In situ Formation of Metal Nanoparticles on Natural Rubber Latex Film

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A Report Submitted in Partial Fulfillment of the Requirements
for the Degree of Bachelor of Engineering (Petrochemical Engineering),
Department of Chemical Engineering, Faculty of Engineering,
King Mongkut's Institute of Technology Ladkrabang
Academic Year 2018

การสังเคราะห์อนุภาคนาโนของโลหะบนผิวยางธรรมชาติ

ชนม์นิภา จันทร์หอม

ปริญญานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรวิศวกรรมศาสตรบัณฑิต

สาขาวิชาวิศวกรรมปิโตรเคมีภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์

สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง

ปีการศึกษา 2561

Title	*In situ* Formation of Metal Nanoparticles on Natural Rubber Latex Film
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Field of Study	Petrochemical Engineering
Advisor	Asst. Prof. Dr. Teeraporn Suteewong

Accepted by the Faculty of Engineering, King Mongkut's Institute of Technology Ladkrabang in Partial Fulfillment of the Requirements for the Degree of Bachelor of Engineering (Petrochemical Engineering).

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Abstract

In the present work, surface modification of sulphur prevulcanized natural rubber (SPNR) film was studied in order to decrease the surface friction coefficient and to improve the antibacterial activity of the rubber. Poly (methyl methacrylate) (PMMA) and silver nanoparticles (AgNPs) were formed both on the surface and underneath of the SPNR films using the two-step *in situ* emulsion polymerization. First, SPNR film was immersed in a solution of sodium dodecyl sulphate, *tert*-butyl hydroperoxide, methyl methacrylate (MMA) and silver nitrate. Then, the rubber film was immersed in an alkaline solution of ferrous ion and fructose for polymerization. The presence of PMMA/AgNPs on the rubber film and the surface morphology were investigated by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX) and atomic force microscopy (AFM) in non-contact mode. Concentration of silver nitrate and reaction time affect the average surface roughness (Ra) and surface morphology of rubber film.

Keywords: Natural rubber, Poly(methyl methacrylate), Silver nanoparticles

เรื่อง	การสังเคราะห์อนุภาคนาโนของโลหะบนผิวยางธรรมชาติ
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บทคัดย่อ

งานวิจัยนี้ทำการศึกษาการปรับสมบัติพื้นผิวของแผ่นฟิล์มยางธรรมชาติที่ผ่านการพรีวัลคาไนซ์ด้วยซัลเฟอร์ (SPNR) เพื่อลดค่าสัมประสิทธิ์แรงเสียดทานพื้นผิวและปรับปรุงสมบัติการต้านเชื้อแบคทีเรียของแผ่นยาง โดยการสังเคราะห์พอลิเมทิลเมทาคริเลต(PMMA)และอนุภาคนาโนเงิน(AgNPs) ขึ้นทั้งบนและใต้ผิวของแผ่นยางผ่านกระบวนการอิมัลชันพอลิเมอร์ไรซ์เซชันโดยขั้นตอนแรกนำแผ่นยางจุ่มลงในสารละลายที่ประกอบด้วยโซเดียมโดเดซิลซัลเฟต(SDS) เทซิเอรีบิวทิลไฮโดรเปอร์ออกไซด์ (*t*-BuHP) เมทิลเมทาคริเลต (MMA) และซิลเวอร์ไนเตรทที่เวลาต่างๆกัน จากนั้นนำแผ่นยางจุ่มในสารละลายของไอออนเหล็กและฟรุกโตสที่มีความเป็นด่าง ทำการศึกษาโครงสร้างสัณฐานวิทยาและลักษณะของ PMMA/AgNPs บนแผ่นยางด้วยกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราดที่มีเครื่องกระเจิงรังสีเอกซ์ (SEM/EDX) และกล้องจุลทรรศน์แบบแรงอะตอม (AFM) ในโหมด non-contact จากการทดลองพบว่าความเข้มข้นของซิลเวอร์ไนเตรทและเวลาที่ใช้ในการทำปฏิกิริยาส่งผลต่อความขรุขระของพื้นผิวเฉลี่ย (R_a) และโครงสร้างสัณฐานที่ผิว

คำสำคัญ: ยางธรรมชาติ พอลิเมทิลเมทาคริเลต อนุภาคนาโนเงิน

Acknowledgements

I would like to express my special thanks and gratitude to my advisor Asst. Prof. Dr. Teeraporn Suteewong, who gave me the opportunity and guidance to do the project. Without her continuous encouragement and support, this study would hardly have been completed. I also express my gratitude to my co-advisor, Prof. Dr. Pramuan Tangboriboonrat. Her guidance of emulsion polymerization has been essential during this work.

I would like to thank Waranya Ratirotjanakul who gave guidance and teach me about the emulsion polymerization experiment.

I would like to thank my friends, who helped me a lot in finishing this project.

Finally, I would like to acknowledge with gratitude, the support of my family. They all kept me going, and this project would not have been possible without them.

Chonnipa Junhom

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CHAPTER I
INTRODUCTION

1.1 Background

Natural rubber (NR) latex is natural polymer obtained from rubber tree, *Hevea brasiliensis* [1]. Today, more than 90 percent of the world's rubber comes from Southeast Asia. Thailand is one of the world's largest producers and exporters of NR. Owing to its excellent properties, for example, film forming ability, high strength, elasticity and abrasion resistance, NR has been used to produce automotive sectors, daily used and medical products as well as other relatively high valued products. However, NR latex has some disadvantages. The first is high surface friction of NR film. For example, gloves, one of NR film products, have surface friction and bunching, starch or talc is then applied on the surface [2]. Although, starch can alleviate the problem, it is considered as contamination in electronic and bio-medical applications [2]. Another is protein allergy. From the mid 1980's, there has been an increasing number of reports indicating that protein in NR latex causes allergy, particularly amongst health care workers and children with spina bifida and/or subjected to multiple surgical procedures [3]. Therefore, it is necessary to find other alternatives to modify the surface of NR to reduce surface friction and to minimize the contact of allergen protein.

Surface modification techniques of polymer are extensively studied, for example, plasma treatment and coating. Plasma treatment uses chemically reactive to generate functional groups, e.g. oxygen or ammonia, on the polymer surface [4]. Results of plasma treatment are given for plenty of advantages. Not only applicable to any kind of polymer surface, this technique does not change the bulk properties of polymer. It can also generate the uniform functional groups over the whole surface. Nevertheless, this technique was operated at high temperature, which could degrade polymer. The other technique is coating. Coating provides many advantages, such as applicable to various shape, easy to control coating thickness, minimal thermal degradation of the substrate and low processing cost. Instead of regular liquid coating, deposition of particles on the substrate surface can be used to modify the surface of polymer. Abu Bakar et al. [5] applied coating method by forming silver nanoparticles (AgNPs) on the NR surface,

using rubber protein as reducing agent and stabilizer for nucleation and growth of AgNPs. In addition, Necula et al. [6] synthesized the titanium medical alloy coating on the very rough surface using porous titanium oxide (TiO_2)-Ag composite. It was found that bacterial activities of composite were enhanced due to the presence of Ag particles. From the previous work, Sanguansap et al. [2] modified NR surface by two-step PMMA Emulsion polymerization. The presence of poly (methyl methacrylate) (PMMA) on the NR surface caused the increase in surface roughness (R_a) and hardness as well as decrease surface friction. Besides, Wongpreecha et al. [7] synthesized AgNPs stabilized with chitosan using silver nitrate ($AgNO_3$) as precursor by one-pot green technique and fabricated chitosan-coated AgNPs on the SPNR film. It was found that reaction temperature was a key in the formation of AgNPs and antibacterial efficiency was a function of $AgNO_3$ concentration.

In this work, we present the novel one-pot synthesis of AgNPs and PMMA on the rubber film using induced redox/Emulsion polymerization technique. It is a green process, in which AgNPs were formed in the absence of toxic reducing/stabilizing agent and organic solvent. AgNPs were formed during polymerization of MMA. Effect of dipping time and concentration of $AgNO_3$ precursor on the Ra, amount and size of AgNPs were investigated using scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX) and atomic force microscopy (AFM). Formation mechanism of PMMA and AgNPs on SPNR films will also be discussed.

1.2 Objective

To increase the surface roughness and to reduce the surface friction of SPNR by coating PMMA and AgNPs on the rubber film.

1.3 Scopes of Work

1.3.1 Synthesis of AgNPs/PMMA nanoparticles on the SPNR film using induced redox/Emulsion polymerization technique

1.3.2 Characterization of AgNPs/PMMA-modified SPNR films

1.3.3 Study of surface morphology and roughness using scanning electron microscopy (SEM) and atomic force microscopy (AFM)

1.3.4 Investigation of nanoparticles formation using scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX)

1.4 Expected Outputs

1.4.1 Friction of AgNPs/PMMA-modified SPNR surface is reduced.

1.4.2 Antibacterial activities of AgNPs/PMMA-modified SPNR surface film is enhanced.

CHAPTER II
LITERATURE REVIEW

2.1 Natural rubber (NR)

2.1.1 General information of NR

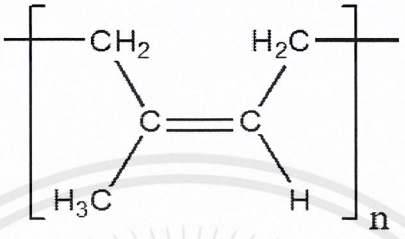


Figure 2.1 Poly-cis-1,4-isoprene.

Natural rubber is poly-cis-1,4-isoprene, as showed in Figure 2.1, obtained from Hevea Brasiliensis. Natural rubber latex is a colloidal system that contains rubber particles dispersed in water. Size of NR particles ranges from 0.05 to 3 μm. The colloidal system contains 45% weight of rubber molecules (cis-1,4 polyisoprene), 50% of water, and 5% of other constituents such as protein, lipids, and carbohydrates [1]. These other constituents are surrounded on surface of rubber particles and dispersed in the water. Fresh latex from tapping will still in colloidal form for up to 6 hours because of bacteria in the air and rubber tree. Degradation of rubber by bacteria generates various types of gases such as carbon dioxide, methane, which affect pH of latex and colloidal stability. In the fact that stability of NR depends on pH, small amount of ammonia or its combination with secondary stabilizers, for example, dithiocarbonates, combination of tertramethylthiuram disulfide and ZnO, lauric or boric acid, are added into the latex for stabilization reason.

Although Thailand is the world's largest producer and exporter of NR and its products, Thailand confronts of low-price rubber crisis. About 90% of exported natural rubber, are in the form of raw rubber. So, it is necessary to convert raw rubber to value-added products such as pharmaceutical and medical product.

2.1.2 Properties of NR

Typically, NR can be divided into two forms, i.e., dry rubber and latex.

2.1.2.1 Dry rubber [1]

Dry rubber is prepared by adding strong acid, such as sulfuric acid into fresh NR latex. Adding diluted sulfuric acid in latex, lead to the formation of 2 phases, i.e. coagulated rubber and aqueous solution. Water trapped in coagulated NR is eliminated by rolling with two rollers. Two main methods used to dry the rubber are fumigate rubber and crepe rubber [1].

2.1.2.2 NR latex

Before being used, NR latex is prevulcanized, generally with sulfur. Vulcanization is a chemical process to increase strength of NR. NR latex has some disadvantages such as its protein allergy. In the case of products with direct contact e.g. gloves, it is necessary to reduce the amount of rubber protein by extracting protein from NR, deproteinized rubber. Another disadvantage is high surface friction of NR latex film. Applying starch or talc is a common technique, however, it causes contamination in electronic and bio-medical applications [2]. Therefore, it is necessary to find other alternatives to modify surface of NR to reduce surface friction and to minimize the contact of protein allergy.

2.2 Surface Modification of Natural Rubber Latex (NRL) Film

2.2.1 Plasma treatment

Plasma treatment is one of interesting modification process which modify the surface of substrate by using oxygen, ammonia as well as air to generate reactive functional groups [4]. Yorsaeng and coworker modified NR latex film was surface-modified with a dielectric barrier discharge (DBD) plasma treatment under an air environment [8]. They reported that hydrophilicity and roughness of

NR surface was increased by increasing plasma treatment time. Nevertheless, the mechanical properties of NR were decreased.

2.2.2 Grafting

Grafting is a technique to generate polymer on the surface [9]. Similar to other polymers, it can modify the molecules of NR to alters its properties. Several monomers were used to graft on NR molecules including polystyrene (ST), methyl methacrylate (MMA), styrene and methyl methacrylate (MMA-ST comonomer), dimethyl amine ethyl methacrylate (DMAEMA), dimethyl methacrylate, methyl methane phosphate (DMMMP) and maleic anhydride (MA) [9]. Thongnuanchan et al. [10] synthesized the modified NR with grafted poly (acetoacetoxyethyl methacrylate-co-methyl methacrylate). The results show that hydrophilicity and adhesion properties of NR was increased after grafting modification.

2.2.3 Fabrication of nanoparticles (NPs)

Nanotechnology is widely determined as a technology to produce new materials and products with unique properties. Nanoparticles are particles which at least one dimension should be in range of 1 to 100 nm [11]. Fabrication of NPs can be done by applying the surface with the prepared solution. Then the particles are formed on the surface of the substrate. Recently, metallic nanoparticles were attached to improve properties of polymer substrate such as antibacterial activities and cytoxicity [7]. In this work, silver nanoparticles (AgNPs) are of interest.

AgNPs are classified as metal-based nanoparticles. They present interested properties such as unique optical, electrical, thermal properties and antibacterial activities. Therefore, they have been used in biomedical and food packaging applications. Normally, AgNPs are synthesized by the reduction of silver precursor (e.g. $AgNO_3$) using reducing agents, such as, enzymes/proteins, amino acids, polysaccharides and vitamins [12]. Therefore, reducing agent is one of key parameter that can control size of nanoparticles. Guidelli et al. [13] and Abu bakar et al. [5] successfully synthesized the AgNPs on the NR surface by mixing rubber latex with silver nitrate before drying overnight at 50°C. They reported that

present of protein in NR was an important key of growth and stabilization of AgNPs on the NR surface.

2.3 Emulsion polymerization

2.3.1 Overview of emulsion polymerization

Emulsion polymerization is a simple technique to form polymer latexes. Emulsion polymerization occurs in the colloidal system which consists of monomer, dispersing medium, emulsifying agent, water-soluble initiator and transfer agent [14]. Particle nucleation can be divided into two types: homogeneous nucleation and micellar nucleation.

In the case of homogeneous nucleation, nucleation can occur in the absence of surfactants. The initiator is ionized in water by heat or chemical reaction to generate free radicals. Covalent bonds are formed with dissolved monomers and free radicals. Then, particles occur. After that, the monomer phase gradually moves through the water to dissolve in the starting particle and form into a polymer. Due to the low polymerization rate mechanism, the homogeneous nucleation is not commonly used in industrial scale.

In addition, emulsion system of micelle nucleation occurs when concentration of a surfactant in aqueous solution is above critical micelle concentration, CMC and then surfactant molecules aggregate into micelles. After that, monomer and initiator are added into the emulsion system. Monomer in the system is divided to three group, monomer droplets, monomer which dissolves in aqueous phase and monomer which swells in the micelles. In aqueous, initiator and small fraction of monomer are present. Initiator initiates radicals and reacts with the monomer in aqueous phase to form oligoradical. Then oligoradical enters to monomer swollen micelle. The droplets act as monomer stores and monomers diffuse from the monomer droplets to growth particles. The Figure 2.2 shows the schematic representation of the components of the reaction medium at various stages of emulsion polymerization [14].

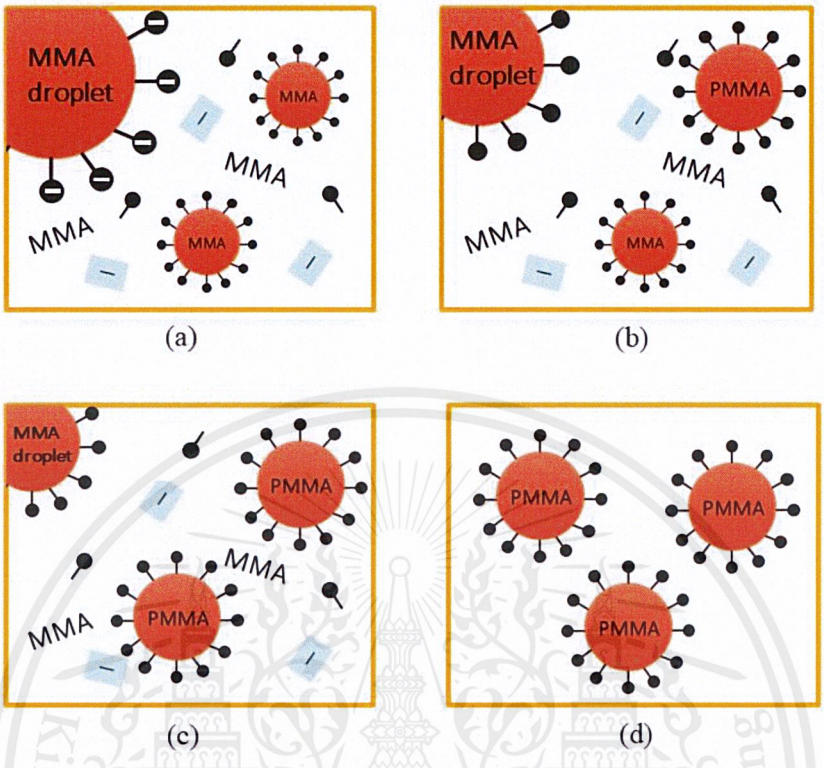


Figure 2.2 Representation of stages of an ideal emulsion polymerization.

2.3.2 Applications of emulsion polymerization

Emulsion polymerization is a widely used technique to synthesize large quantities of latex products as well as to fine tune applications such as surface coatings and bulk polymer [4]. Normally, water is used as the dispersion medium because it is environmentally friendly, i.e. compared with using other volatile organic solvents, and allows excellent heat dissipation during polymerization process [14]. Sanguansap et al. [2] was modified NR rubber film by polymerization of methyl methacrylate (MMA) in water-based system to reduce surface friction of NR film. The results demonstrated that the surface roughness of NR film was increased by increasing polymerization time. So, surface friction of NR film was reduced. Besides, emulsion polymerization was applied to modify surface of epoxidized natural rubber (ENR) latex film by Amornchaiyapitak et al. [15]. They reported that the PMMA mainly existed near the rubber surface in the nodular morphology. These nodules increased the surface roughness and reduced surface friction of the ENR surface

2.4 Literature review

Currently, natural polymer as rubber can be modified to obtain required properties by using chlorination, epoxidation, hydrogenation and grafting method. Grafting process is generated by emulsion polymerization. Styrene, methyl methacrylate, comonomer of styrene and methyl methacrylate and maleic anhydride are monomer that used in emulsion polymerization process [14].

Emulsion polymerization in the water-based system was applied to surface modification of natural rubber. This process consisted of two steps. First, monomer was swollen into the natural rubber in aqueous solution of monomer, redox initiator and surfactant. Then, polymerization was activated on the swollen rubber by using an aqueous solution of ferrous ion [2]. Advantages of emulsion polymerization in the water-based system are easily to control the swelling kinetics and to reduce the generation of hazardous substances to environment. In the research, the result showed that the presence of PMMA on the surface of rubber lead to increase surface roughness and hardness. Thus, the surface friction of rubber was reduced. Protein is present on the surface of rubber. The protein is cause of latex allergy. Reaction of metallic nanoparticles and protein on the surface of rubber can blind the latex allergy cause. Coating silver nanoparticles, metallic nanoparticles, on the surface of rubber can cover the functional group of protein that is the allergy cause [11] and improve the antimicrobial activities of the rubber [12].

CHAPTER III
RESEARCH METHODOLOGY

This work aims to modify the surface of SPNR film by lowering surface friction and installing additional antibacterial properties. SPNR strip was first dipped into an aqueous emulsion solution containing anionic surfactant (SDS), *tert*-butyl hydroperoxide (*t*-BuHP), Methyl methacrylate (MMA) monomer and silver nitrate ($AgNO_3$). To activate polymerization, the MMA-swollen rubber was then dipped into an alkaline aqueous solution of fructose and ferrous ion. In this work, effect of dipping time and concentration of $AgNO_3$ on the surface roughness amount and amount as well as particle size of AgNPs formed on the rubber film were studied.

3.1 Chemicals

1) Aluminum oxide (basic), Brockmann I grade, SIGMA-ALDRICH
2) Aluminum oxide (neutral), Brockmann I grade, SIGMA-ALDRICH
3) Ammonium iron (II) sulphate hexahydrate, AR grade, KEMAUS
4) *tert*-Butyl hydroperoxide (70%) (*t*-BuHP), SIGMA-ALDRICH
5) D- (-)-Fructose, ≥99%, SIGMA-ALDRICH
6) Deionized water
7) Methanol, commercial grade
8) Methyl methacrylate (MMA), 99%, ACROS ORGANICS
9) Silver nitrate ($AgNO_3$), ≥99.0%, SIGMA-ALDRICH
10) Sodium dodecyl sulphate (SDS), ≥98.5%, SIGMA-ALDRICH
11) Sulphur Prevulcanized Natural Rubber (SPNR) latex, Lucky four Co. Ltd.

3.2 Apparatus

1) Aluminum foil
2) Aluminum sieves (250 mesh)
3) Amber glass bottle
4) Analytical balance
5) Atomic Force Microscope
6) Beaker

7) Centrifugal tubes
8) Cotton
9) Filter paper
10) Glass column
11) Jacket reactor (300 ml)
12) Magnetic bar
13) Magnetic stirrer
14) Para film
15) Plastic bag
16) Plastic film
17) pH paper
18) Oven
19) Rubber gloves
20) Sonicating bath
21) Spatula
22) Stainless steel scissors
23) Temperature-controlled magnetic stirrer

3.3 Experimental

3.3.1 Preparation of SPNR sheet

1) Pour 300 ml SPNR latex through 250-mesh sieve to filter SPNR latex. Then scoop bubbles out from the latex.
2) Gently, pour filtered SPNR latex to a glass plate.
3) Dry SPNR latex at 60°C overnight.

3.3.2 Cleaning SPNR sheet

1) Cut SPNR sheet into 1.5x4 cm^2.
2) Put SPNR strip in centrifugal tubes and pour methanol into the tubes.
3) Sonicate the rubber strip in the sonicating bath for 15 minutes.
4) Drain methanol and repeat step 1-2 and change from methanol to deionized water.
5) Store cleaned SPNR strip in box containing silica gel.

3.3.3 Purification of MMA monomer

1) Insert cotton into the tip of glass column.
2) Add neutral aluminum oxide and basic aluminum oxide into the column, respectively.
3) Wrap the column with aluminum foil and pack the ice pads to cool the system.
4) Pour non-purified MMA monomer into the prepared column. Collect the purified MMA monomer and store in an amber glass bottle at 4°C.

3.3.4 *In situ* formation of AgNPs and PMMA on SPNR sheet

1) Prepare an aqueous emulsion solution containing purified MMA monomer (62.5 g), 2% aqueous solution of SDS (191.2 g), 70% *t*-BuHP (6.7 g) and 1% aqueous solution of $AgNO_3$ (20 ml) and stir at 400 rpm for 1 h.
2) Dip cleaned rubber strip in the emulsion solution in step 1 and stir at 400 rpm for 20 minutes.
3) Dip MMA-swollen rubber strip with deionized water and stir at 400 rpm for 10 minutes to clean the residue MMA emulsion and excess $AgNO_3$ on the rubber strip.
4) Prepare 150 ml mixture of an aqueous solution of 2% fructose and 10 ppm ferrous ion at pH 10 in jacket reactor and heat to 60°C.
5) Dip cleaned MMA-swollen rubber in the alkaline aqueous solution (from step 4) at 60°C for 6 h.
6) Dip surface-modified rubber sheet with deionized water and stir at 400 rpm for 10 minutes.
7) Store samples (AgNPs/PMMA-modified SPNR films) in the box containing silica gel.

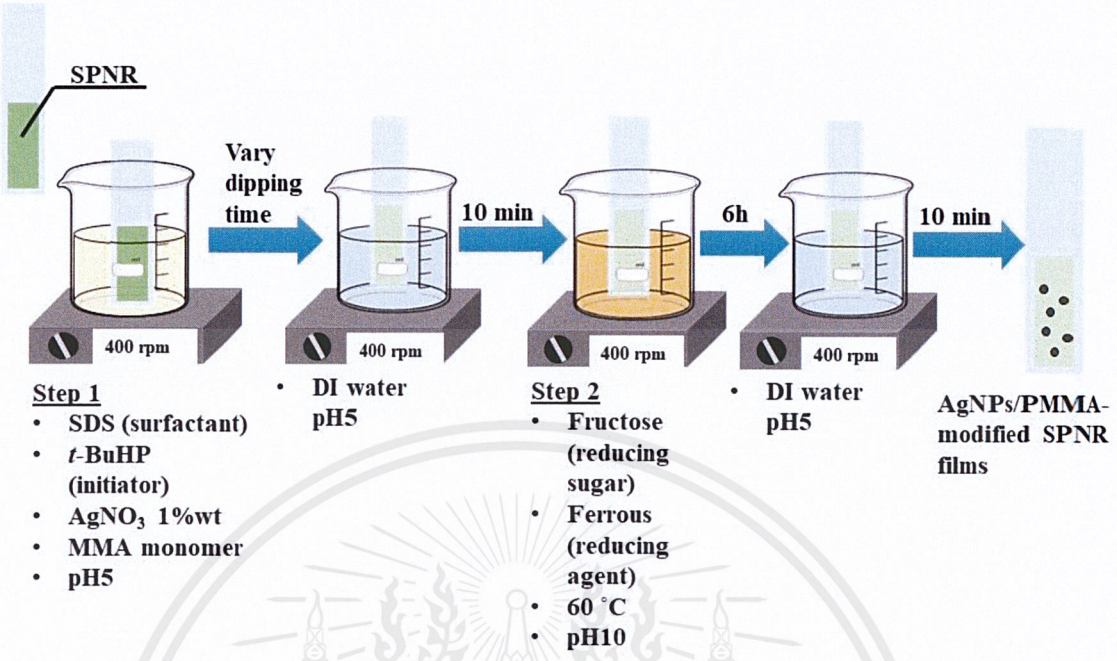


Figure 3.1 *In situ* formation of PMMA/AgNPs on SPNR sheet

3.3.5 Characterization

1) Average surface roughness using atomic force microscopy (AFM), non-contact mode, SPA400
2) The surface morphologies of samples, coated with a thin layer of platinum and palladium, and elemental analysis using scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX), Hitachi SU8010
3) The amount of AgNPs deposited per unit area on SPNR film surface, or surface coverage (C_s) using equation: $C_s\ (\%) = \frac{N}{N_{max}} \times 100$

   Where N is the number of particles per unit area and N_{max} is the maximum number of particles on the area assuming a dense packing

CHAPTER IV
RESULTS AND DISCUSSION

This work aims to fabricate PMMA and AgNPs on SPNR film using induced redox/Emulsion polymerization technique. Effects of dipping time and concentration of silver nitrate ($AgNO_3$) on the surface roughness (R_a) and content of AgNPs were investigated by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX) and atomic force microscopy (AFM). The amount of AgNPs per unit area on SPNR film surface or surface coverage (C_S) was determined. To elucidate the formation mechanism of AgNPs/PMMA on rubber sheet, effect of MMA monomer and $AgNO_3$ on MMA emulsion were also investigated.

4.1 Direct formation of AgNPs on SPNR films (1%wt $AgNO_3$)

With the aim to lower the skin allergy caused by non-rubber protein on NR-based product, we then prepared AgNPs directly on SPNR films using non-rubber proteins as reducing and stabilizing agent. Figure 4.1 and 4.2 show AFM and SEM micrographs of SPNR as well as SEM micrographs of AgNPs-coated on SPNR film, respectively.

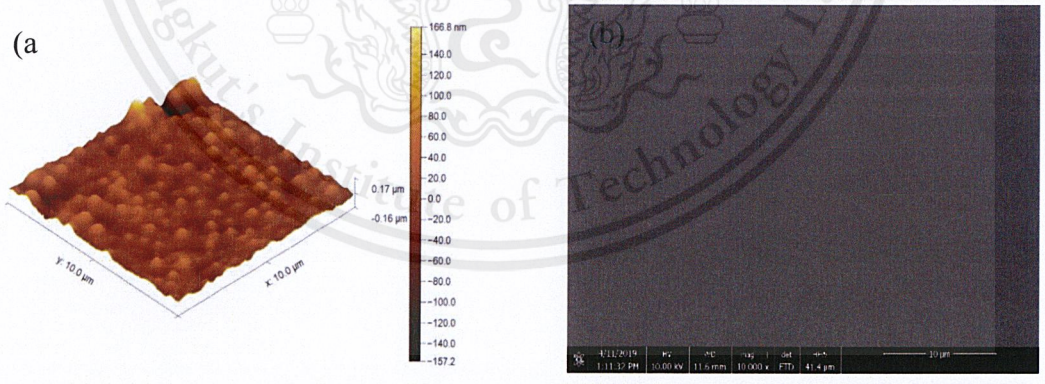


Figure 4.1 (a) AFM and (b) SEM micrographs of SPNR film, respectively.

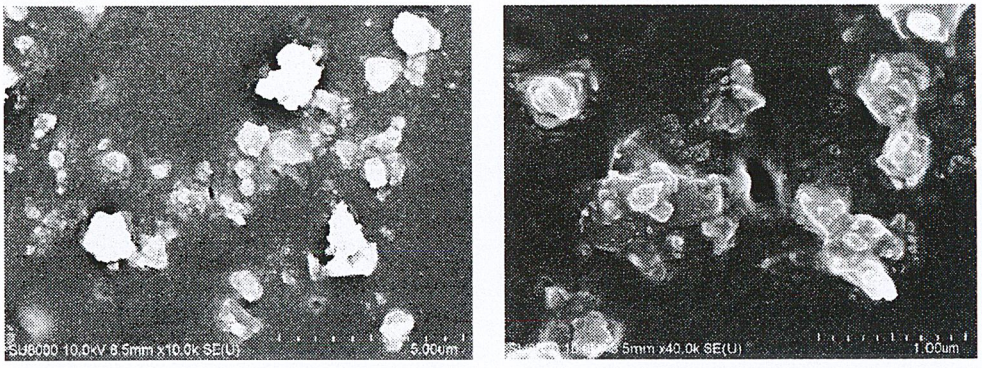


Figure 4.2 SEM micrographs of AgNPs-coated on SPNR film.

SEM and AFM micrographs of SPNR show relatively smooth surface of rubber film with R_a of 20.5 ± 3.69 nm. After dipping SPNR film in $AgNO_3$ solution at room temperature for 20 minutes, it was clearly observed that the morphology of rubber film surface was changed. SEM micrographs show aggregate of AgNPs was formed on the SPNR film. A small amount of AgNPs was sparingly formed possibly due to the presence of dispersed non-rubber protein on the surface in the reduction of Ag ion [5]. Another reason is the submersion of NPs in the low T_g polymeric substrate [16]. Alternative method, increasing rigidity and roughness of rubber film prior to formation of AgNPs was then introduced.

4.2 Emulsion polymerization of PMMA on SPNR film

Figure 4.3(a-b) shows the AFM and SEM micrographs of PMMA-modified SPNR films using Emulsion polymerization technique. SEM of PMMA-modified film (Figure 4.3(b)) shows that its surface was rougher than that of SPNR film, and its R_a is 175.6 nm. It is clearly observed that the formation of PMMA can increase the surface roughness of SPNR film. The increase of R_a results in a lower adhesive friction against substrate so the surface friction of the PMMA-modified film is reduced [2].

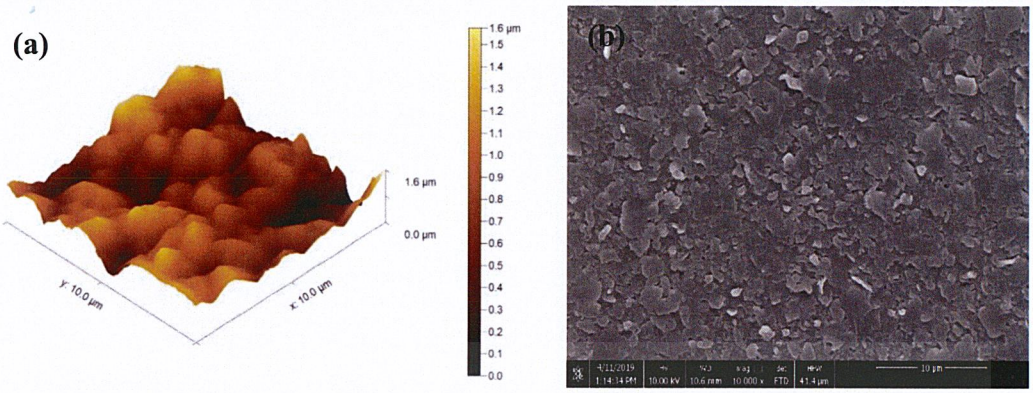


Figure 4.3 (a) AFM and (b) SEM micrographs of PMMA-modified SPNR, respectively.

4.3 Effect of dipping time on the formation of AgNPs

To increase the amount of AgNPs on PMMA-modified SPNR films, $AgNO_3$ (1%wt) was mixed in the first step of preparation of PMMA-modified film, swelling of MMA emulsion. The dipping time, i.e., the time that SPNR film immersed in the emulsion, was varied from 20 to 60 minutes. Then, the swollen rubber films were immersed in the alkaline solution of ferrous ion and fructose at 60°C for 6 h to initiate the polymerization.

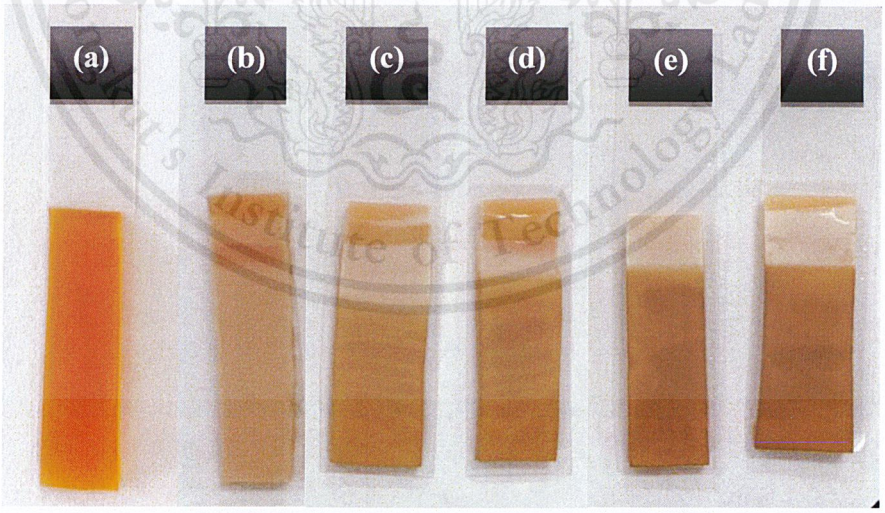


Figure 4.4 Photographs of (a) SPNR, (b) PMMA-modified and AgNPs/PMMA-modified SPNR films prepared at various dipping times of (c) 20, (d) 30, (e) 40 and (f) 60 mins.

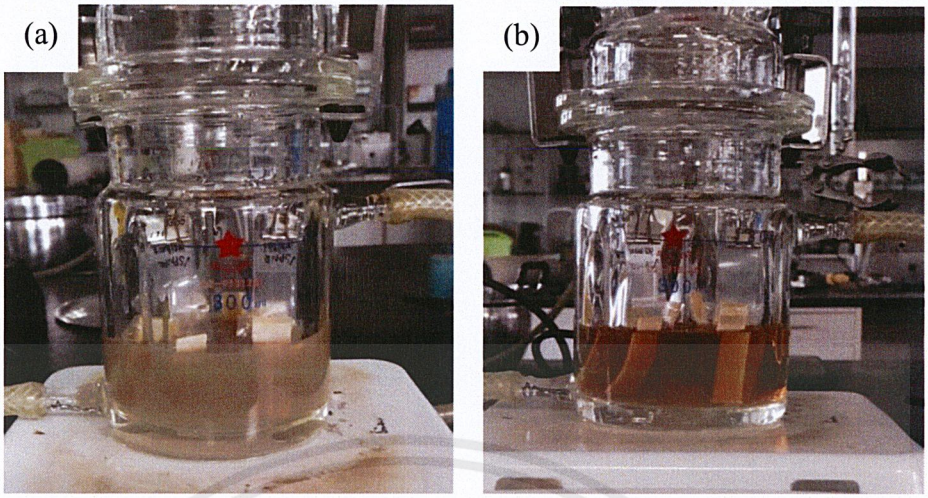


Figure 4.5 Images of polymerization reaction at (a) 4 and (b) 6 h, respectively.

Figure 4.4(a-f) shows photographs of SPNR, PMMA-modified and AgNPs/PMMA-modified SPNR films, respectively. The change in color of rubber films from orange of SPNR to turbid yellow of PMMA-modified and light brown of AgNPs/PMMA-modified SPNR films implies the change in surface characteristics. Moreover, brown color of AgNPs/PMMA-modified SPNR films implies the presence of AgNPs on the rubber surface.

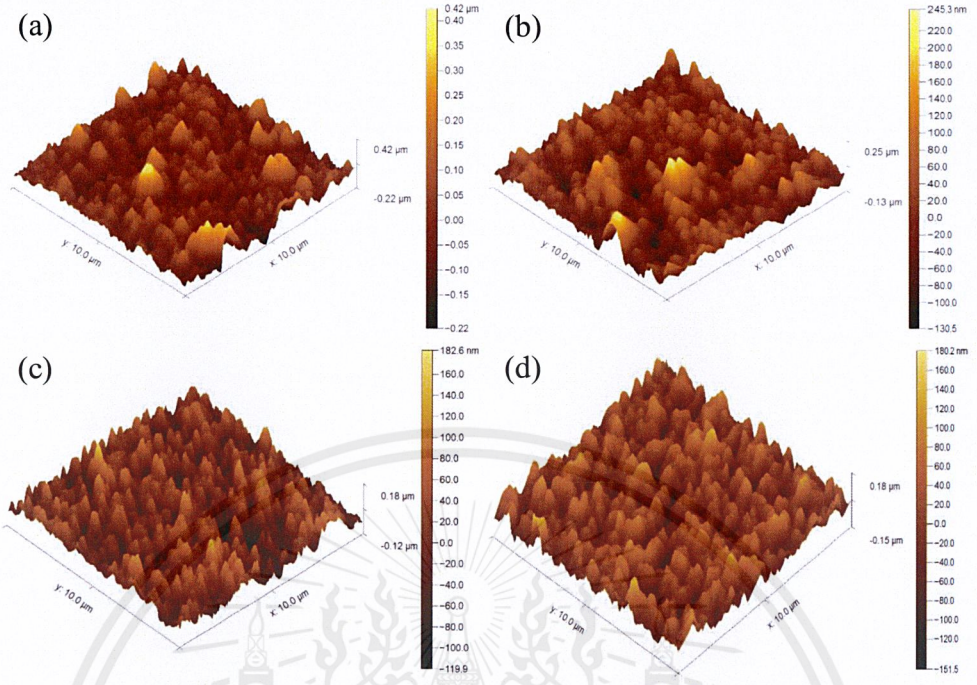


Figure 4.6 AFM images of AgNPs/PMMA-modified SPNR films prepared at various dipping times of (a) 20, (b) 30, (c) 40 and (d) 60 mins.

Figure 4.6(a-d) present AFM images of AgNPs/PMMA-modified SPNR films prepared at various dipping times. AFM images of AgNPs/PMMA-modified SPNR films at dipping time 20 and 30 minutes, Figure 4.4(a-b), contains high nodes, while AFM images of samples prepared at higher dipping times do not.

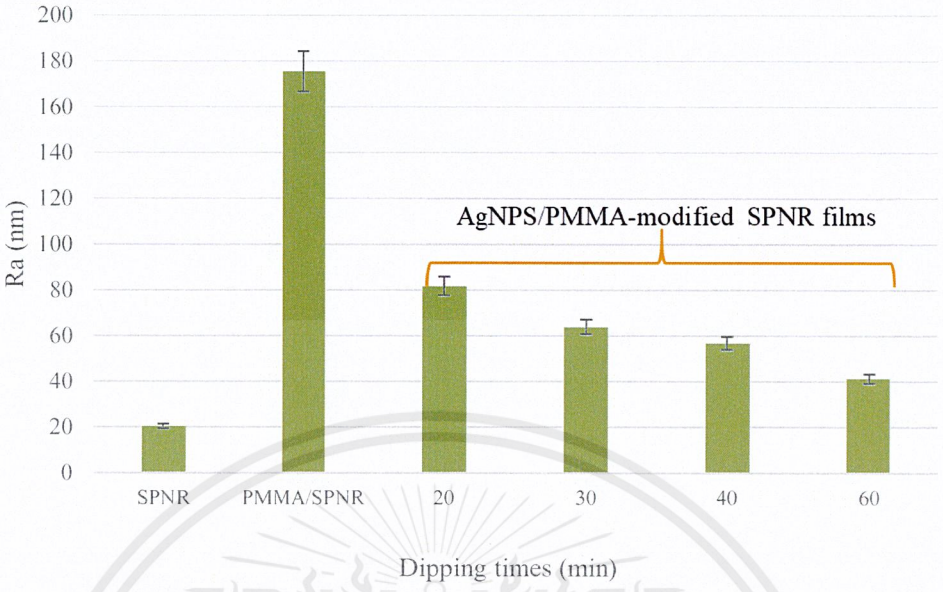


Figure 4.7 Graph plotted between R_a (nm) and dipping times (min).

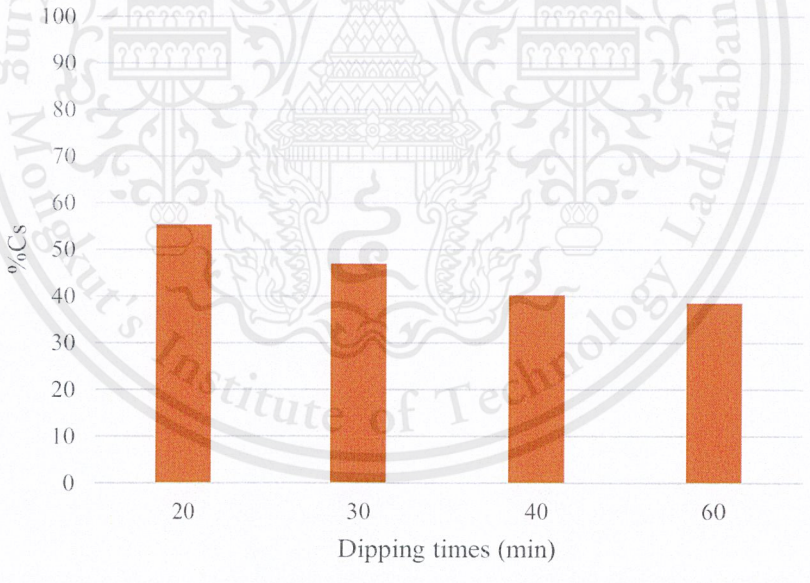


Figure 4.8 Graph plotted between $\%C_s$ and dipping times (min).

Figure 4.7 shows R_a of AgNPs/PMMA-modified SPNR films as a function of dipping time. R_a of untreated rubber film is 20.5 ± 3.69 nm while R_a of treated rubber films prepared at various dipping times, (20, 30, 40 and 60 minutes), are 81.78 ± 10.93, 64.00 ± 7.11, 56.92 ± 11.84 and 41.38 ± 4.76 nm, respectively. All AgNPs/PMMA-

modified SPNR films have higher R_a than that of untreated SPNR films, however, are still much lower than PMMA-modified films.

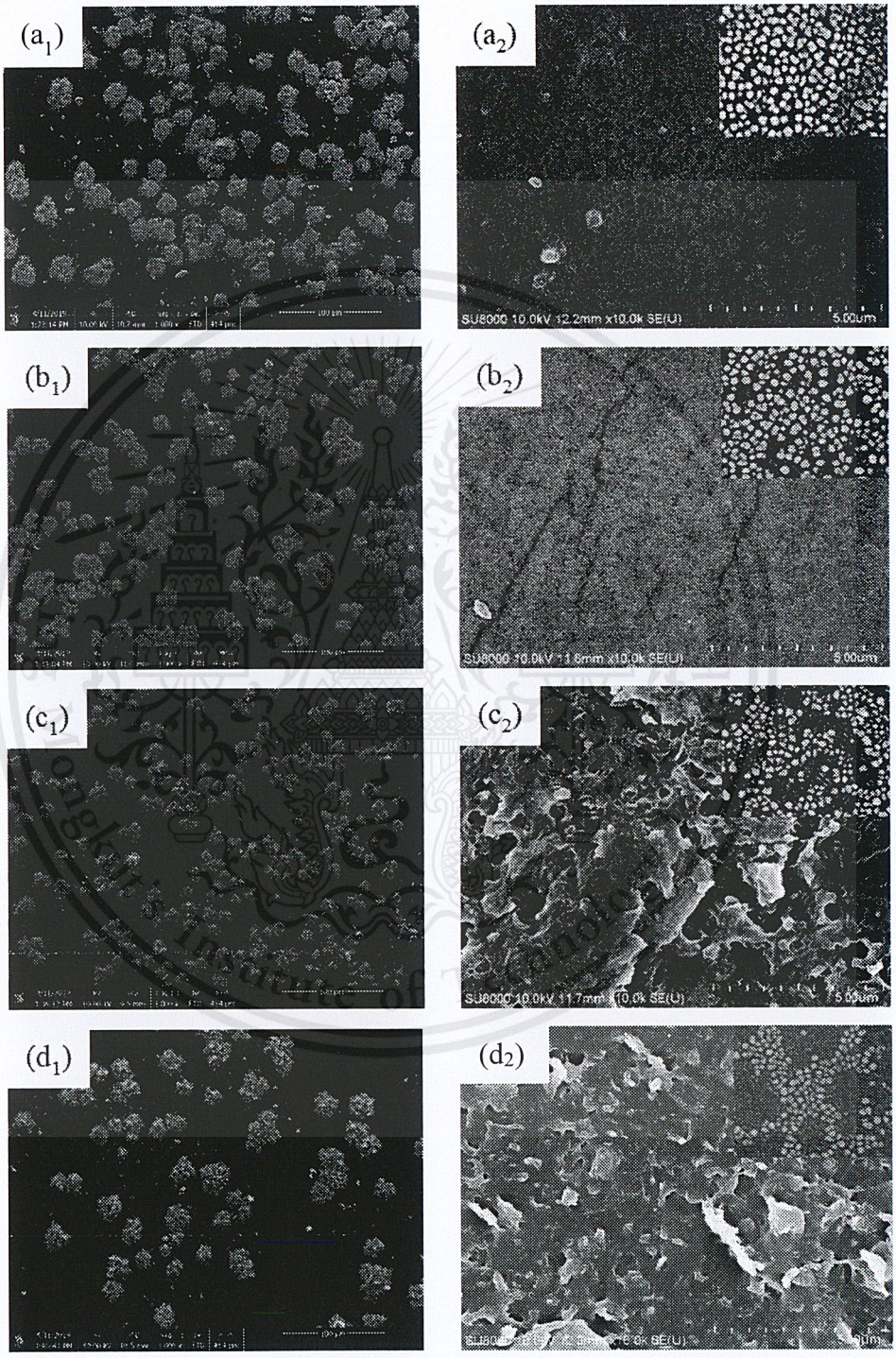


Figure 4.9 SEM images of AgNPs/PMMA-modified SPNR films prepared at various dipping time of (a) 20, (b) 30, (c) 40 and (d) 60 mins.

SEM of AgNPs/PMMA-modified SPNR films are shown in Figure 4.9(a-d). Difference from PMMA-modified SPNR film surface that shows relatively uniform roughness, all surfaces of AgNPs/PMMA-modified SPNR films have clusters of PMMA and AgNPs mostly formed on the rubber surface. The aggregation of PMMA leads to high peak-to-valley roughness, the distance between the highest peak and the lowest valley on the measured surface. Therefore, R_a of AgNPs/PMMA-modified SPNR are lower than that of PMMA-modified SPNR. In addition, SEM micrographs, Figure 4.9 (a_2, b_2, c_2 and d_2), show the morphology of AgNPs. Particles size of AgNPs on the modified SPNR prepared at 20, 30, 40 and 60 minutes of dipping times, are 25.25 ± 5.33, 25.92 ± 3.35, 25.79 ± 5.03 and 25.14 ± 3.24 nm. It was observed that particles size is dipping time independent. Many literatures report that AgNPs can be synthesized using bioorganic compounds such as sugar, protein and polysaccharides [12]. For example, AgNPs were successfully synthesized by L-Valine-based oligopeptide [12]. Its sulphur content controls the shape and size of AgNPs [12]. In our case, the combination of ferrous/fructose solution was fixed for all experiment, which could be the reason of similar size of AgNPs.

The amount of AgNPs per unit area on SPNR film surface or surface coverage (C_s) is shown in Table 1. It was found that C_s decreases with increasing dipping time. We expected that if dipping times increase, C_s and percentage of silver will increase. Surprisingly, C_s trend was opposite and %Ag did not show a trend. The reduction in C_s might be thermodynamically controlled. At early dipping stage, there is a high concentration gradient between rubber surface and bulk solution, which drives the Ag^+ to the rubber surface and adsorption occurs. Later, adsorption-desorption of Ag^+ may reach equilibrium, which cause the lower C_s. The adsorption of Ag^+ might be done through the electrostation interaction between anionic surfactant (SDS), MMA emulsion and cationic Ag^+.

Table 1. Surface mean roughness (R_a), percent of surface coverage (C_s), percentage of Ag and average particles size of AgNPs of AgNPs/PMMA-coated SPNR films prepared at various dipping times

Dipping times (min)	R_a (nm)	%C_s	%Ag	Average particle size of AgNPs (nm)
20	81.78 ± 10.93	55.46	38.81	25.25 ± 5.33
30	64.00 ± 7.11	47.09	40.79	25.92 ± 3.35
40	56.92 ± 11.84	40.35	23.01	25.79 ± 5.03
60	41.38 ± 4.76	38.68	38.35	25.14 ± 3.24

%Ag: silver percentage was obtained using selected-area EDX analysis.

From much different R_a of PMMA-modified SPNR and AgNPs/PMMA-modified SPNR, silver ion might interrupt formation of MMA emulsion and lead to the cause of decreasing R_a. Therefore, the relation between MMA emulsion and formation silver particles was studied in the next experiment.

4.4 Effect of $AgNO_3$ concentration

In order to study effect of $AgNO_3$ concentration, the concentration of $AgNO_3$ in the synthesis was varied. The dipping time was fixed at 20 minutes.

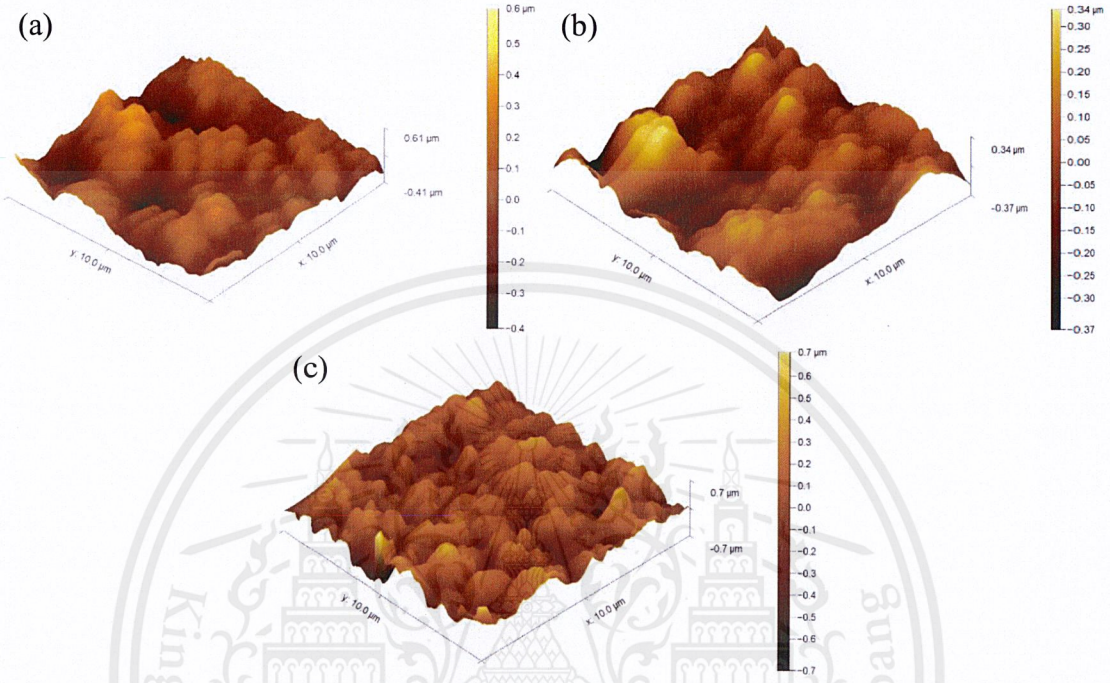


Figure 4.10 AFM micrographs of AgNPs/PMMA-modified SPNR films prepared by adding various $AgNO_3$ concentrations at (a) 1%wt (b) 3%wt and (c) 5%wt.

The results show that R_a of AgNPs/PMMA-modified SPNR films prepared by adding various $AgNO_3$ concentrations at 1%wt, 3%wt and 5%wt are 85.7, 107.6 and 132.0 nm, respectively. It is indicated that concentration of $AgNO_3$ increase with roughness. R_a of AgNPs/PMMA-modified SPNR films is a function of $AgNO_3$ concentration. AgNPs/PMMA-modified SPNR films prepared by adding 5%wt $AgNO_3$ have the highest R_a. Therefore, this condition is selected to study the antibacterial activity of the rubber films.

4.5 Effect of emulsion components on formation of AgNPs

4.5.1 Effect on MMA monomer on the formation of AgNPs

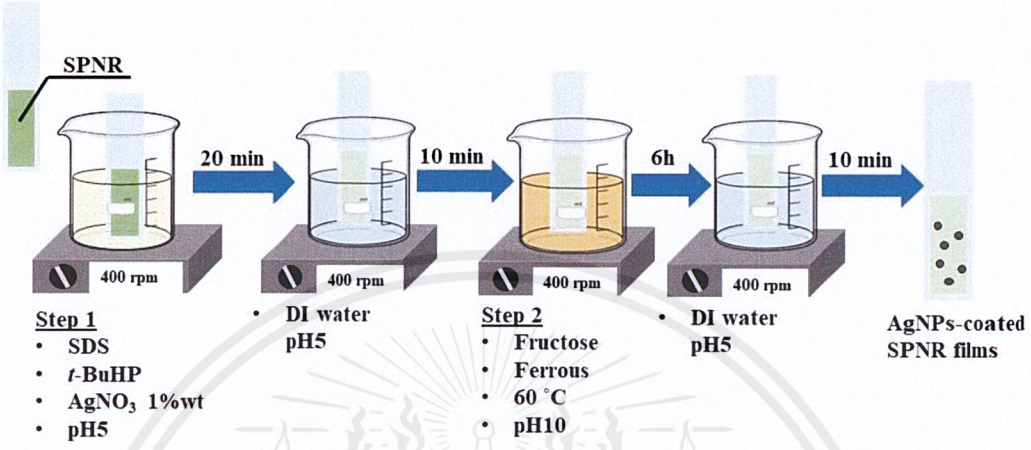


Figure 4.11 *In situ* formation of AgNPs-coated SPNR sheet.

To prove our assumption, the solution in step I was prepared by mixing SDS, *t*-BuHP and 1%wt $AgNO_3$. No MMA was added. The rubber film was dipped in this solution for 20 minutes, prior to immerging in solution II for 6 h at 60°C.

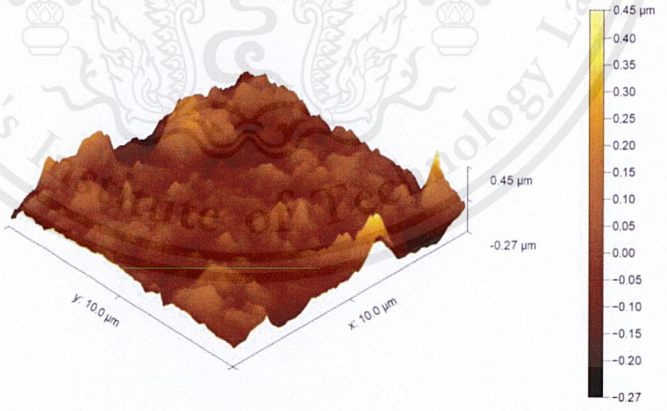


Figure 4.12 AFM image of AgNPs-coated SPNR film.

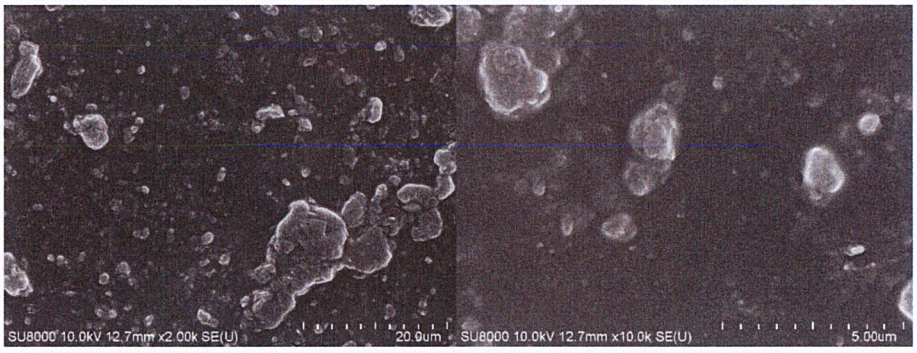
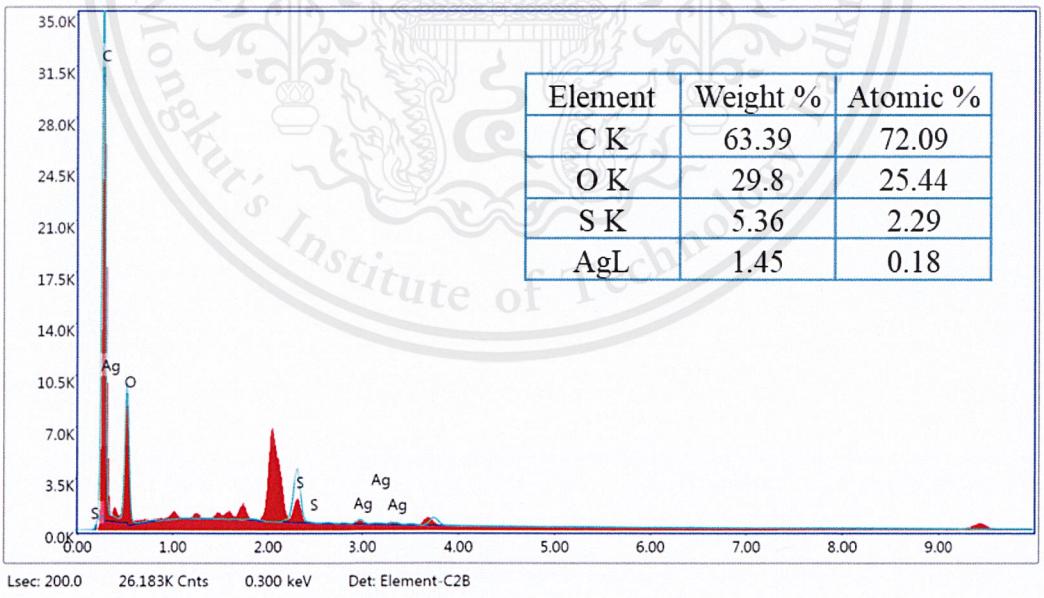


Figure 4.13 SEM images of AgNPs-coated SPNR film.

AFM image (Figure 4.12) shows the rough surface of AgNPs-coated SPNR film having R_a 47.44 nm. From Figure 4.20, there are lots of shiny aggregation on the SPNR surface. However, the EDX analysis proved that the aggregation was not silver. Silver was detected and the weight percentage is 1.45. This is to confirm that MMA monomer is necessary for forming AgNPs on the SPNR surface. The adsorption of Ag^+ caused by the chelation between MMA and Ag^+.



Element	Weight %	Atomic %
C K	63.39	72.09
O K	29.8	25.44
S K	5.36	2.29
AgL	1.45	0.18

Figure 4.14 EDX spectra of AgNPs-coated SPNR film.

4.5.2 Effect of MMA emulsion on the formation of AgNPs

To prove the assumption, next experiment was performed by mixing of SDS, *t*-BuHP and MMA monomer first for 30 minutes then $AgNO_3$ was added in the solution. SPNR strip was dipped in the solution for 20 minutes. After that, MMA-swollen rubber strips were dipped in ferrous/fructose at 60°C for 6 h.

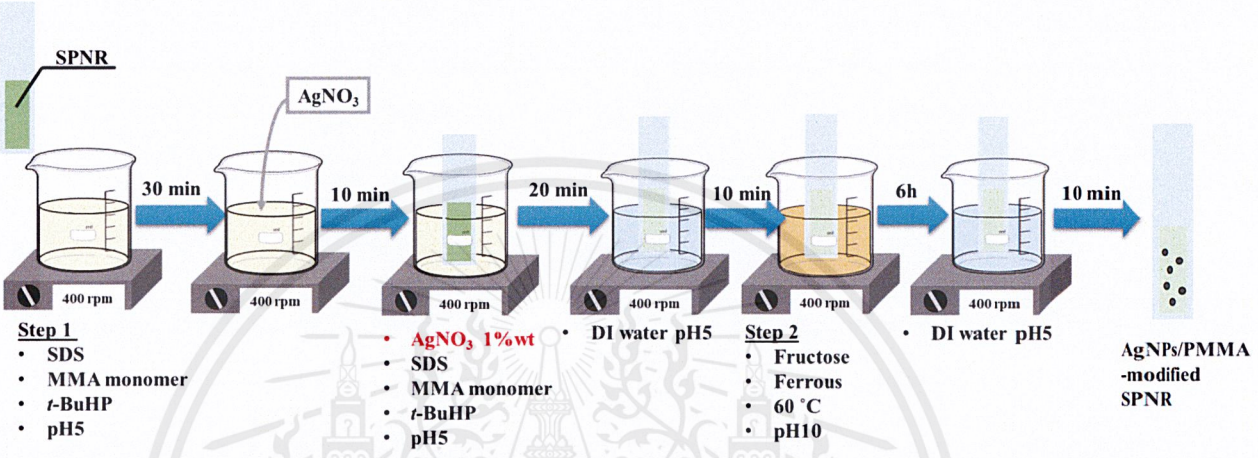


Figure 4.15 *In situ* formation of PMMA/AgNPs on SPNR sheet by adding $AgNO_3$ after formation of MMA emulsion for 30 minutes.

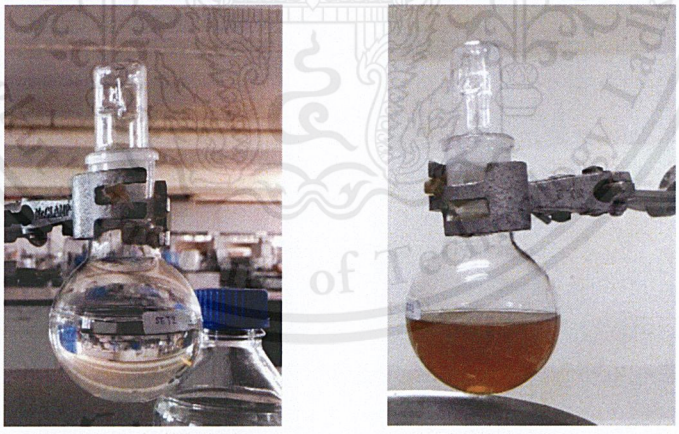


Figure 4.16 Color of ferrous/fructose solution at (a) 0 and (b) 6 h (after heating).

After the swollen-MMA rubber strips were dipped in the ferrous/fructose for 6 h, the color of solution was changed from colorless to brown as shown in Figure 4.16 This was confirmed the formation of AgNPs.

Figure 4.17 shows the slightly rough surface of AgNPs/PMMA-modified SPNR films prepared by adding $AgNO_3$ solution in the emulsion solution in step I.

R_a of the rubber film is 52.56 nm, which much lower than PMMA-modified SPNR and AgNPs/PMMA-modified SPNR.

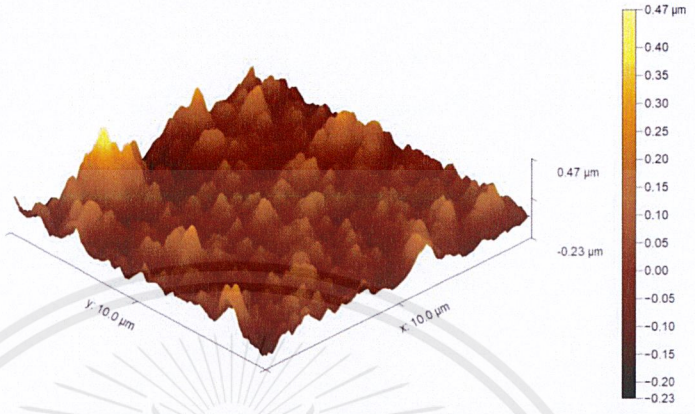


Figure 4.17 AFM image of of AgNPs/PMMA-modified SPNR films prepared by adding $AgNO_3$ solution after formation of MMA emulsion for 30 minutes.

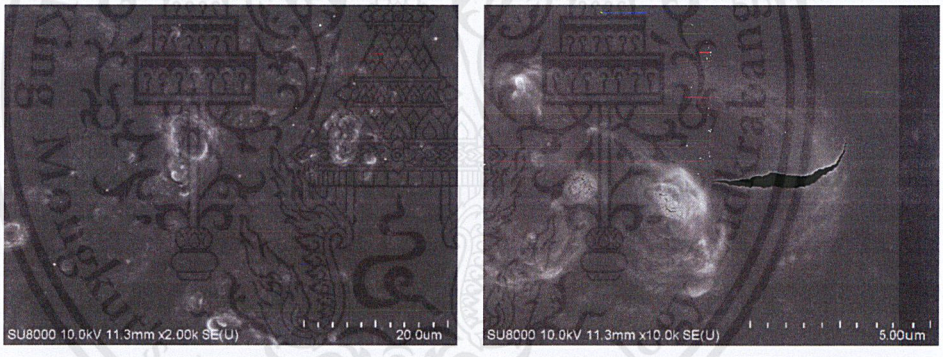


Figure 4.18 SEM micrographs of AgNPs/PMMA-modified SPNR.

SEM micrographs (Figure 4.18) show that the rubber was rough and swollen. MMA monomer might be diffused to underneath the rubber surface. The crack was occurred while the surface morphology was investigated. This suggests that heat resistance of the rubber decreased. AgNPs were not observed.

Based on these results, it suggested that adsorption of Ag^+ associated with the presence of MMA, SDS and/or MMA emulsion. We would like to further understand how the AgNPs are formed and their effect on the formation of PMMA on SPNR film. So, the next experiment was performed. Instead of mixing $AgNO_3$ in the MMA emulsion, $AgNO_3$ was mixed with the mixture of

ferrous/fructose in step II. The MMA-swollen rubber strips were dipped in solution II at 60°C for 6 h.

4.6 Effect of ferrous/fructose on formation of AgNPs

In order to study what is the reducing agent in the formation of AgNPs, $AgNO_3$ solution was added in the ferrous/fructose in step II instead.

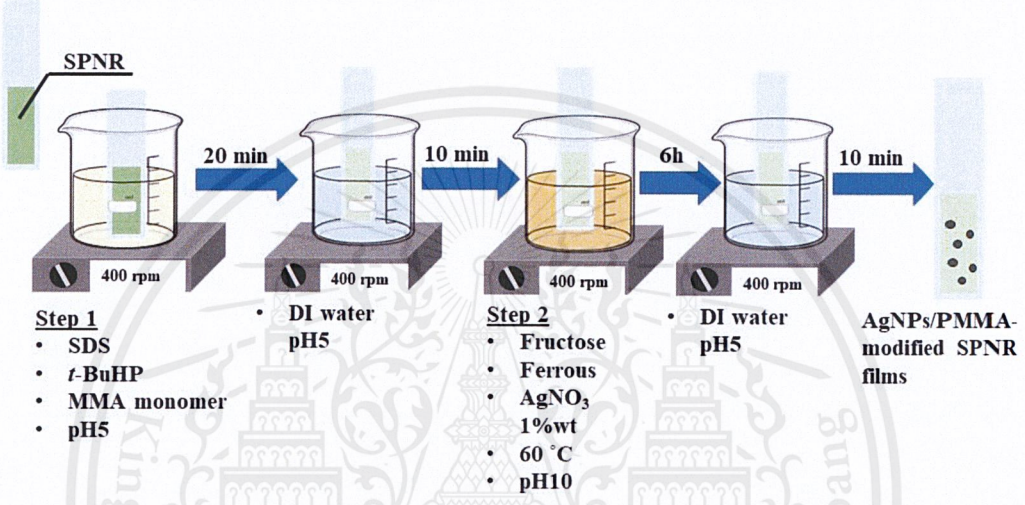


Figure 4.19 *In situ* formation of AgNPs/PMMA on SPNR film (adding $AgNO_3$ solution in the second polymerization step).

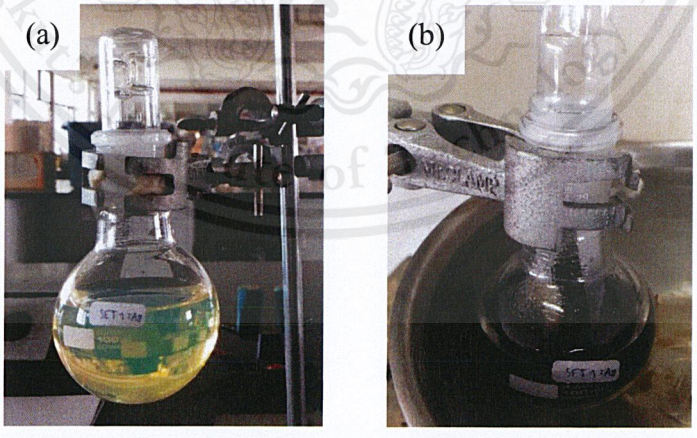


Figure 4.20 Color of ferrous/fructose solution after mixing $AgNO_3$ at (a) 0 and (b) 20 min (without heating).

After mixing $AgNO_3$ in ferrous/fructose solution, the pale-yellow solution turns to dark brown in 20 minutes without heating, (Figure 4.20). This phenomenon suggests the formation of AgNPs occurred by reduction of ferrous/fructose solution.

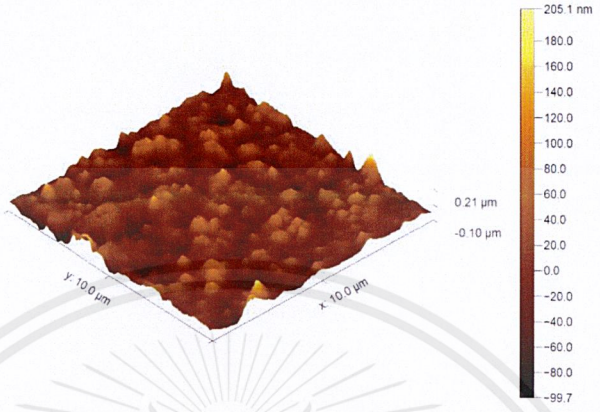
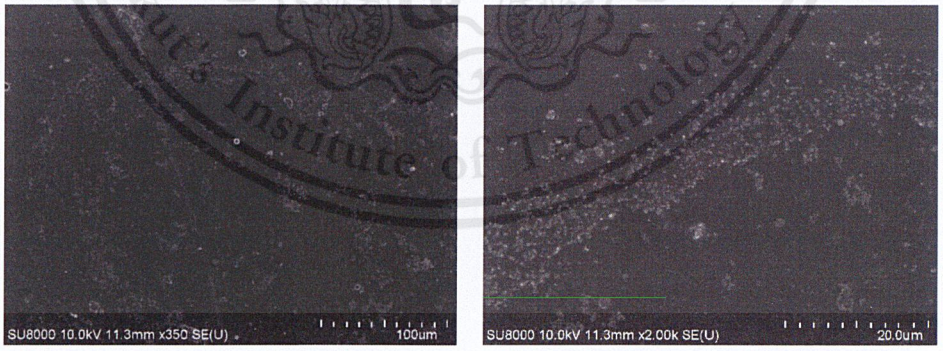


Figure 4.21 AFM image of of AgNPs/PMMA-modified SPNR films prepared by adding $AgNO_3$ solution in the second polymerization step.

Figure 4.21 shows the slightly rough surface of AgNPs/PMMA-modified SPNR films prepared by adding $AgNO_3$ solution in the ferrous/fructose in step II. R_a of the rubber film is 23.53 nm, which much lower than PMMA-modified SPNR and AgNPs/PMMA-modified SPNR.



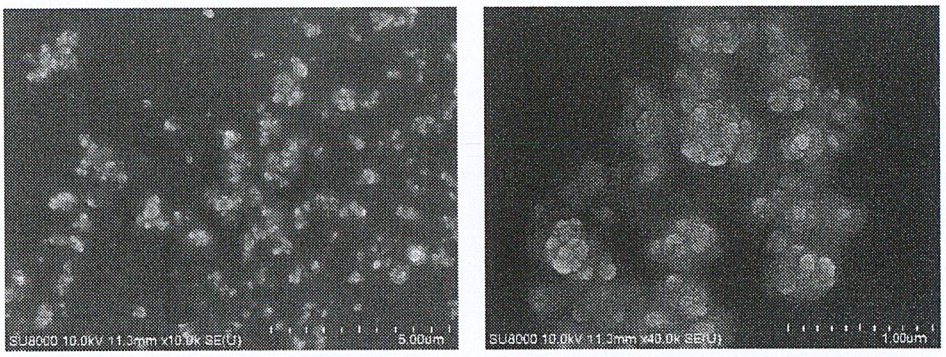


Figure 4.22 SEM images of AgNPs/PMMA-modified SPNR films prepared by adding $AgNO_3$ solution in the second polymerization step.

In addition, SEM micrographs showed that clusters of particles similar to PMMA aggregation. However low R_a and sparingly formed PMMA might be because the ferrous/fructose, emulsion redox initiator, was mainly used in the formation of AgNPs in the solution. Thus, less polymerization occurred. In addition, AgNPs were mostly formed in the aqueous ferrous/fructose solution. No or less AgNPs were seen on rubber film. Since MMA monomer is necessary for the AgNPs formation, in order to prove this hypothesis, we removed MMA monomer and added $AgNO_3$ solution in the first polymerization step.

CHAPTER V
CONCLUSION

AgNPs/PMMA was successfully prepared *in situ* using induced redox/Emulsion polymerization technique. Surface roughness were governed by dipping time and concentration of $AgNO_3$. AgNPs/PMMA-modified SPNR which prepared by dipping for 20 minutes and using 5%wt $AgNO_3$ has the highest surface roughness. In addition, MMA monomer and ferrous/fructose solution are significant for AgNPs formation.

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APPENDIX

A.1 Optical image

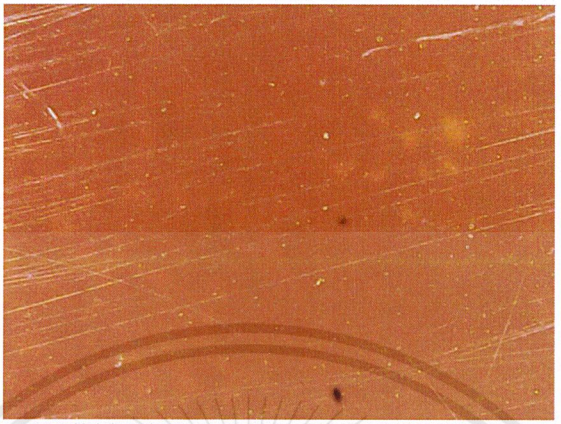


Figure A.1.1 Optical image of SPNR film.

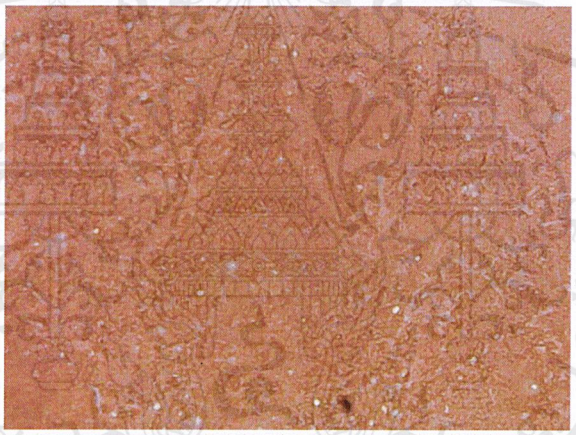
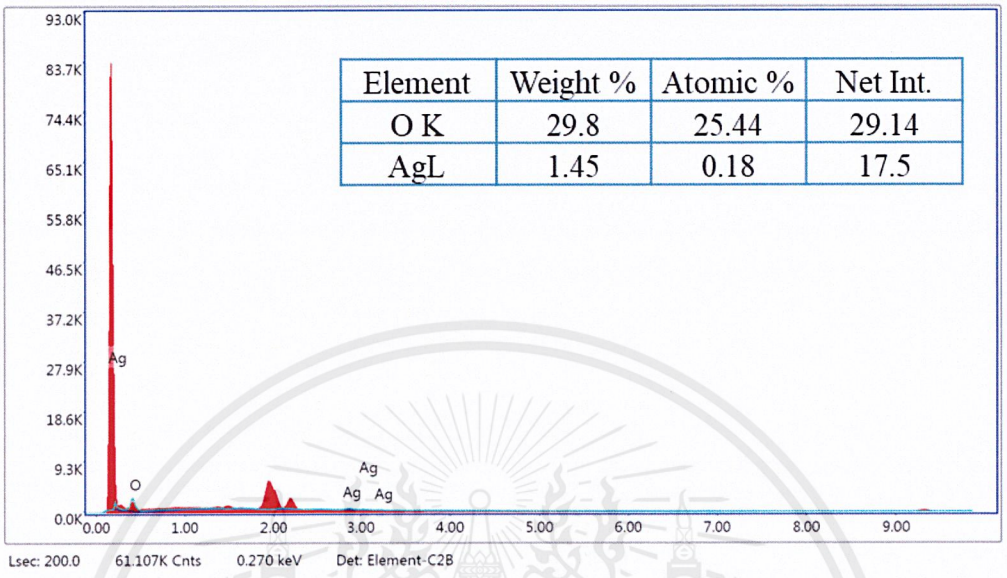


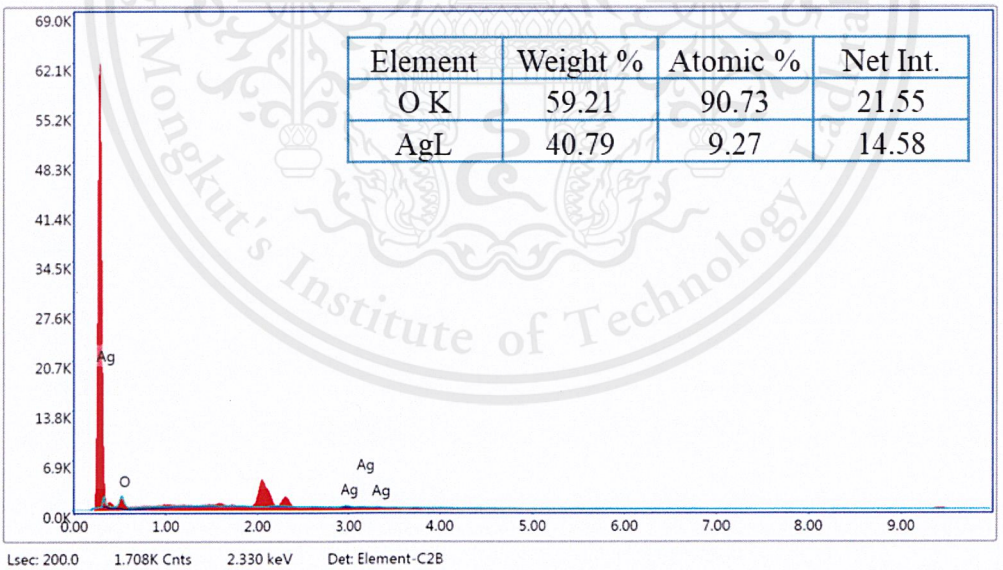
Figure A.1.2 Optical image of AgNPs/PMMA-modified SPNR film.

A.2 Elemental analysis



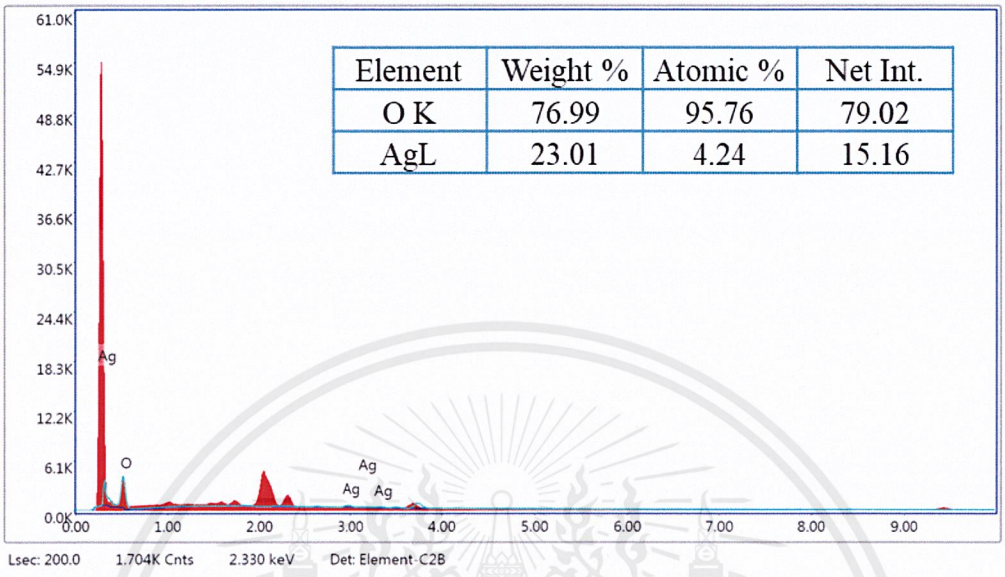
Element	Weight %	Atomic %	Net Int.
O K	29.8	25.44	29.14
AgL	1.45	0.18	17.5

Figure A.2.1 EDX spectra of AgNPs/PMMA-modified SPNR films prepared by dipping for at 20 minutes



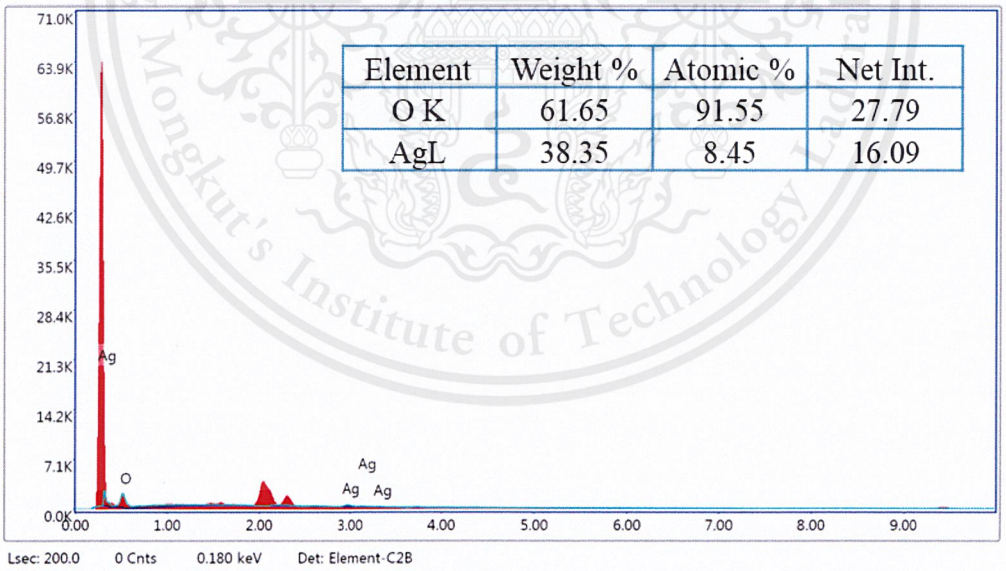
Element	Weight %	Atomic %	Net Int.
O K	59.21	90.73	21.55
AgL	40.79	9.27	14.58

Figure A.2.2 EDX spectra of AgNPs/PMMA-modified SPNR films prepared by dipping for at 30 minutes



Element	Weight %	Atomic %	Net Int.
O K	76.99	95.76	79.02
AgL	23.01	4.24	15.16

Figure A.2.3 EDX spectra of AgNPs/PMMA-modified SPNR films prepared by dipping for at 40 minutes



Element	Weight %	Atomic %	Net Int.
O K	61.65	91.55	27.79
AgL	38.35	8.45	16.09

Figure A.2.3 EDX spectra of AgNPs/PMMA-modified SPNR films prepared by dipping for at 60 minutes

BIBLIOGRAHPY

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