indicate that PS–PEGMA cores are homogeneously coated with polypyrrole, independently of the oxidation agent. The thickness of the polypyrrole layer deposited on the PS core increases gradually with PPy loading. The obtained composite particles possess core–shell morphology where the shell is composed of small PPy nanodomains. It has been demonstrated that the PEGMA-rich shell layer on the template surface has enhanced the affinity to polypyrrole chains, providing an excellent possibility to control the morphology and thickness of the PPy shell. The shell thickness can be varied by changing PPy loading and by influencing the pyrrole polymerization kinetics in the presence of different oxidants. The type of anions influences the electrical conductivity of the particles, which among others, depends on the polypyrrole content and morphology of films. The highest electrical conductivity was obtained for films prepared using $FeCl_3$ as oxidant.
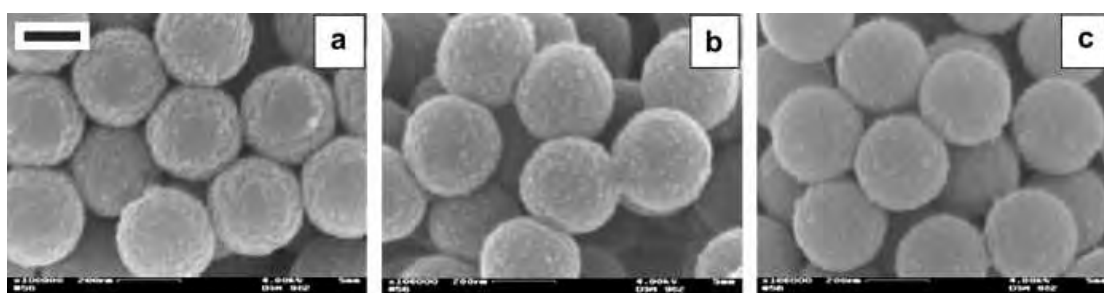
Figure 2.17 SEM images of composite particles prepared with different oxidants ((a) – $Na_2S_2O_8$; (b) – $FeCl_3$; (c) – $H_3PMo_{12}O_{40} \cdot 29H_2O$). The scale of all photographs is given by black bar in (a), which represents 200 nm.

CHAPTER III

MATERIALS AND METHODS

3.1 Chemicals

The chemicals used in this study are listed in Table 3.1. Hydroxymethyl propionic acid and polyester polyol were heat to 105°C and 120°C, respectively under vacuum at 3-5 mmHg for 2 h to remove water before use. N-methyl-2-pyrrolidine was purified before used by refluxing with calcium hydride (CaH_2) for 2 h and then distilling off. The water was removed from chlorobenzene by immersing molecular sieve type 4A for 24 h and then distilling off. Pyridine and pyrrole monomer were purified by distillation before use. Other reagents were used as received without further purification.

The chemicals used in this study are listed in Table 3.1.

Table 3.1 Chemicals used in this study.

Chemicals	Suppliers
1, 6-Hexanediol	ACROS
Acetic anhydride	ACROS
Adipic acid	ACROS
Ammonium peroxydisulfate, 98% (APS)	FLUKA
Chlorobenzene	ACROS
Dibutyltin dilaurate	FLUKA
Hydroxymethyl propionic acid (DMPA)	ACROS

Table 3.1 (cont.) Chemicals used in this study.

Chemicals	Suppliers
Di-*n*-butylamine	FLUKA
Ethylene diamine (EDA)	FLUKA
Ferric chloride	FLUKA
Isophthalic acid	ACROS
Methyl methacrylate (MMA)	FLUKA
n-Butanol	FLUKA
N-methyl-2-pyrrolidone (NMP)	ACROS
Phenolphthalein	FLUKA
Poly (*N*-vinylpyrrolidone) (PVP) (type K90, M = 390,000)	FLUKA
Potassium hydroxide (KOH)	FLUKA
Pyridine	ACROS
Pyrrole	FLUKA
Sodium formaldehyde sulfoxylate	FLUKA
Tertiary butyl hydroperoxide (TBHP)	FLUKA
Toluene	FLUKA
Toluene diisocyanate (TDI)	ACROS
Triethylamine (TEA)	FLUKA

3.2 Apparatus

The apparatus used in the present study are listed in Table 3.2

Table 3.2 List of apparatus used in the present study.

Apparatus	Suppliers/Trade Marks
Dynamic Light Scattering	Malvern, NanoZs
Fourier Transform Infrared Spectroscopy (FTIR)	Bruker, EQUINOX 55
Gel Permeation Chromatography (GPC)	Water, 150-CV
Magnetic Stirrer	IKAMAG-Mini-PIR
Microcentrifuge	Eppendorf
Scanning Electron Microscope (SEM)	Hitachi, S-2500
Transmission Electro Microscope (TEM)	JEOL, JEM-2010
Ultra turrax disperser (UTD)	IKAMAG-Mini-PIR
Ultrasonic Bath	Bandelin, Sonorex RK 100 H
Vacuum Pump	Edwards
Vented Air Oven	Memmert, 400UM
Water Bath	Thermo Haake. DC 10

3.3 Synthesis of polyester polyol

A 500 mL five-neck round bottom glass reactor equipped with a half-moon type mechanical stirrer, a thermometer, a condenser, and a nitrogen gas inlet was used. Polyesterification was carried out under a slow stream of nitrogen to avoid oxidation due to atmospheric oxygen. The progress of reaction was solely monitored from acid value and the quantity of water of esterification accumulated during the

course of reaction. Reaction temperature was controlled using a heating mantle. Figure 3.1 illustrates the apparatus for the synthesis of polyesterpolyol.

The 1,6-hexanediol, adipic acid and isophthalic acid, 5:3:1 mole ratio, were introduced into the reactor. The reaction was carried out at 280°C for 9 h under nitrogen atmosphere. This reaction had been described by Otts et al. [29].
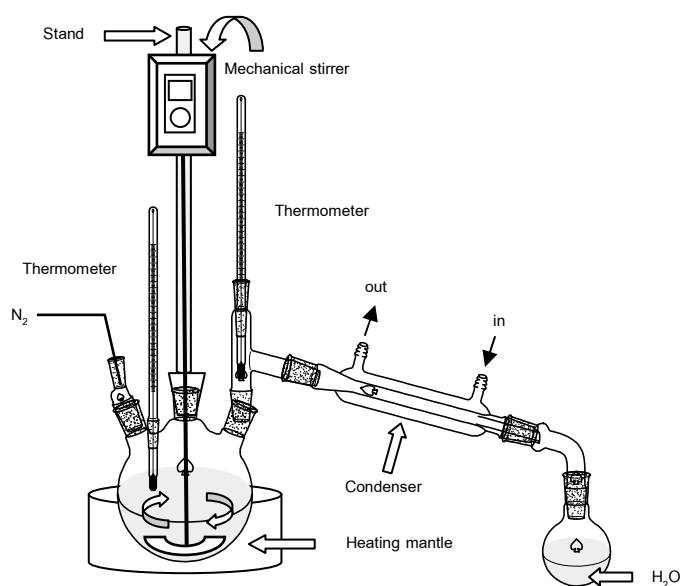
Figure 3.1 The apparatus for the synthesis of polyester polyol.

3.3.1 Characterization of polyester polyol

3.3.1.1 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.

$$ROH \quad + \quad (CH_3CO)_2 \quad \longrightarrow \quad RO\text{-}COCH_3 \quad + \quad CH_3COOH$$
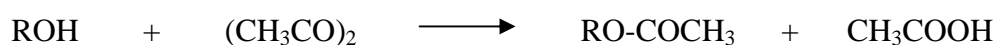
Reagents

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. The hydroxyl value was calculated from the equation 3.1.

$$\text{Hydroxyl value (mg KOH/g sample)} = \frac{(B - S) \times M \times 56.1}{W} \tag{3.1}$$

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)

3.3.1.2 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 color 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. The acid value was determined from the equation 3.2.

$$\text{Acid value on solid} = \frac{V \times 5.61}{W \times N} \qquad (3.2)$$

    V = Volume of alcoholic KOH 0.1 N (mL)

    W = Weight of sample (g)

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

3.3.1.3 Determination of $\overline{M}w$ and MWD

      The $\overline{M}w$ and MWD of polyester polyol (one hundred microliters of a 0.5% solution) was determined by gel permeation chromatography (GPC) (Water, 150-CV) using tetrahydrofura (THF) as the eluent at a flow rate of 1.0 mL/min at 30°C through two PLgel 10 µm mixed B 2 columns and reflactive index detector.

3.3.1.4 Chemical structure analysis

Fourier transform infrared (FTIR) spectra of polyester polyol were recorded on a Bruker Tensor 27 FTIR spectrometer in the range 400–4000 cm^{-1} with 32 scans at room temperature. Sample was prepared by casting 0.5 wt.% polyester polyol on KBr pellets, followed by vacuum drying at 50°C for 48 h.

3.4 Synthesis of aqueous polyurethane dispersion

Aqueous polyurethane (PU) dispersion was prepared by prepolymer mixing process [30] in two steps via synthesis of NCO- terminated prepolymer and preparation of dispersion by introducing anionic centers to acid dispersion. Isocyanate terminated was prepared in a 500 mL round bottom, five-necked glass reactor equipped with a mechanical stirrer, thermometer, a reflux condenser with drying tube, a nitrogen gas and dropping funnel. The polyester polyol and DMPA were charged into the reactor. While stirring, NMP (20 wt.% based on the total reaction mass) was added and stirring was continued until a homogeneous mixture was obtained. After that slowly adding TDI, where the mole ratio of –NCO in TDI to –OH in polyester polyol is 1.5 - 2.5 from the dropping funnel about 30 min. When the TDI addition was completed, add the DBTDL (0.03 wt.% based on total solids) as catalyst to the reactor. Then the mixture was heated to 90ºC and hold for 1.5 h. Upon reaching the theoretical NCO value. The NCO content of the prepolymer was determined by di-*n*-butylamine back titration method [31].

The prepolymer was chain extended by the addition of ethylene diamine (EDA), and allowed to react for 2 h at 90°C to make the polyurethane polymer. The final polymer was neutralized the carboxylic acid in DMPA by the addition of triethylamine (TEA) over 30 min while maintaining the temperature at 55°C. With the change of TEA amount, the degree of neutralization was controlled (Table 3.1). After that the neutralized polyurethane solution was dispersed in deionized water at 45-50°C with Ultra turrax disperser (UTD). The stirring was continued at the same

temperature for additional 30 min. Figure 3.2 shows the apparatus for the synthesis of aqueous polyurethane dispersion.

Table 3.3 Recipe for preparing of aqueous PU dispersion: effect of TEA/DMPA mole ratio

Components	Amount (g)
DI water	120
TEA	variable*
PU prepolymer	100

*Variable: mole ratio TEA/DMPA = 0 – 1.0
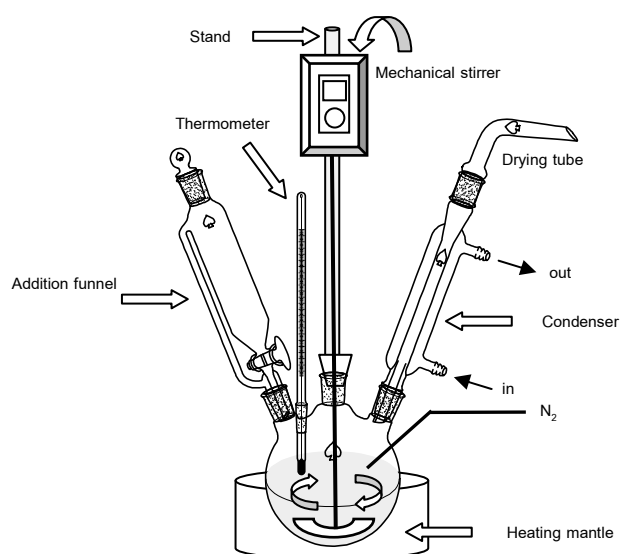
Figure 3.2 The apparatus for preparing water-base polyurethane dispersion.

3.4.1 Characterization of aqueous polyurethane dispersion

3.4.1.1 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 1.00 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. The %NCO was calculated by using equation 3.3.

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

(3.3)

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)

3.4.1.2 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 ± 2.5°C. After heating for 24 h, weigh the dish. The %NV was calculated from using the equation 3.4.

$$\%NV \ = \ \frac{(C-A) \times 100}{S}$$
(3.4)

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

3.4.1.3 Determination of $\overline{M}w$ and MWD

The $\overline{M}w$ and MWD of aqueous polyurethane dispersion were determined as described in section 3.3.1.3.

3.4.1.4 Chemical structure analysis

Fourier transform infared (FTIR) spectra of aqueous polyurethane dispersion were obtained as described in Section 3.3.1.4.

3.4.1.5 Measurement of size of aqueous polyurethane dispersion

The size of aqueous polyurethane dispersion after ultrasonication was measured by using dynamic light scattering apparatus (Malvern, NanoZS). The charge density of aqueous polyurethane dispersion was determined by applying a microelectrophoresis apparatus (Malvern, Zeta sizer nanoZS).

3.5 Synthesis of PU/PMMA latex

The PU/PMMA latex was prepared by soap free emulsion polymerization technique [27]. A predetermined quantity of aqueous PU dispersion prepared in the previous step was taken in a 500 mL five-neck round bottom glass reactor equipped with the same accessories used in the previous step. 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 introduce 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.

3.5.1 Characterization of PU/PMMA latex

3.5.1.1 Chemical structure analysis

Fourier transform infared (FTIR) spectra of aqueous polyurethane dispersion were obtained as described in Section 3.3.1.4.

3.5.1.2 Measurement of size of PU/PMMA latex

Particle size of PU/PMMA latex was measured as described in Section 3.4.1.5.

3.5.1.3 Morphological study

The morphology of particles in PU/PMMA latex was investigated under transmission electron microscopy (TEM) JEM-200CX model. The specimens were optained from dropping the diluted latex onto the copper grid and allowed to dry in a desiccator at room temperature.

3.6 Synthesis of PPy/PU/PMMA latex

The PU/PMMA latex (1:1) constituted the medium for the polymerization of pyrrole. The latex was placed in stirred reactor. An appropriate pyrrole amount was injected with a syringe and the mixture was stirred for 15 min under nitrogen flow at 25°C. A water solution of oxidant ($FeCl_3$) was added dropwise to start the pyrrole polymerization. After 5-10 min the dispersion became coloured (blue or dark red colour appeared) indicating that the pyrrole polymerization started. After 6 h the formed composite particles were removed from the reaction vessel. The relative amount of pyrrole was varied.

3.6.1 Characterization of PPy/PU/PMMA latex

3.6.1.1 Chemical structure analysis

Fourier transform infared (FTIR) spectra of aqueous polyurethane dispersion were obtained as described in Section 3.3.1.4.

3.6.1.2 Measurement of size of PPy/PU/PMMA latex

Particle size of PU/PMMA latex was measured as described in Section 3.4.1.5.

3.6.1.3 Morphological study

The morphology of particles in PPy/PU/PMMA latex was investigated as described in Section 3.5.1.3.

3.7 Corrosion study

The corrosion study was carried out with electrochemical method. This device allowed program controlled cycles for immersion of iron 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 iron 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.

3.7.1 Characterization of coating degradation

3.7.1.1 Morphology of the coating degradation

The morphology of metal surface coated with PPy/PU/PMMA latex after immersion in the salt solution 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 Preparation of aqueous polyurethane dispersion

In this research, aqueous polyurethane dispersion was prepared based on 2,4-toluene diisocyanate and polyester polyol according to a prepolymer mixing process. 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 of 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 should be obtained with hydroxyl (OH) end groups. The equation of the reaction is shown in Scheme 4.1.
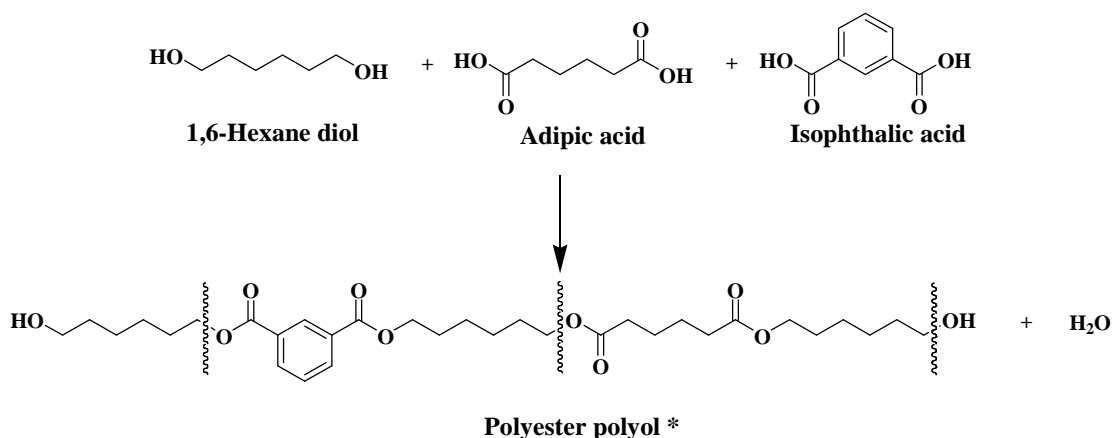
* From now on, the structure of polyester polyol will be represented as $HO \sim\!\sim\!\sim\!\sim OH$

Scheme 4.1 Synthesis of polyester polyol.

The reaction time was varied and the acid value of the mixture was determined at a certain time by titrating with alcoholic KOH solution as shown in Table 4.1. During the reaction, water was collected into graduated receiver as a by-product. The reaction was complete within 9 hours when no more water was collected. The amount of water related with a theoretic value. The product was obtained as waxy white viscous fluid at room temperature and the molecular weight 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 product were 2,078 and 3,256, respectively.

Table 4.1 Determination of acid value of the synthesized polyester polyol.

Reaction time (h)	Acid value
4	68.05
5	39.90
6	21.15
7	9.56
8	3.39
9	2.29

It was found that the acid value decreased when the reaction time increased. Finally, the acid value was found to be 2.29 at 9 h of the reaction time. This result indicates that almost all dicarboxylic acid of adipic acid and isophthalic acid were converted to the corresponding ester. This reaction had been described by Otts *et al*. [29]

Figure 4.1 shows FTIR spectra of product, adipic acid, isophthalic acid. Both starting dicarboxylic acids, adipic acid and isophthalic acid, exhibit the broad absorption bands of the carboxyl group at the range of 3300-2400 cm^{-1} and the carbonyl group at 1695 cm^{-1} which are characteristics of the carboxylic acid groups. The disappearance of both absorption bands and the appearance of the small

absorption band at the range of 3600-3400 cm^{-1} (OH stretching) and the sharp absorption band at 1729 cm^{-1} (C=O stretching of an ester) in the FTIR spectrum of the film of the product indicate the formation of an 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 3300-2400 cm^{-1} and the presence of alcoholic OH in the structure of the product. The other absorption band at 2936 and 2864 cm^{-1} are due to C-H stretching.

In addition, the acid value of the as-prepared product is very low, which is probably due to the trace amount of adipic acid and isophthalic acid left in the mixture. These results clearly confirmed the existence of polyester polyol.
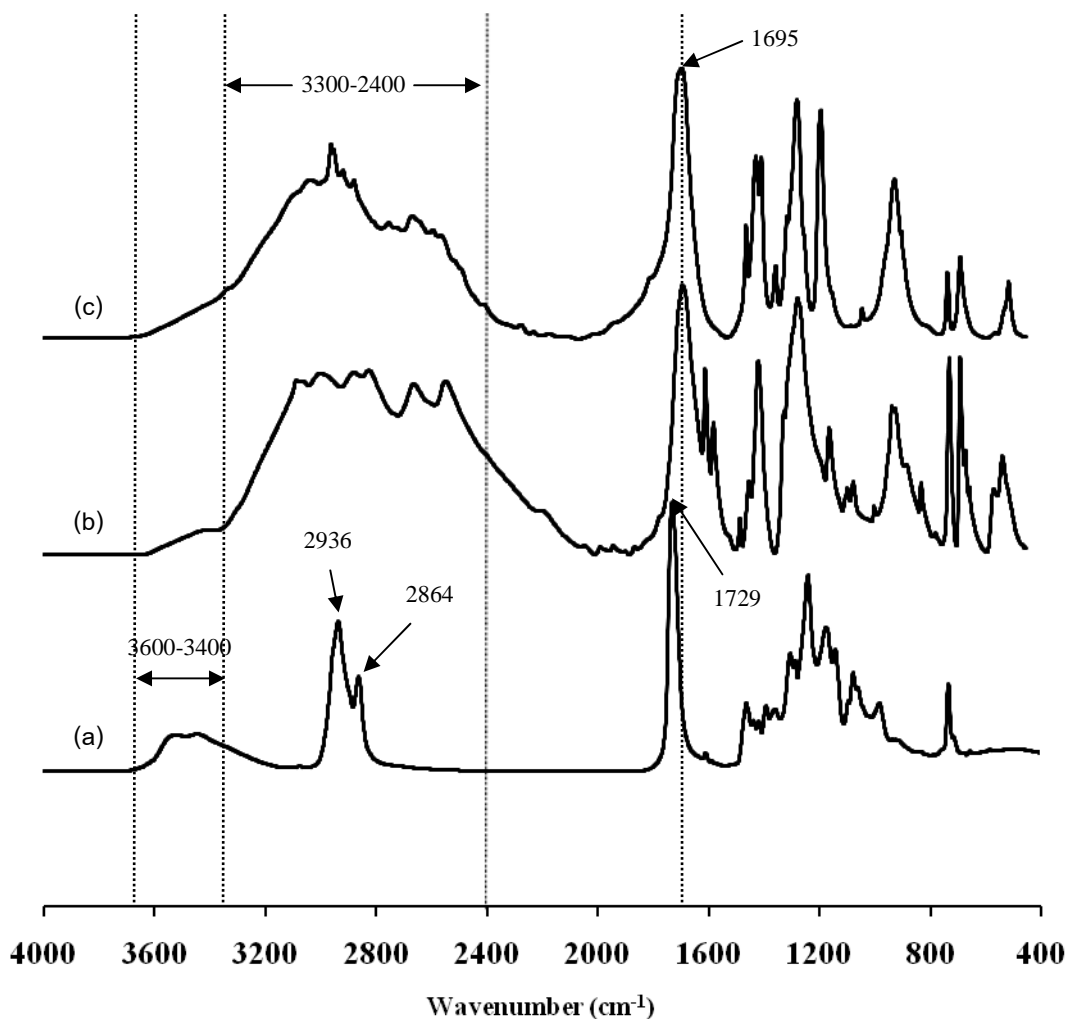
Figure 4.1 FTIR spectra of the product (a, film), adipic acid (b, KBr), and isophthalic acid (c, KBr).

4.1.2   Synthesis and characterization of aqueous polyurethane dispersion

The synthesis of the aqueous polyurethane dispersion is shown in Scheme 4.2. Aqueous polyurethane dispersion was prepared by prepolymer mixing process. Prior to the synthesis, 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 determined as 120 mg KOH/g and then was taken for calculating the use of TDI for polymerization. The NCO groups of TDI were sufficiently reacted with hydroxyl groups of polyol and DMPA at the first step and with the EDA at the next step. Relative amount of residual NCO group was 5.09% which was investigated by back titration medthod with di-n-butylamine [31]. The appearance of aqueous polyurethane dispersion was translucent. It had solid content 32 % and pH 8-9. The polyurethane particles were dispersed in the water by self anionic emulsifier, -COO$^-$HN$^+$(C$_2$H$_5$)$_3$ [32].

OCN—⟨ring⟩—**NCO** + **HO**—C(**CH₃**)(**COOH**)—**OH** + **HO**〜〜〜**OH**

2,4-Toluene diisocyanate **Hydroxymethyl propionic acid** **Polyester polyol**

NCO - Terminated prepolymer

Triethylamine

H₂N—CH₂CH₂—**NH₂**
Ethylene diamine

H₂O

Aqueous polyurethane dispersion
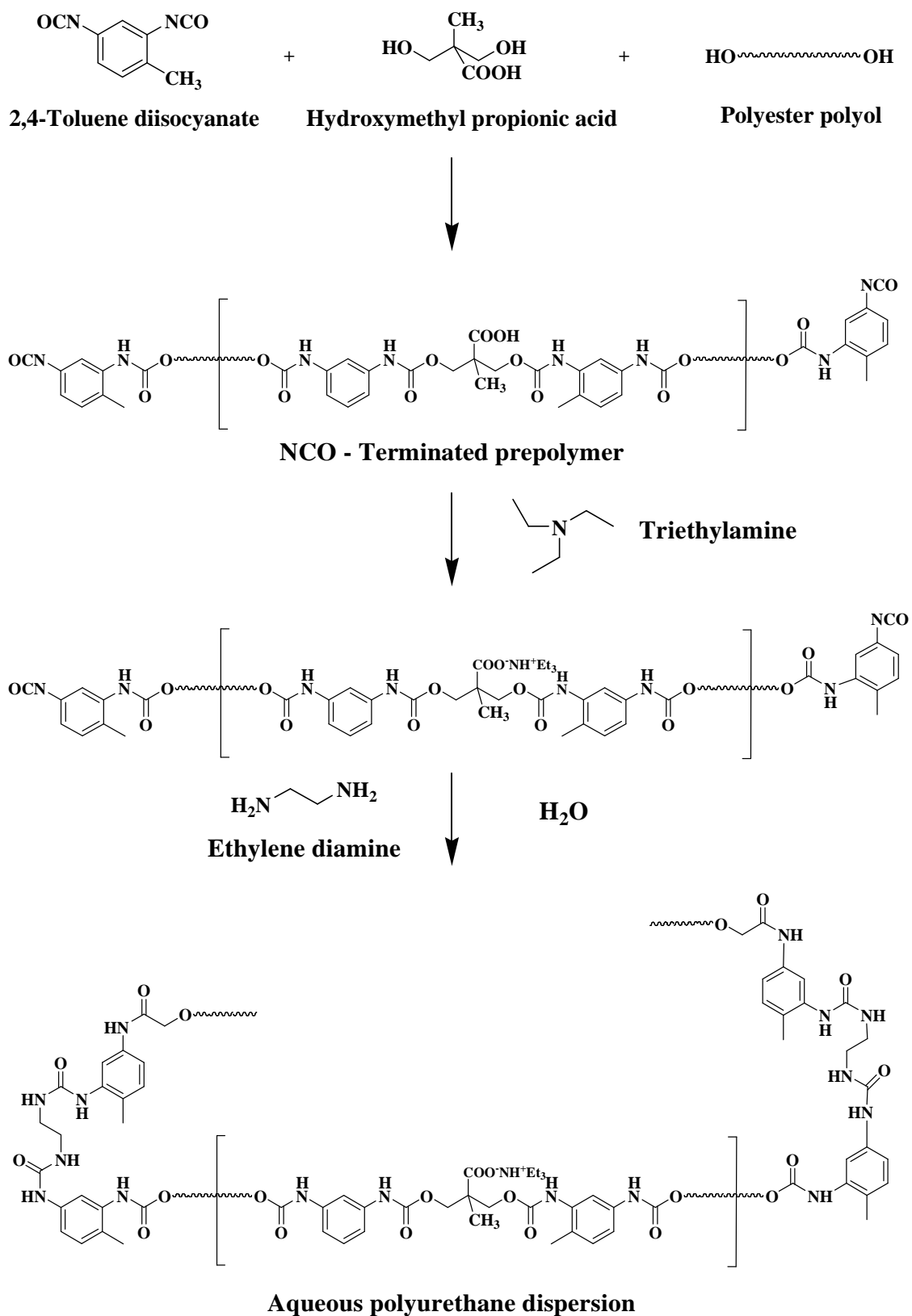
Scheme 4.2 Synthesis of aqueous polyurethane dispersion

Figure 4.2 demonstrates the typical FTIR spectra of dried film from polyester polyol and liquid from product. As for the product, there was no absorption band of –NCO at 2265 cm^{-1}, it was concluded that all the residual –NCO groups were consumed and disappeared after chain extension. The appearance band at the range of 3400-3200 cm^{-1} is due to O-H stretching of water in latex and also N-H stretching of amino group in polyurethane structure. The sharp absorption band at 1682 cm^{-1} is due to C=O stretching in polyester polyol and also urethane linkage. The other absorption band at 2942 and 2860 cm^{-1} are due to C-H stretching. These results agree with report Jhon, Y.K. *et al*. [33]
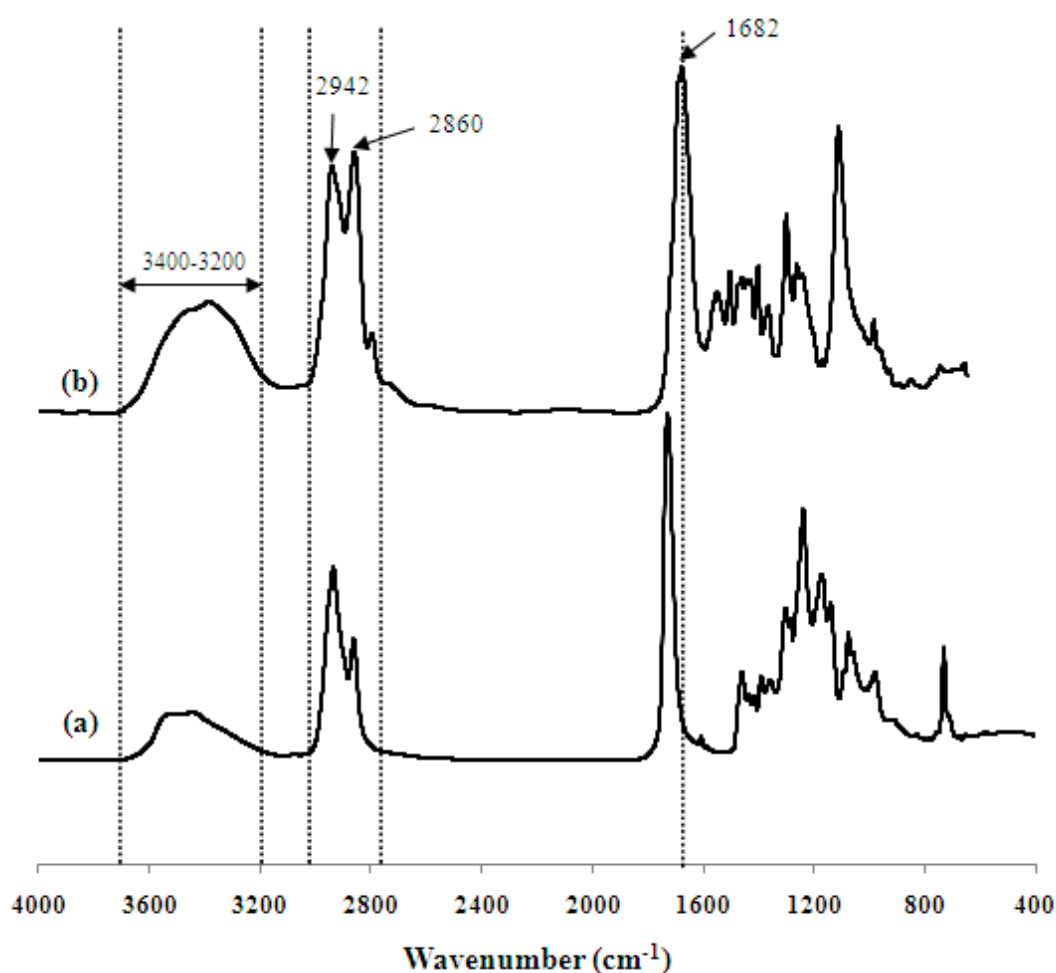
Figure 4.2 FTIR spectra of polyester polyol (a, film) and product (b, liquid).

4.1.2.1 The particle size of aqueous polyurethane dispersion

4.1.2.1.1 Effect of NCO/OH molar ratio of aqueous polyurethane dispersion on the particle size

The effect of the different NCO/OH molar ratio of aqueous polyurethane dispersion on the particle size is shown in Figure 4.3. With the increase of NCO/OH molar ratio of aqueous polyurethane dispersion, the urea content in aqueous polyurethane dispersion is increased. The presence of the more hydrogen bonding can result in the aggregation between polyurethane molecules. Consequently, the average particle size of aqueous polyurethane dispersion is also increased. D means diameter and P means polydispersity.

Figure 4.3 Particle size distributions curves of aqueous polyurethane dispersion with different molar ratios of NCO/OH: (a) 1.5 (D =80 nm, P = 0.076), (b) 2.0 (D = 97, P = 0.071), and (c) 2.5 (D = 108, P = 0.076).

4.1.2.1.2 Effect of TEA/DMPA mole ratio of aqueous polyurethane dispersion on the particle size

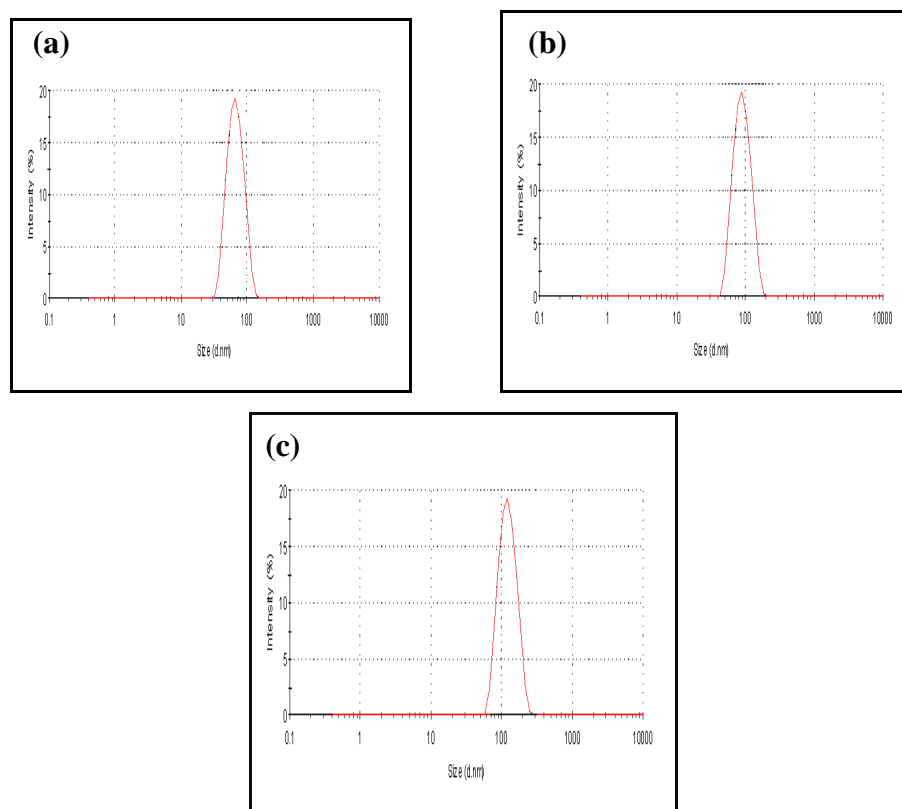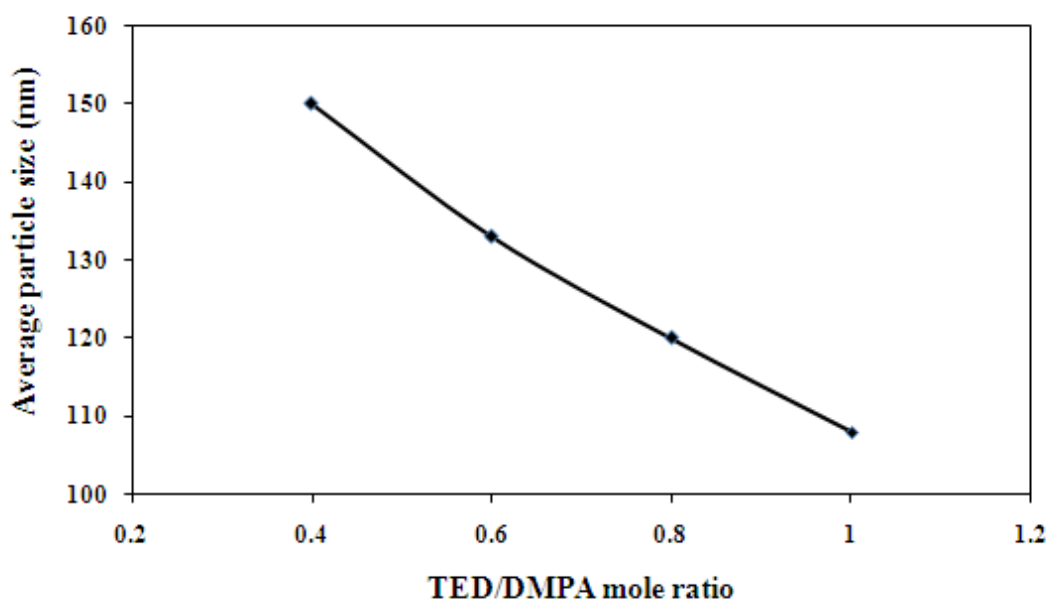**Figure 4.4** The effect of TEA/DMPA mole ratio on average particle size of aqueous PU dispersion (NCO/OH = 2.5).

The effect of on the average particle size of aqueous PU dispersion is shown in Figure 4.4. Regardless of the TEA/DMPA mole ratio, a similar tendency was observed. The lower the concentration of carboxyl groups per unit chain length, the larger the particle size of aqueous PU dispersion. The PU particle sizes decreased as the degree of neutralization increased, because the dissociated carboxyl groups were capable of stabilization.

4.2 Preparation of PU/PMMA latex

One of the approaches to develop polyurethane dispersion with superior performances which can compete with solvent-type counterparts is to produce emulsions with a multi-phase structure in each emulsion particle with a core-shell type polymerization technology. Aqueous PU 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 [23].

4.2.1 Synthesis and characterization of PU/PMMA latex

In this study, the polyurethane (PU)/poly (methyl methacrylate) (PMMA) latex emulsion was prepared by soap free emulsion polymerization method using aqueous PU dispersion as the colloidal stabilizer or emulsifier for the polymerization of hydrophobic MMA monomers. The PU/PMMA latex was synthesized at different weight ratios of aqueous polyurethane dispersion and PMMA by changing the amount of the MMA monomers introduced while keeping the amount of PU constant. 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.

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.
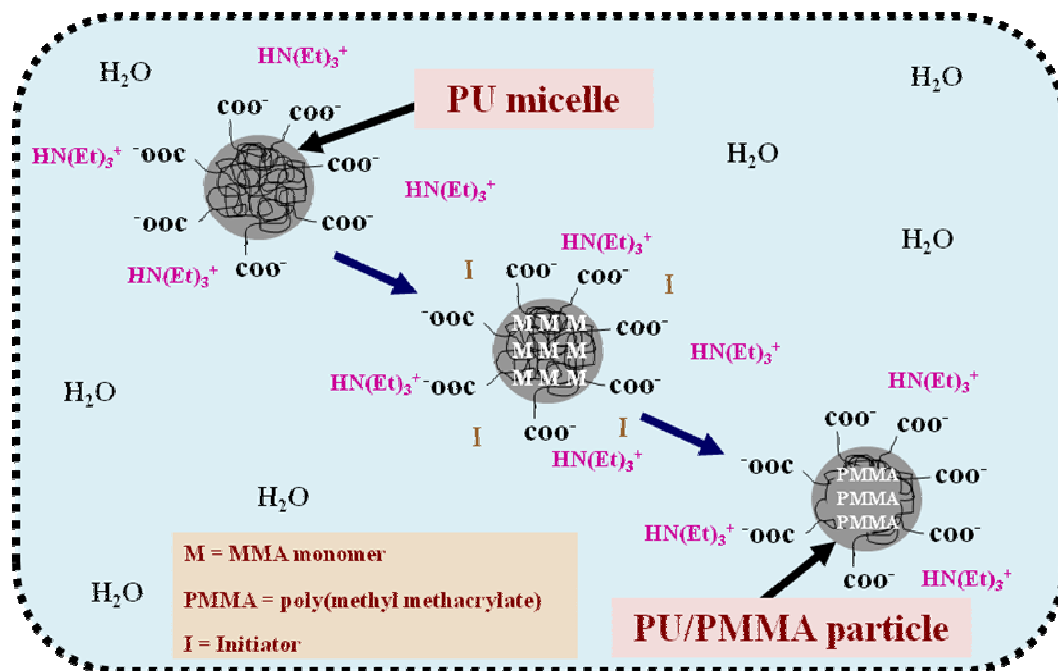
Figure 4.5 Schematic formation of PU/PMMA latex.
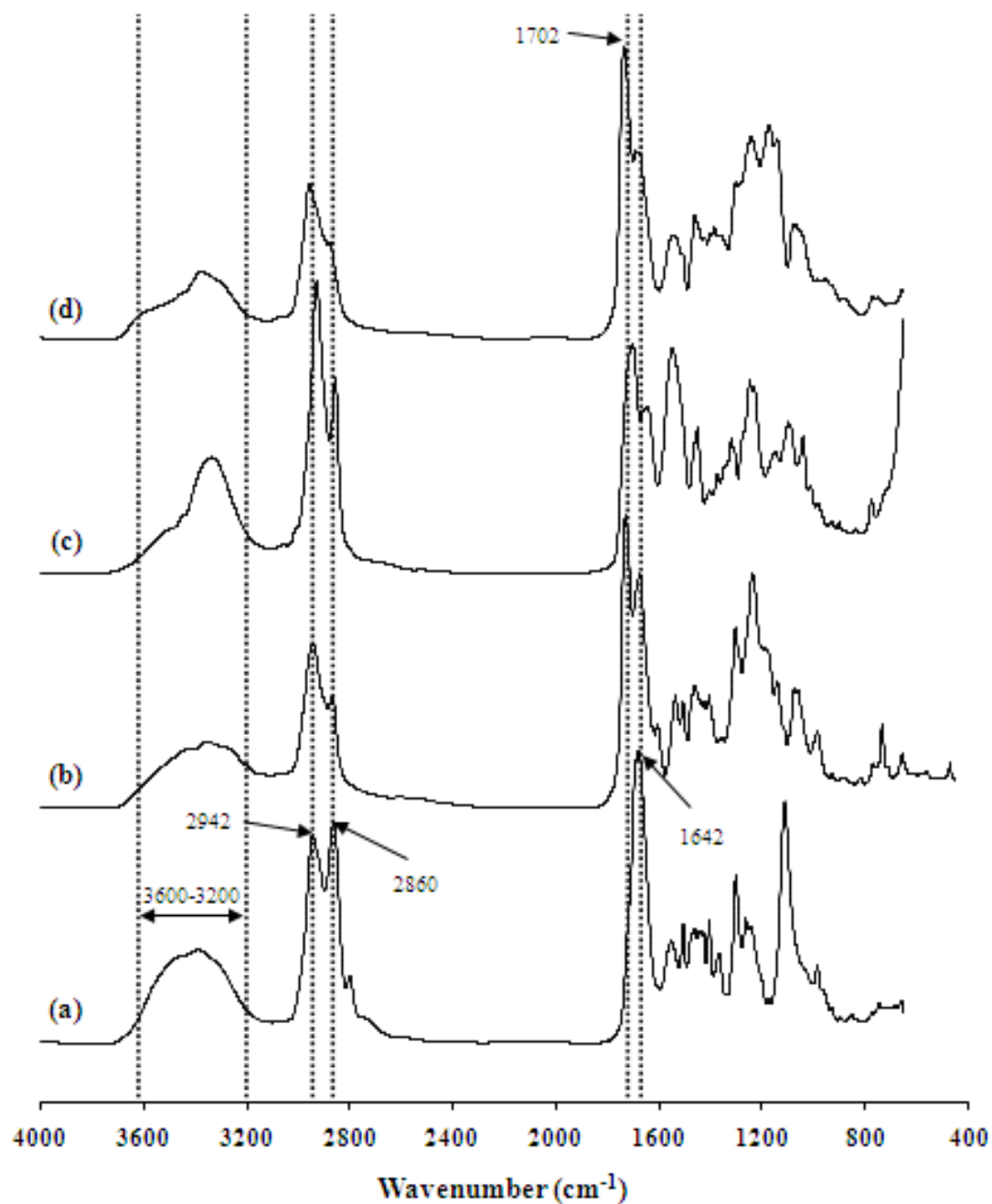
Figure 4.6 FTIR spectra of aqueous PU (a) and various weight ratios of PU/PMMA; 2:1 (b), 1:1 (c), 1:2 (d).

The assignment of the most characteristic absorption bands are given in Figure 4.6. The increase in the PMMA content causes an increase in the relative intensity of the C=O stretching bands at 1702 and 1642 cm^{-1}. The absorption band range between 3600 - 3200 cm^{-1} is due to O-H stretching of water in aqueous polyurethane and N-H

stretching of the amino group in PUD structure. The sharp and intense absorption band at 1702 and 1642 attributed to the C=O stretching of PU and PMMA, which they overlap in various weight ratios of PU/PMMA spectra. When PMMA content was increased, it was obviously found the additional shoulder peak around 1642 cm^{-1}. It is plausibly attributed to the C=O stretching of PMMA. These FTIR spectra confirm the formation of a polyurethane and PMMA structure. Furthermore, there is no apparent difference in absorption peaks among these four FTIR spectra. This indicates that there is no occurrence of chemical reaction between aqueous PU dispersion and MMA monomer during the polymerization reaction of MMA. In addition, these PU/PMMA FTIR spectra are similar to the work reported by Hirose M. *et al*. [6]

4.2.1.1 The particle size of PU/PMMA particle

Particle size distribution curves of the PU/PMMA composite latex were measured with the particle size analyzer of a dynamic light scattering instrument. From Figure 4.7, it was found that the particle size distributions of all PU/PMMA latexes were narrow. The effects of the PU/PMMA weight ratios on the particle size of PU/PMMA composite emulsion are shown in Figure 4.7(a-c). *D* means diameter and *P* means polydispersity. They were obtained from various weight ratios of PU/PMMA. PU (NCO/OH = 2.5) was used as the medium.
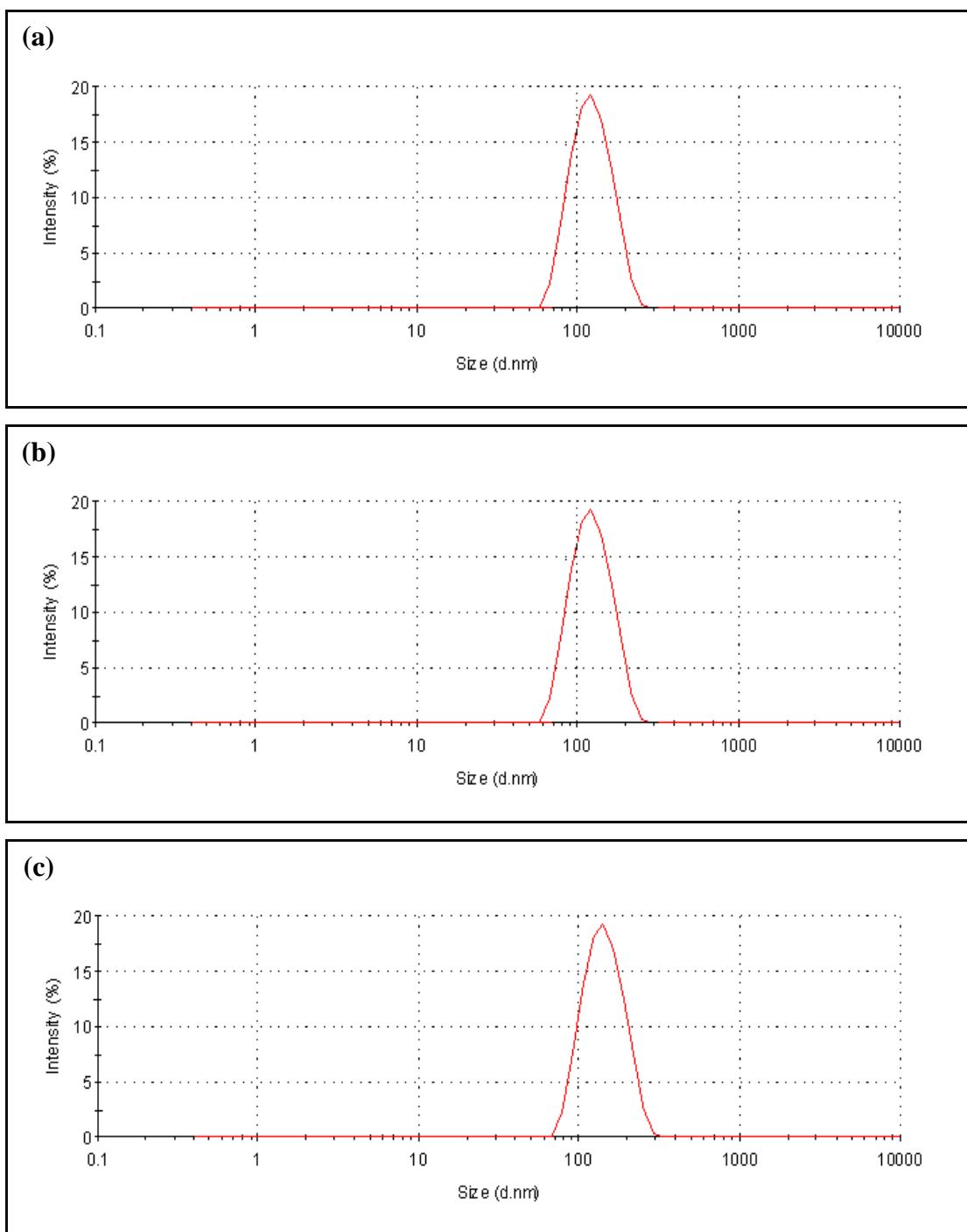
Figure 4.7 Particle size distributions curves of PU/PMMA latex with different PU/PMMA weight ratios: (a) 2:1(D =111 nm, P = 0.076), (b) 1:1 (D = 115, P = 0.071), and (c) 1:2 (D = 136, P = 0.076).

Analysis of the data in Figure 4.7 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 no detected in the particle size distribution. It represented good stability of the synthesized PU/PMMA latex.

4.2.1.1.1 Effects of MMA content on the particle size of PU/PMMA latex

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 Index
1:0	108	0.08
2:1	111	0.07
1:1	115	0.07
1:2	136	0.08

When the PU/PMMA ratio was greater than 1:1, the average diameters of PU/PMMA composite emulsions increased with increase in the amounts of the methyl methacrylate monomers. This was in good agreement with the regular rule.

In addition, the average diameters of the three PU/PMMA composite emulsion system using different PU/PMMA ratios were larger than those of the PU seed dispersions. This is also in good agreement with the regular rule.

The results clearly indicated that the particle size of PU/PMMA was enlarged by higher amount of PMMA with respect to PU. Since the surface area of PU particles cannot be entirely covered by the hydrophilic carboxyl groups. Therefore, the PU particle in aqueous dispersion is an open or water-swollen structure [27], it can

accommodate the acrylic emulsion particle up to a certain content without expansion as demonstrated in Figure 4.8 (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 4.8 (c).
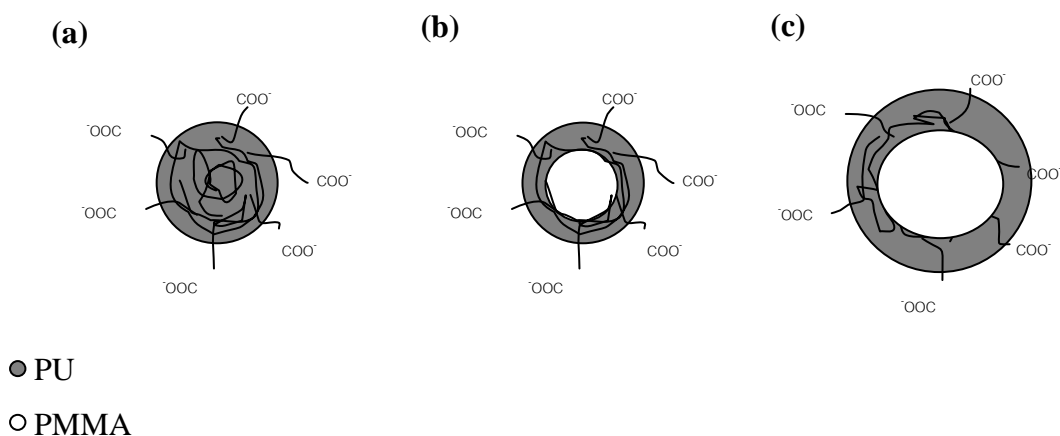

● PU
○ PMMA

Figure 4.8 Schematic representation of the effect of MMA content on PU/PMMA particle.

Figure 4.9 shows some TEM photographs of the PU/PMMA latex obtained from stable composite emulsion of PU/PMMA latex [Figure 4.9 (b)]. This composite emulsion system was core-shell structured sphere. In this core-shell particle, the darker region of the outer layer was PU domain, and the lighter region in the core was poly(methyl methacrylate)(PMMA). On the one hand, the electronic cloud density around the PU chains was higher than that around PMMA because PU had greater polarity in comparison with the PMMA chains. The more hydrophilic chains in amphiphilic PU/PMMA latex composite system were selectively located in the shell region, and the hydrophobic chains were concentrated in the core region of the emulsion particle in the course of phase-inversion process. 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 [6,18].
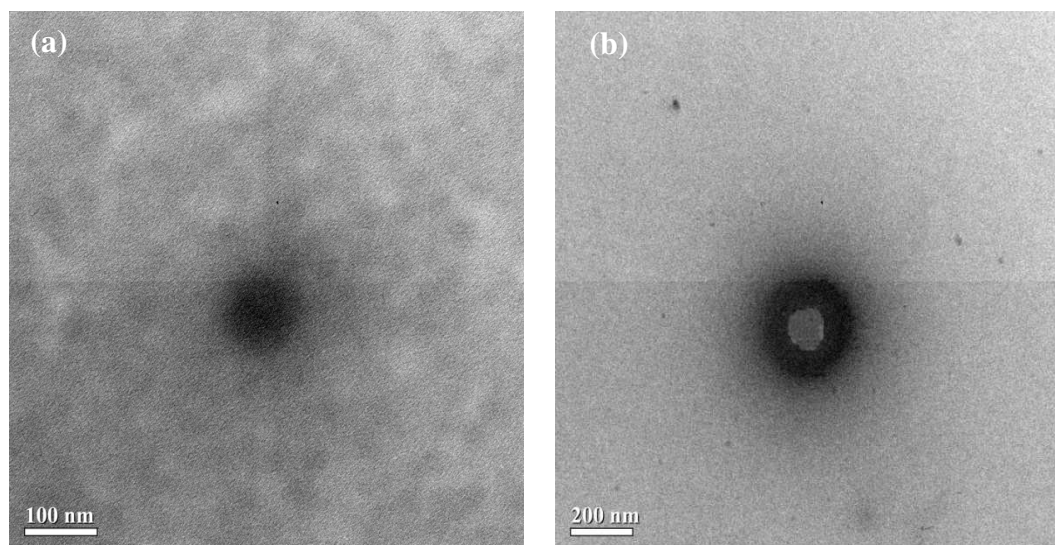
Figure 4.9 TEM photographs of aqueous polyurethane dispersion (a) and PU/PMMA latex at 1:1 weight ratio (b).

4.3 Preparation of PPy/PU/PMMA latex

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

4.3.1 Synthesis and characterization of PPy/PU/PMMA latex

The PPy/PU/PMMA latex was prepared by using PU/PMMA latex (1:1 ratio) as medium for polymerization. The reaction was the oxidative polymerization using ferric chloride as an oxidant.

The synthesis of PPy/PU/PMMA latex was performed according to section 3.5.4. Therefore PPy/PU/PMMA latex was obtained and characterized by FTIR spectroscopy. Figure 4.10 exhibits the comparison of PPy, PU/PMMA, and PPy/PU/PMMA latex.
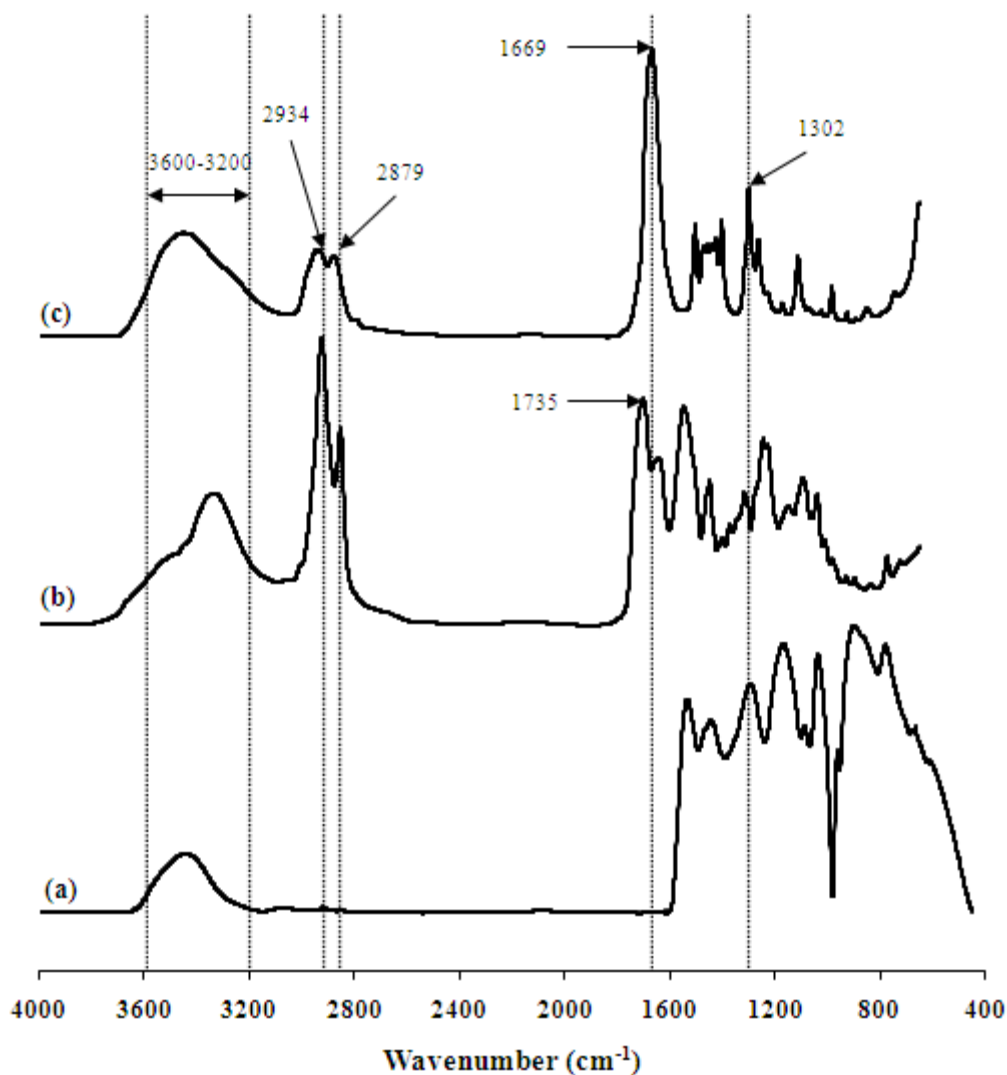
Figure 4.10 FTIR spectra of PPy (a, KBr) PU/PMMA (b, liquid), and PPy/PU/PMMA (c, liquid).

The pattern of the spectrum of the PPy/PU/PMMA latex is similar to both of the PPy and PU/PMMA latex. The small absorption band at the range 3600-3200 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 polypyrrole and polyurethane. The sharp and intense absorption bands at 1735 and 1669 cm^{-1} are characteristic of C=O stretching of PU/PMMA and PPy/PU/PMMA, respectively. The sharp and intense absorption band of N-H stretching at 1302 cm^{-1} confirmed the structure of PPy and

PPy/PU/PMMA. Accordingly, FTIR spectra prove that the synthesis of PPy/PU/PMMA latex was successful.

4.3.1.1 The particle size of PPy/PU/PMMA particle

In the synthesis of PPy/PU/PMMA latex, the concentration of pyrrole was varied from 1.2 – 1.5 wt.%. The results were shown in Table 4.3.

This could be attributed to the insufficiency of PVP for entrapping the growing polypyrrole particle in the reaction mixture which caused polypyrrole partially formed to aggregate. This phenomenon had been described by J. Stejskal *et al.* as shown in Figure 4.11 [34, 35].

(a)   (b)   (c)
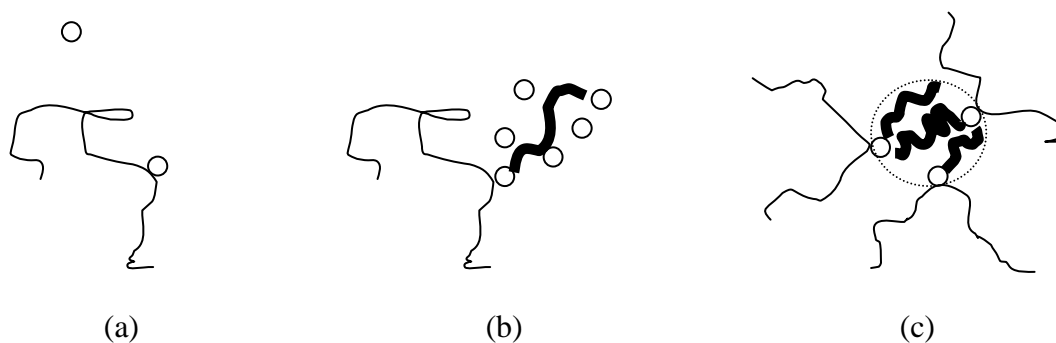
Figure 4.11 Polypyrrole particle formation in aqueous phase [19,20].

Pyrrole oligomers were produced in the early stages of pyrrole oxidation polymerization and adsorbed at stabilizer chains (Figure 4.11(a)), the growth of polypyrrole started at the stabilizer chains (Figure 4.11(b)). The polypyrrole particle was sequentially produced from these nuclei (Figure 4.11(c)) until monomer or oxidant or both were used up. Steric stabilizer, PVP, entrapped at the polypyrrole 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 pyrrole was varied, PPy/PU/PMMA latex were obtained with particle size and polydispersity as illustrated in Table 4.4. It can be seen that the particle size

of PPy/PU/PMMA was slightly larger than PU/PMMA. The results indicated PPy plausibly heterocoagulated with PU/PMMA.

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

Polydispersity of all PPy/PU/PMMA latex were about the same and approximately equal to PU/PMMA.

Table 4.3 The effect of concentration of pyrrole on diameter and polydispersity.

Concentration of pyrrole monomer (wt.%)	Diameter (nm)	Polydispersity Index
0.0[*]	115	0.08
1.2	117	0.13
1.3	119	0.13
1.4	121	0.12
1.5	125	0.16

[*] PU/PMMA

While PU/PMMA latex was milky color, the visual appearance of PPy/PU/PMMA latex at all various concentration of pyrrole monomer were milky gray, which the dark color represented PPy form [36, 37]. When the concentration of pyrrole was increased, the color of PPy/PU/PMMA latex became more intense.

Figure 4.12 Particle size distribution curves of PPy (---) and PPy/PU/PMMA latex (–) with different wt.% of pyrrole (PY) monomer: (a) 1.2 (D = 117 nm, P = 0.133), (b) 1.3 (D = 119 nm, P = 0.133), (c) 1.4 (D = 121 nm, P = 0.119), and (d) 1.5 (D = 126 nm, P = 0.164) wt.%.

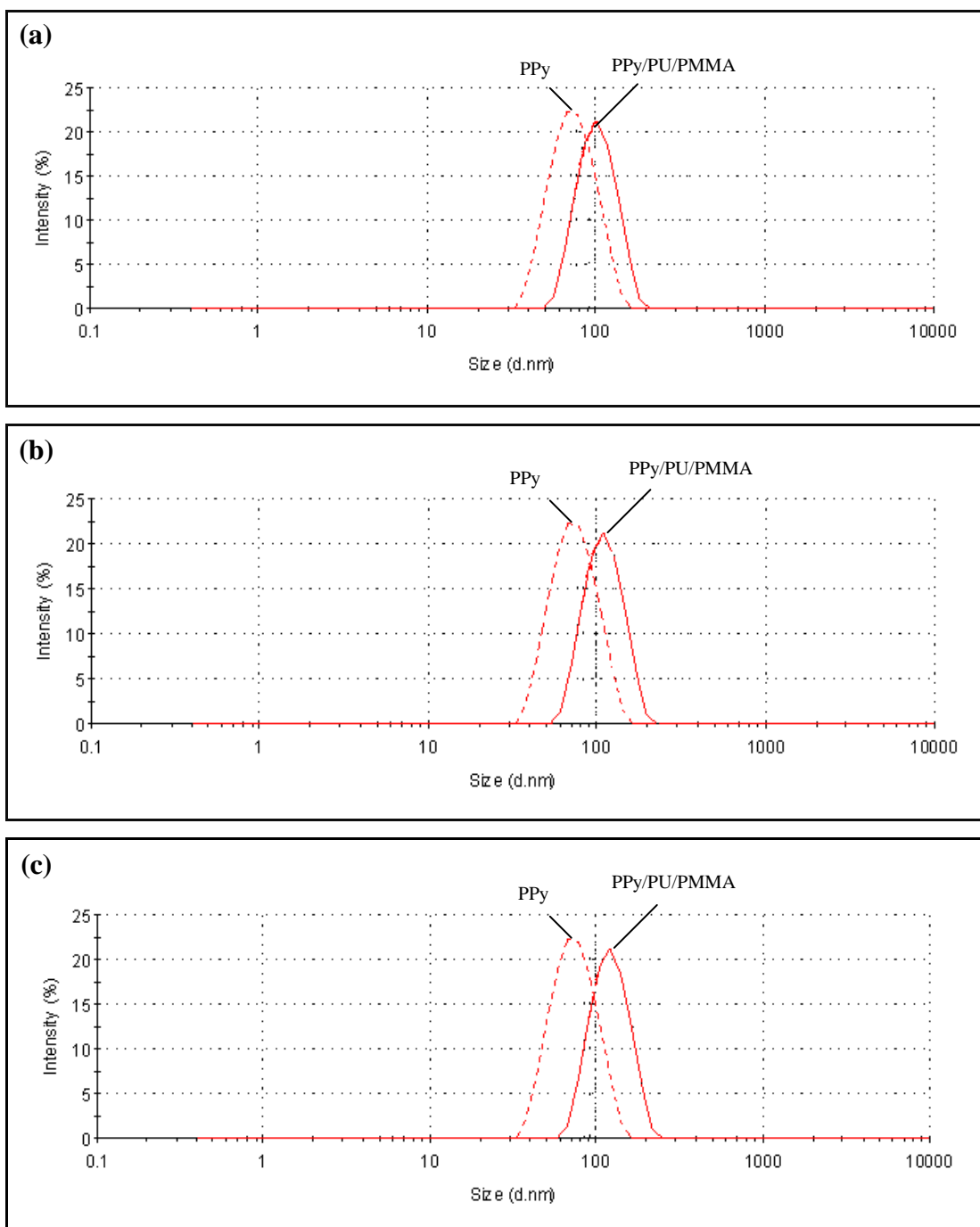**Figure 4.12** (cont.) Particle size distribution curves of PPy (---) and PPy/PU/PMMA latex ($-$) with different wt.% of pyrrole (PY) monomer: (a) 1.2 ($D = 117$ nm, $P = 0.133$), (b) 1.3 ($D = 119$ nm, $P = 0.133$), (c) 1.4 ($D = 121$ nm, $P = 0.119$), and (d) 1.5 ($D = 126$ nm, $P = 0.164$) wt.%.
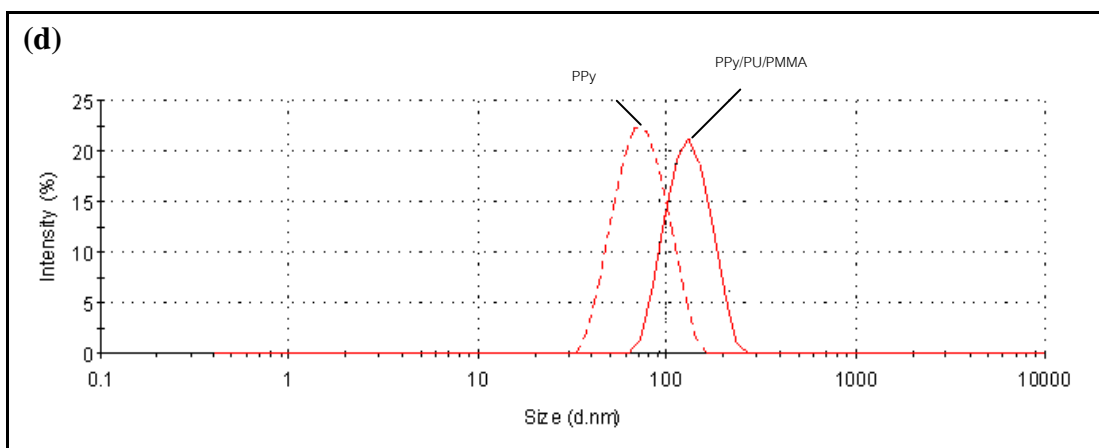
Analysis of the data in Figure 4.12 revealed that no other materials besides PPy/PU/PMMA were in the latex, particularly free PPy. This conclusion was confirmed by the polymerization of pyrrole monomer was the same concentration and reaction condition as for the preparation of PPy/PU/PMMA. PPy was formed with the average particle in the range of 76-78 nm. Therefore, if free PPy 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 PPy was rather found on the surface of PU/PMMA.

Figure 4.13 illustrates the formation of PPy/PU/PMMA latex. In reaction mixture, the PU/PMMA particles and polypyrrole particles were both dispersed in aqueous phase as shown in Figure 4.13(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 PPy stabilized by PVP. Polypyrrole was heterocoagulated on the PU/PMMA particle and the polymer steric stabilizer, PVP, continued to act as a stabilizer for the entire PPy/PU/PMMA particle as shown in Figure 4.13 (b).
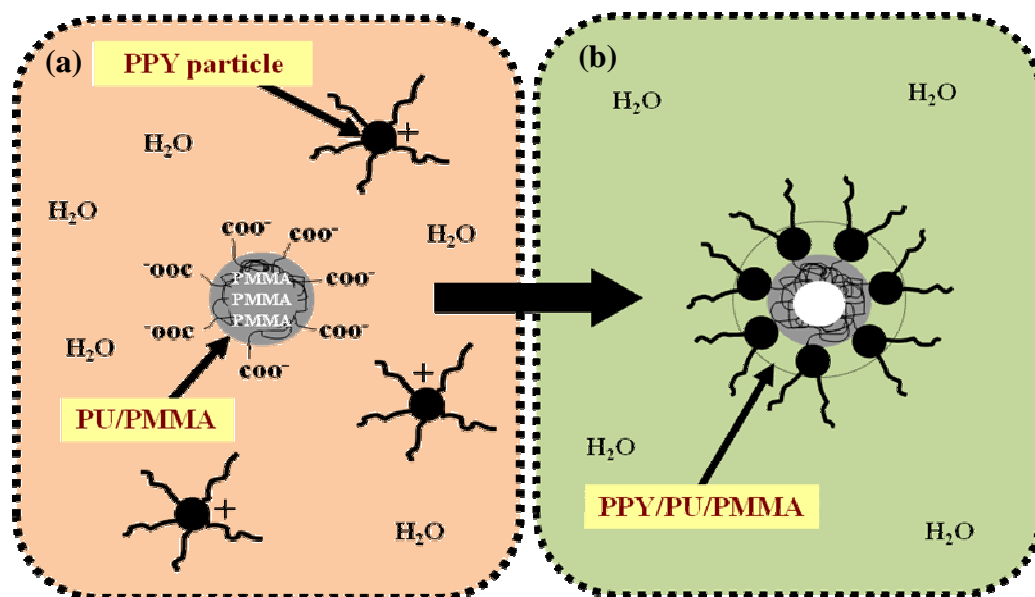
Figure 4.13 Diagrammatic representation of PPy/PU/PMMA particle**.**

Figure 4.14 shows the particle morphology of PPy/PU/PMMA and PU/PMMA. PU/PMMA and PPy/PU/PMMA particles looked very much alike. It was plausible that PPy was only a thin overlayer on PU/PMMA particle. However, PPy/PU/PMMA particle size was measured to be 2-10 nm larger than PU/PMMA particle indicating the possible overlayer of PPy.

Furthermore, no free PPy particle, which was dark and opaque in a rice grain shape, was obtained as shown in Figure 4.14(b). It can thus be assumed that PPy had been developed right on PU/PMMA particle.

Figure 4.14 TEM photographs of PU/PMMA (a), and PPy/PU/PMMA (b).

4.4 Corrosion study

The contact of iron 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 [24].
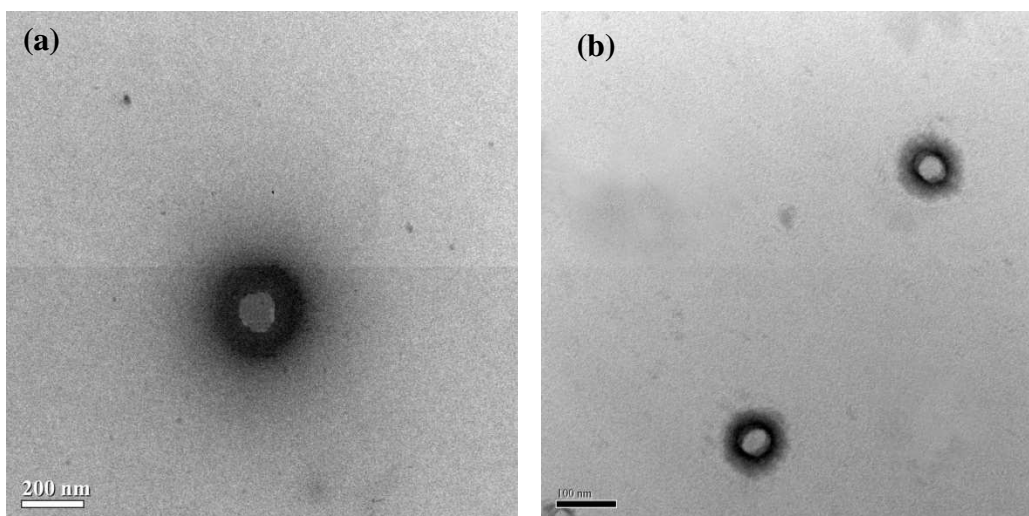
Finally, in this section described the corrosion performance of the panels coated with latexes specially indicated for iron and marine environment. The samples were tested in the NaCl solution (3.5 wt.%) 30 days. The degradations of coating surfaces were observed using digital camera and scanning electron microscope after immersed in the NACl solution. Results are compared between PU, PU/PMMA and PPy/PU/PMMA coating.

4.4.1 Morphology of the coating degradation

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

Figure 4.15(d) shows the iron 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 iron. However, inspection to the PPy/PU/PMMA coating reveals that the initial smooth surface is almost intact, Figure 4.15(e). Thus, the degree of corrosion detected in its surface was noticeably lower than that found for the PU/PMMA films.

Figure 4.16 shows the iron coated with PPy/PU/PMMA latex at all various concentration of pyrrole, which all samples of PPy/PU/PMMA coating to perform slight degradation of iron surface, when compared with PU/PMMA coating in Figure 4.15(d). In summary, polypyrrole can enhance corrosion protection property of PU/PMMA latex coating. Therefore, the PPy/PU/PMMA latex had a corrosion resistance.

Sample	Photographs of the tested samples (2 cm x 2 cm)	SEM micrographs of the surface
(a)		
(b)		
(c)		

Figure 4.15 Photographs and SEM micrographs of the surface of tested samples; initial sample (a), no coating (b), coated with PU latex (c), PU/PMMA latex (d) and PPy/PU/PMMA latex (e); (b), (c), (d) and (e) immersed in NaCl solution (3.5 wt.%).

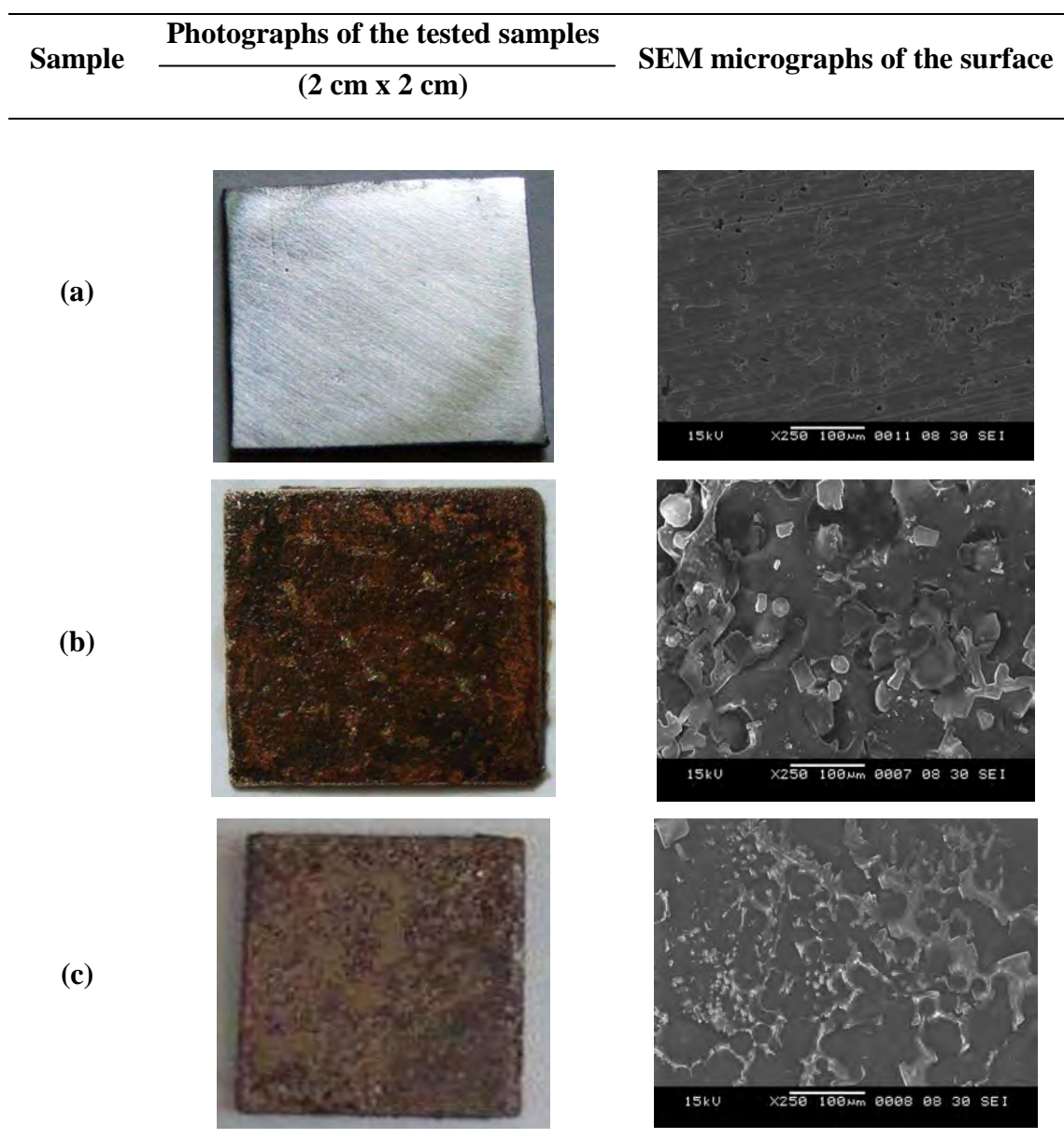| Sample	Photographs of the tested samples 2 cm x 2 cm	SEM micrographs of the surface
(d)		
(e)		

Figure 4.15 (cont.) Photographs and SEM micrographs of the surface of tested samples; initial sample (a), no coating (b), coated with PU latex (c), PU/PMMA latex (d) and PPy/PU/PMMA latex (e); (b), (c), (d) and (e) immersed in NaCl solution (3.5 wt.%).
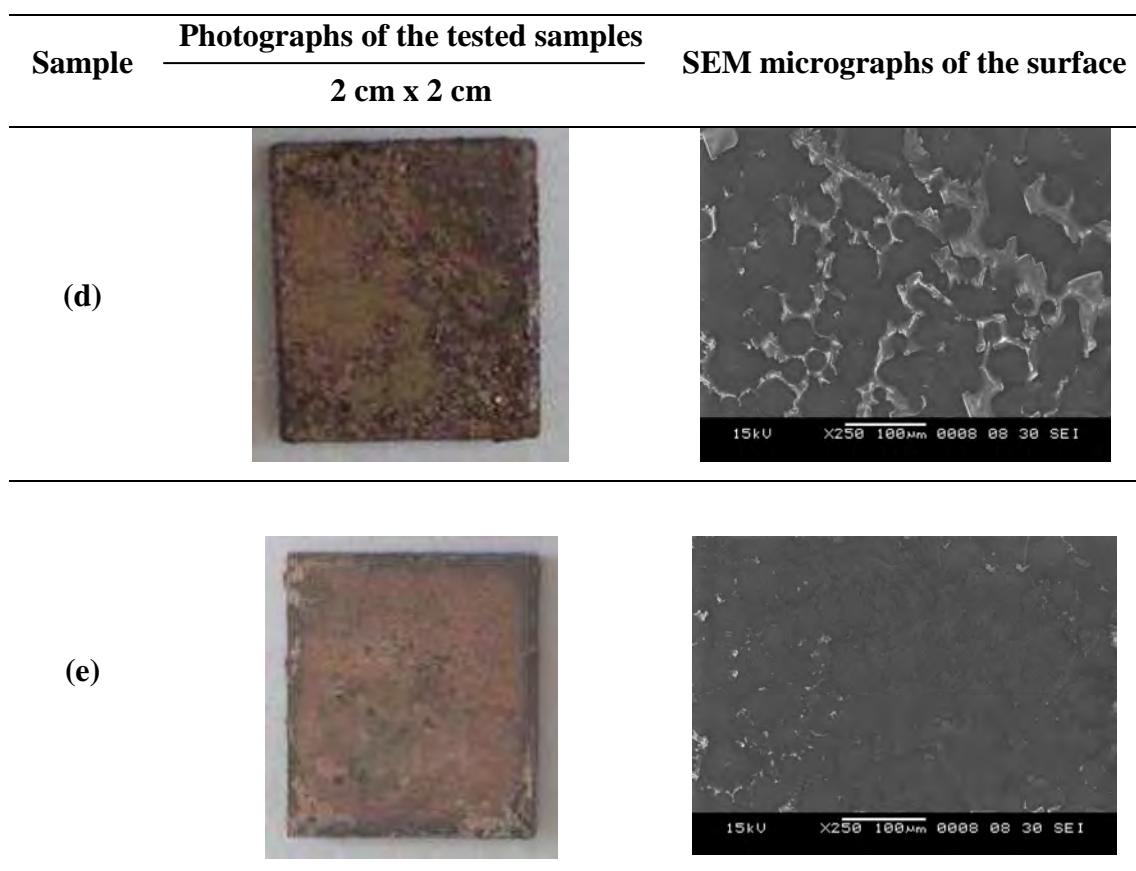
Sample	Photographs of the tested samples 2 cm x 2 cm	SEM micrographs of the surface
(a)		
(b)		
(c)		

Figure 4.16 Photographs and SEM micrographs of the surface of tested samples coated with PPy/PU/PMMA latex at 1.2 (a), 1.3 (b), 1.4 (c), and 1.5 (d) mol L^{-1}of pyrrole after immersed in NaCl solution (3.5 wt.%) for 30 days.

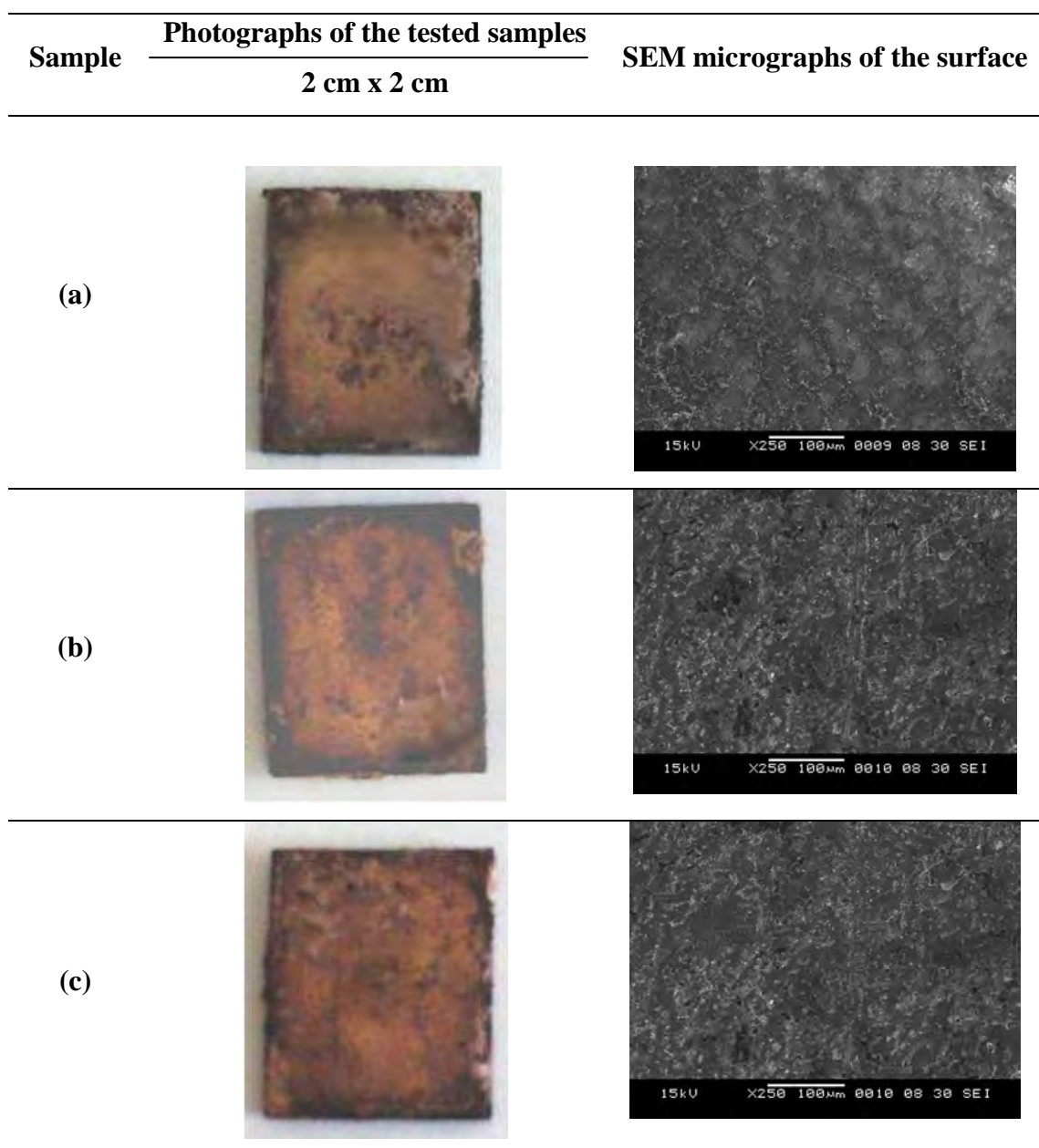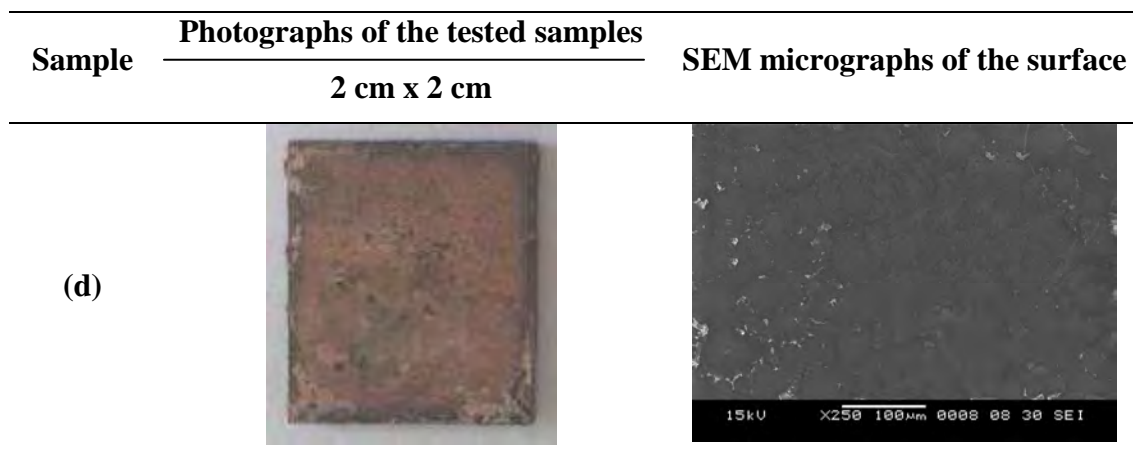| Sample	Photographs of the tested samples 2 cm x 2 cm	SEM micrographs of the surface
(d)		

Figure 4.16 Photographs and SEM micrographs of the surface of tested samples coated with PPy/PU/PMMA latex at 1.2 (a), 1.3 (b), 1.4 (c), and 1.5 (d) mol L^{-1} of pyrrole after immersed in NaCl solution (3.5 wt.%) for 30 days.

The role of polypyrrole in active corrosion protection is due to its ability to intercept electrons at the metal surface [19]. 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, polypyrrole 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 polypyrrole, and negative charge of metal surface invoked by electron transfer from polypyrrole could prevent anodic iron dissolution near corrosion potential due to the cathodic protection effect.

Anodic partial reaction:

$$2Fe \longrightarrow 2Fe^{2+} + 4e$$

Cathodic partial reaction:

$$O_2 + 2H_2O + 4e \longrightarrow 4OH^-$$

Corrosion product:

$$Fe^{2+} \xrightarrow{OH^-} Fe_3O_4, Fe_2O$$
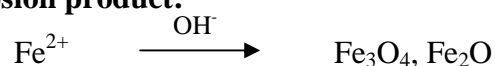
Scheme 4.3 Corrosion mechanism of iron when attacked by water and oxygen.

CHAPTER V

CONCLUSIONS AND SUGGESTIONS

A series of new polypyrrole (PPy)/polyurethane (PU)/ poly (methyl methacrylate) (PMMA) latex has been successfully synthesized. Firstly, polyester polyol was synthesized by condensation polymerization using excess amount of diol and gradually increase in heating the mixture to complete the reaction. In the preparation of aqueous PU dispersion, it was found that the most critical parameters on its particle size were due to the molar ratios of NCO/OH in prepolymer mixing process and TEA/DMPA in aqueous PU dispersion using NCO/OH = 2.5 could form a good film while at the other molar ratios no film forming could be obtained. PU/PMMA latex was then obtained by soap free emulsion polymerization of MMA in PU dispersion. When PU/PMMA weight ratio was greater than 1:1, the average particle size of PU/PMMA latex became larger than PU particle.

The oxidative polymerization of pyrrole in PU/PMMA latex was used for PPy/PU/PMMA synthesis. The addition of pyrrole in the reaction was limited at 1.5% of the solid content of PU/PMMA latex. The average particle size of PPy/PU/PMMMA slightly increased around 6-9 nm from original PU/PMMA particle. This PPy/PU/PMMMA latex had good film forming. Their corrosion protection performance on iron surface was studied. The results exhibited that PPy/PU/PMMA coating could retard corrosion compared with PU/PMMA, PU and no coating, in a sequence.

5.1 Further works

The more relevant method for the corrosive study need to be taken for reconfirmed the results of our work and the sample of PANI/PU/PMMA were required to comparative study with PPy/PU/PMMA in the corrosion test.

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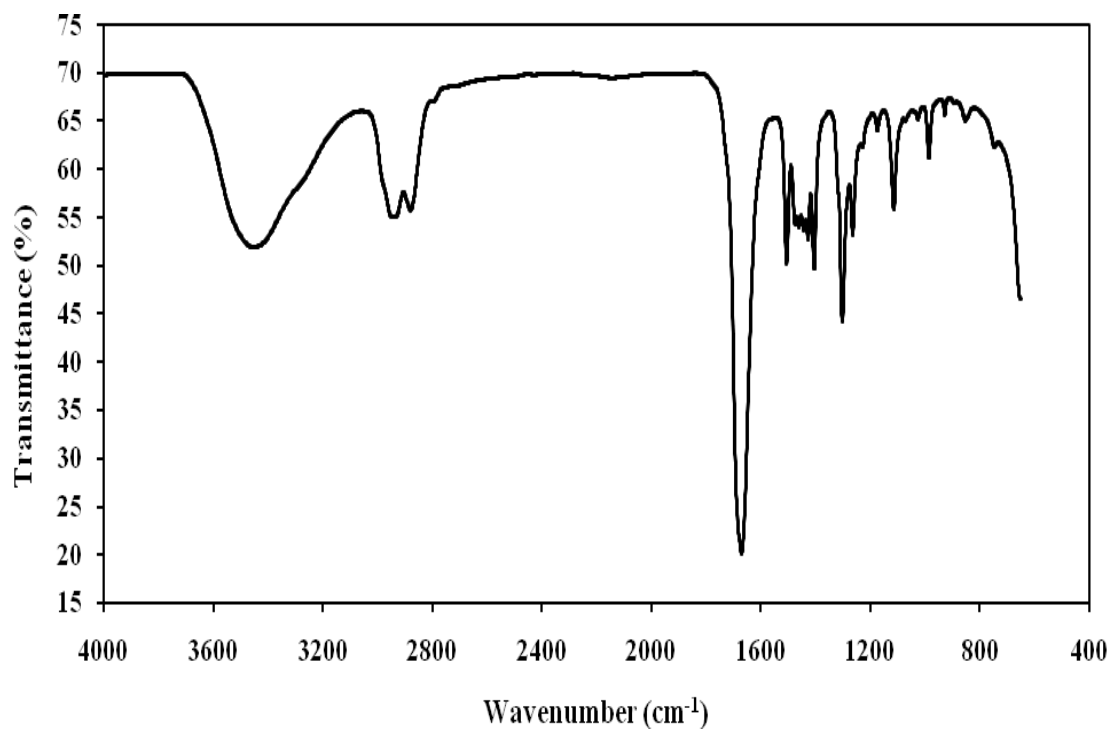
Appendices

Appendix A

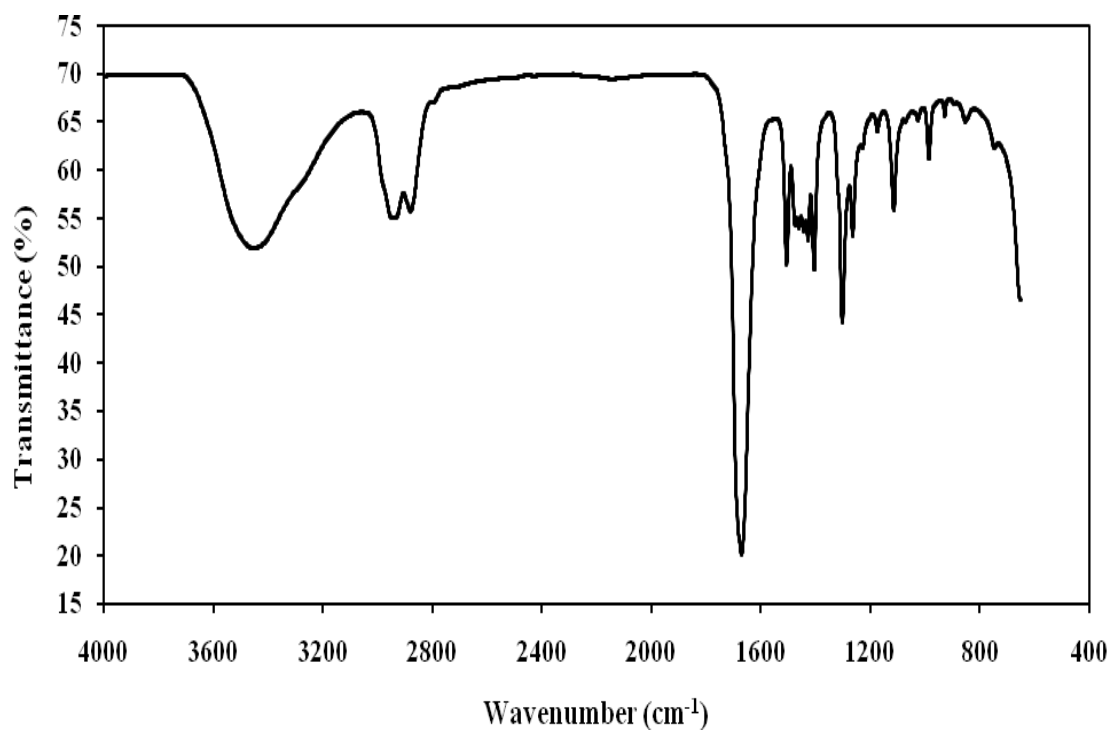**Figure A-1** FTIR spectrum of PPy/PU/PMMA latex; pyrrole 1.2 wt.%.

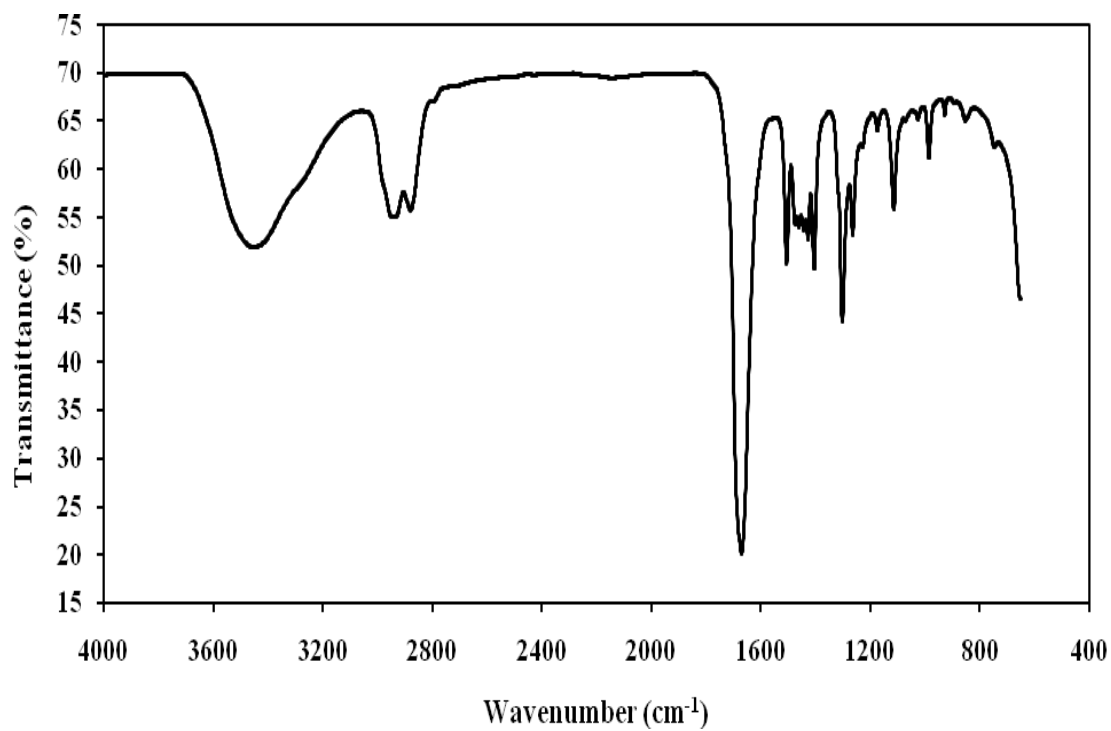**Figure A-2** FTIR spectrum of PPy/PU/PMMA latex; pyrrole 1.3 wt.%

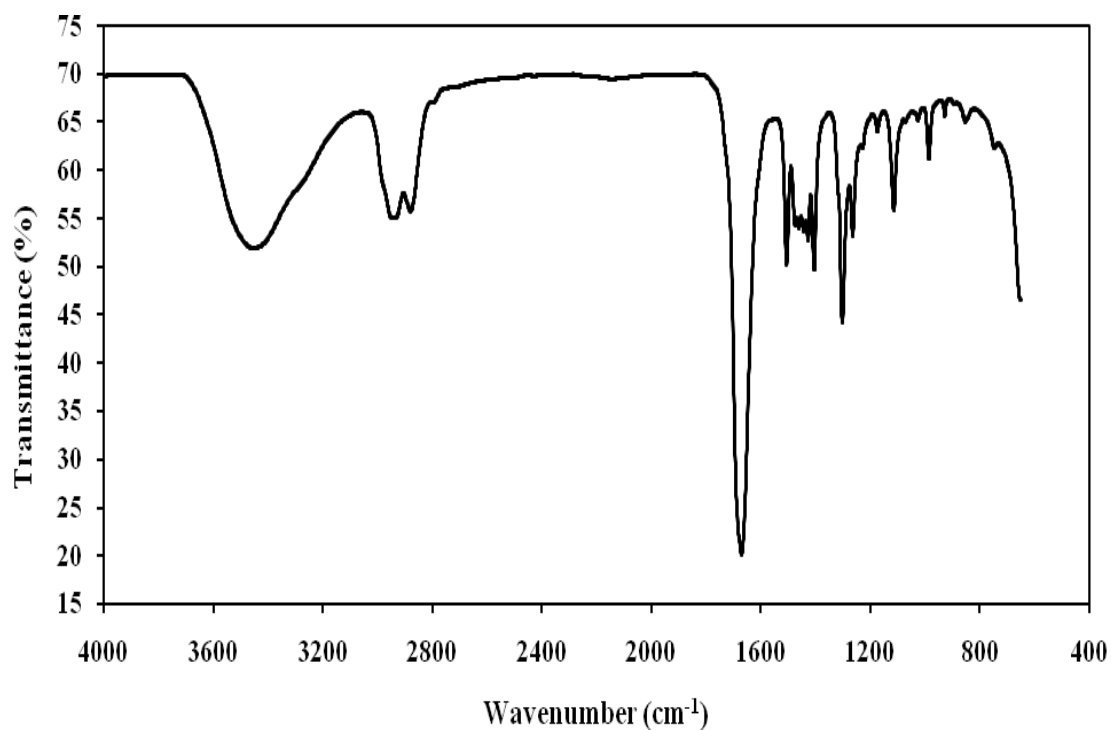**Figure A-3** FTIR spectrum of PPy/PU/PMMA latex; pyrrole 1.4 wt.%.

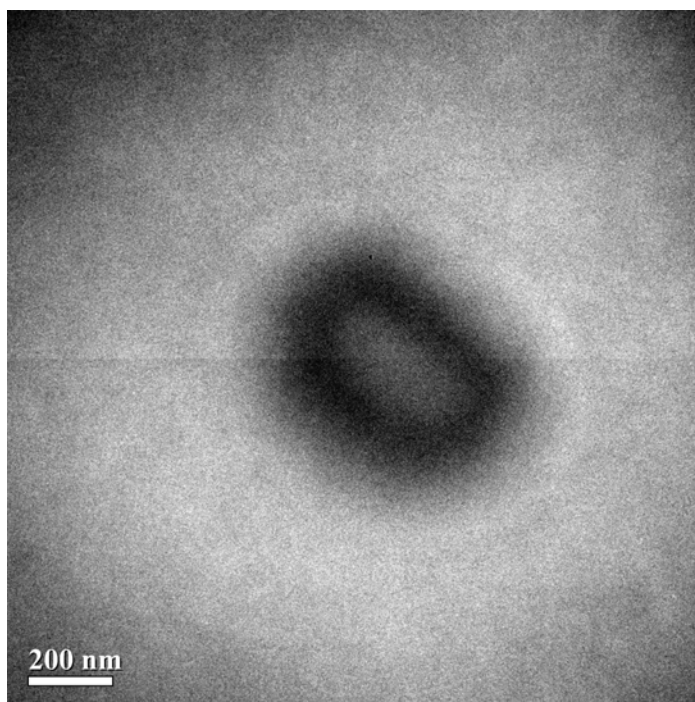**Figure A-4** FTIR spectrum of PPy/PU/PMMA latex; pyrrole 1.5 wt.%.
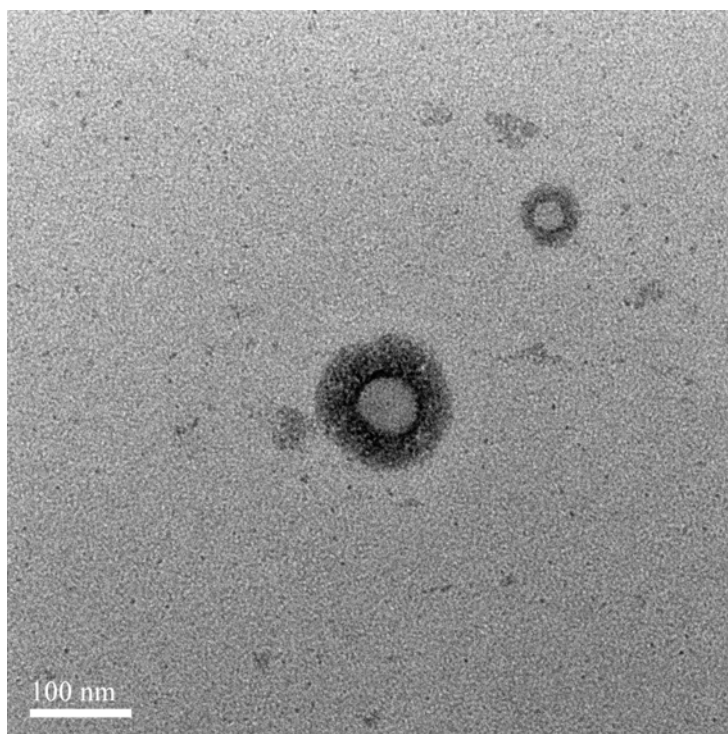
Appendix B

Figure B-1 TEM photograph of PU/PMMA particle.
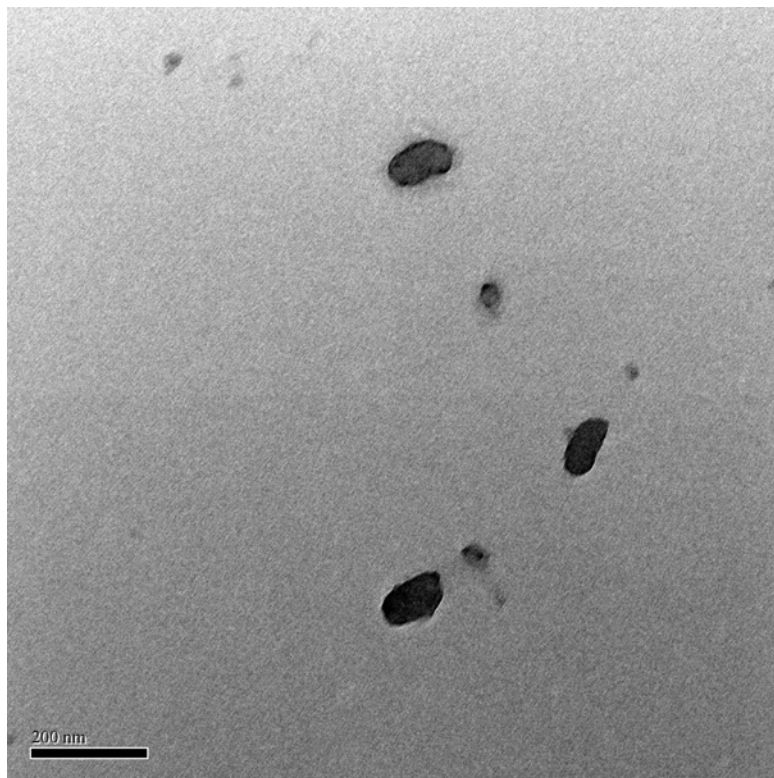

Figure B-2 TEM photograph of PU/PMMA particle.

Figure B-3 TEM photograph of PPy particle.

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