การเตรียมและสมบัติของยางธรรมชาติกราฟต์ด้วยพอลิ(บิวทิลอะคริเลต-*โค*-ฟลูออริเนเตดอะคริเลต)

นางสาวกชมน ยิ้มหมุด

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2559

PREPARATION AND PROPERTIES OF NATURAL RUBBER GRAFTED WITH POLY(BUTYL ACRYLATE-*CO*-FLUORINATED ACRYLATE)

Miss Kotchamon Yimmut

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
Faculty of Science
Chulalongkorn University
Academic Year 2016

Thesis Title	PREPARATION AND PROPERTIES OF NATURAL RUBBER GRAFTED WITH POLY(BUTYL ACRYLATE-*CO*-FLUORINATED ACRYLATE)
By	Miss Kotchamon Yimmut
Field of Study	Petrochemistry and Polymer Science
Thesis Advisor	Associate Professor Napida Hinchiranan, Ph.D.

Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

....Dean of the Faculty of Science
(Associate Professor Polkit Sangvanich, Ph.D.)

THESIS COMMITTEE

....Chairman
(Professor Pattarapan Prasassarakich, Ph.D.)

....Thesis Advisor
(Associate Professor Napida Hinchiranan, Ph.D.)

....Examiner
(Assistant Professor Kanoktip Boonkerd, Ph.D.)

....External Examiner
(Assistant Professor Suwadee Kongparakul, Ph.D.)

กชมน ยิ้มหมุด : การเตรียมและสมบัติของยางธรรมชาติกราฟต์ด้วยพอลิ(บิวทิลอะคริเลต-*โค*-ฟลูออริเนเตดอะคริเลต) (PREPARATION AND PROPERTIES OF NATURAL RUBBER GRAFTED WITH POLY(BUTYL ACRYLATE-*CO*-FLUORINATED ACRYLATE)) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร. นพิดา หิญชีระนันทน์, 77 หน้า.

กราฟต์โคพอลิเมอไรเซชันของ 2,2,2-ไตรฟลูออโรเอทิลเมทาคริเลต บนยางธรรมชาติถูกสังเคราะห์ในระบบการอิมัลชันโดยใช้โพแทสเซียมเปอร์ซัลเฟตเป็นตัวริเริ่มปฏิกิริยา เนื่องด้วยสภาพขั้วที่แตกต่างกันของยางธรรมชาติและ 2,2,2-ไตรฟลูออโรเอทิลเมทาคริเลตทำให้มอนอเมอร์ 2,2,2-ไตรฟลูออโรเอทิลเมทาคริเลตไม่สามารถกราฟต์ลงบนยางธรรมชาติได้โดยตรง บิวทิลอะคริเลตถูกเลือกมาใช้เป็นมอนอเมอร์ร่วมเพื่อเพิ่มประสิทธิภาพในการกราฟต์ของระบบนี้ ศึกษาโครงสร้างทางเคมีของยางธรรมชาติก่อนและหลังการกราฟต์โคพอลิเมอไรเซชันด้วยเทคนิคเอเทนูเอทโท้ทิลรีเฟคแทนซ์ฟูเรียร์ทรานสฟอร์มอินฟาเรดสเปกโตรสโกปีและนิวเคลียร์แมกเนติกเรโซแนนซ์สเปกโตรสโกปี ศึกษาผลความเข้มข้นของตัวริเริ่มปฏิกิริยา อัตราส่วนโดยน้ำหนักของบิวทิลอะคริเลต/2,2,2-ไตรฟลูออโรเอทิลเมทาคริเลต อุณหภูมิ และเวลาที่ใช้ในการเกิดปฏิกิริยาต่อการเปลี่ยนแปลงของมอนอเมอร์ สมบัติการกราฟต์ และประสิทธิภาพการกราฟต์ ปริมาณสูงสุดของธรรมชาติกราฟต์ด้วยพอลิ(บิวทิลอะคริเลต-*โค*-2,2,2-ไตรฟลูออโรเอทิลเมทาคริเลต) ที่ 72.8% โดยน้ำหนักพบที่การใช้อัตราส่วนบิวทิลอะคริเลต/2,2,2-ไตรฟลูออโรเอทิลเมทาคริเลต ที่ 30/70 โดยน้ำหนัก และใช้โพแทสเซียมเปอร์ซัลเฟต 1.5 ส่วนต่อร้อยส่วนของยางที่ 60 องศาเซลเซียส นาน 8 ชม. จะได้ยางธรรมชาติกราฟต์สูงสุดถึง 25.3% โดยน้ำหนัก 2,2,2-ไตรฟลูออโรเอทิลเมทาคริเลต ที่เกิดการกราฟต์ 68.5%โดยโมลลาเท็กของผลิตภัณฑ์กราฟต์ที่ได้แสดงสัญฐานวิทยาแบบแกนขเปลือก สมบัติเชิงความร้อน เชิงกล มุมสัมผัสและพลังงานพื้นผิวถูกวิเคราะห์เพื่อใช้ในการประเมินผลของการเติมผลิตภัณฑ์กราฟต์ต่อความเข้ากันได้ระหว่างวัฏภาคยางธรรมชาติและพอลิ(บิวทิลอะคริเลต-*โค*-2,2,2-ไตรฟลูออโรเอทิลเมทาคริเลต) ในฟิล์มผสมของยางธรรมชาติ/พอลิ(บิวทิลอะคริเลต-*โค*-2,2,2-ไตรฟลูออโรเอทิลเมทาคริเลต) (20/80 โดยน้ำหนัก) ผลการทดลองแสดงให้เห็นว่าการเติมผลิตภัณฑ์กราฟต์ 10% โดยน้ำหนักเพิ่มความเข้ากันได้ขององค์ประกอบพอลิเมอร์ในแผ่นฟิล์ม ทำให้ความไม่ชอบน้ำถูกปรับปรุงโดยมีมุมสัมผัสสูง (109°) และมีความเหนียวเพิ่มขึ้น นอกจากนี้ความต้านทานการบวมตัวในน้ำของฟิล์มที่ได้ยังมีค่าสูงกว่าฟิล์มทางการค้า สามารถผนึกได้ด้วยตัวเองอย่างเช่น Parafilm M^{R} ที่ใช้กันมากในห้องปฏิบัติการ

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต ....

ปีการศึกษา 2559 ลายมือชื่อ อ.ที่ปรึกษาหลัก ....

5771903423 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE

KEYWORDS: NATURAL RUBBER, 2,2,2-TRIFLUOROETHYL METHACRYLATE, BUTYL ACRYLATE, GRAFT COPOLYMERIZATION.

KOTCHAMON YIMMUT: PREPARATION AND PROPERTIES OF NATURAL RUBBER GRAFTED WITH POLY(BUTYL ACRYLATE-*CO*-FLUORINATED ACRYLATE). ADVISOR: ASSOC. PROF. NAPIDA HINCHIRANAN, Ph.D., 77 pp.

Graft copolymerization of 2,2,2–trifluoroethyl methacrylate (3FMA) onto natural rubber (NR) was synthesized in an emulsion system by using potassium persulfate (K_2SO_4) as an initiator. Since the polarity of NR and 3FMA monomer was different, the 3FMA monomer could not be directly grafted onto the NR structure. Thus, butyl acrylate (BA) was selected as a co-monomer to enhance the grafting efficiency (GE) of this system. The chemical structure of NR before and after graft copolymerization was detected by using attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) and nuclear magnetic resonance spectroscopy. The effects of initiator concentration, BA/3FMA wt ratio, reaction temperature and reaction time on monomer conversion, grafting properties and GE of the graft NR (GNR) were investigated. The maximum content of NR-*g*-poly(BA-*co*-3FMA) at 72.8 wt% was obtained by using 30/70 (w/w) BA/3FMA and 1.5 phr K_2SO_4 at 60 °C for 8 h. This condition provided GNR with 25.3 mol% grafted 3FMA content and 68.5% GE. The latex of the graft product exhibited the core-shell morphology. The thermal properties, mechanical properties, contact angle and surface energy were analyzed to evaluate the effect of the addition of graft product on the compatibility between NR and poly(BA-*co*-3FMA) phases in the NR/poly(BA-co-3FMA) films (20/80 (w/w)). The results revealed that the addition of 10 wt% GNR enhanced the compatibility of the polymeric constituents in the films resulting the improved hydrophobicity with high contact angle (109°) and higher toughness. Moreover, the oil swelling resistance of obtained film was higher than that of the commercial self-sealing film using in the laboratory, Parafilm M^R.

Field of Study:	Petrochemistry and Polymer Science	Student's Signature	....
		Advisor's Signature	....
Academic Year:	2016		

ACKNOWLEDGEMENTS

The author would like the express her greatest gratitude to her advisor, Associate Professor Dr. Napida Hinchiranan for her valuable guidance during the course of this research. In addition, the author wishes to thank Professor Dr. Pattarapan Prasassarakich, Assistant Professor Dr. Kanoktip Boonkerd and Assistant Professor Dr. Suwadee Kongparakul for seving as the chairman and members of the thesis committee, respectively.

The author also thanks for the research financial supports from the Program in Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University. The author wishes to express her thankfulness to technicians of the Department of Chemical Technology, Faculty of Science, Chulalongkorn University for providing their assistance throughout this research.

Thanks are going towards all of her friends in the laboratory for their friendship, assistance, suggestion, advice concerning the experimental techniques and encouragement during the course of her graduate research.

Finally, and most of all, the author wishes to express her deepest gratitude to her family; especially, her parents for their love, support and encouragement throughout her entire study.

CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

1.1 The statement of problem

Fluorinated polymers have been applied in various applications owing to their superior performance such as high thermal stability, chemical inertness, excellent weatherability and superb water and oil repellence. These properties are resulted from the strong electronegativity of fluorine atoms in the fluorine-containing groups in these polymers to provide the low surface energy (Hao et al. 2012; Xiao and Wang 2009; Zhou, Zhang, and Ma 2013). 2,2,2-Trifloroethyl methacrylate (3FMA), a fluorinated acrylate monomer containing 34% fluorine content (Li et al. 2014; Liu et al. 2010), can be easily polymerized via free radical mechanism in bulk, solution and emulsion polymerization methods to form poly(3FMA) (P3FMA). Although P3FMA exhibits high performance for coating, the disadvantage of this polymer involves with its high glass transition temperature (T_g) as ca. 80-90 °C resulting in poor elasticity with inferior film-foaming properties (Xu et al. 2016; Zhang, Zhao, et al. 2011). Moreover, it is expensive, which limits to be used in the large scale applications. To solve these problems, Zhang et al. (2011) reported that the introduction of $–CH_2CH_2O-$ functional group into the chain of P3FMA significantly decreased its T_g to ca. 13 °C with retaining good hydrophobicity (water contact angle = 99.9°). The copolymerization of 3FMA with other monomers such as methyl methacrylate (MMA) and butyl acrylate (BA) could also reduce the cost of chemicals and the improved mechanical properties of the copolymer products would be obtained (Ozbay and Erbil 2014). However, MMA is also classified as the rigid polymer due to its high T_g (105 °C). Thus, MMA should not be used alone for copolymerization with 3FMA. BA has been suggested as another co-monomer since its T_g was ca -55 °C and it also provides the higher toughness to produce the higher flexible copolymer film (Ozbay and Erbil 2014).

To consider the elastomeric materials with the awareness of environmental aspect, natural rubber (NR) is one of green natural polymers with excellent mechanical and dynamic properties such as high resilience, great tensile properties, high fatigue resistance and low T_g (ca. -67 °C). It is consequently attractive material to be blended with various brittle polymers such as poly(lactic acid) (Rosli et al. 2016; Zhang, Man, et al. 2011), poly(methyl methacrylate) (Abu Bakar 2012; Oommen 1997) and poly(vinyl chloride) (Arayapranee, Prasassarakich, and Rempel 2004) to produce thermoplastic elastomers with improved mechanical properties. However, these above polymers are classified as polar materials, which are not compatible with NR having low polarity. To solve the polarity mismatch, the structure of NR is chemically modified by various techniques such as epoxidation, maleinization and graft copolymerization (Ozbay and Erbil 2014; Saramolee, Lopattananon, and Sahakaro 2014). Among these techniques, the graft copolymerization is the most popular process to apply polar vinyl monomers such as MMA (Oommen 1997; Ozbay and Erbil 2014) acrylonitrile (Angnanon, Prasassarakich, and Hinchiranan 2011), styrene (Aroonsingkarat and Hansupalak 2013) and glycidyl methacrylate (Juntuek et al. 2011) onto the NR backbone in the states of solid, solution or latex. The obtained graft copolymers contain the segments, which can promote the reactive interaction resulted in the reduction of interfacial tension of the immiscible polymeric parts in the bends.

In the case of fluorinated monomers, there are few previous literatures reported the graft copolymerization of fluorinated monomers onto the NR structure for some applications. Wang et al. (2000) enhanced the hydrophobicity of the NR latex film surface (water contact angle of modified film = 109°) by using argon plasma treatment followed by UV-induced graft copolymerization of 2,2,3,3,4,4,4-heptaflurobutyl acrylate. Hinchiranan et al. (2013) synthesized the P3FMA-*graft*-NR via solid-state graft copolymerization without the assistance of co-monomer. The obtained graft product was applied as the compatibilizer for NR/fluoroelastomer vulcanizates. Although this technique was easy for commercialization, the high reaction temperature was required (> 80 °C), which could promote the high level of gel formation (gel content = ca. 20 – 90%) in the obtained graft product with only 1.34% maximum grafting efficiency.

According to the drawback of the solid-state grafting process as described above, this research focused on the graft copolymerization of P3FMA onto the NR backbone in the emulsion state due to the availability of NR latex with cheaper than the solid form. Moreover, this process provides the good heat transfer control to promote in the fast polymerization rate in the presence of lower reaction temperature (50 – 80°C depended on the initiator type). Due to the polarity difference of NR and 3FMA monomer in the obstruction of directly grafting P3FMA onto NR structure, BA was selected as a co-monomer to enhance the grafting efficiency of this system. The effects of BA/3FMA wt ratio, potassium persulfate (KPS) initiator concentration, reaction temperature and reaction time on the monomer conversion, grafting properties and grafting efficiency of the graft product were investigated. The morphology and size of the NR particles before and after graft copolymerization were comparatively observed. The obtained gross graft NR (GNR) was then applied as the compatibilizer for NR/poly(BA-*co*-3FMA) films. The tensile and thermal properties including water and oil contact angle of the film products were also examined.

1.2 Objectives of the research work

The objectives of this research were stated as followed:

1. To synthesize the graft copolymer derived from graft copolymerization of poly(BA-*co*-3FMA) onto NR backbone in the latex state.

2. To study the effects of reaction parameters such as the wt ratio of BA/3FMA, initiator concentration, reaction temperature and reaction time on the monomer conversion, grafting properties, grafting efficiency of GNR.
3. To characterize the physical, thermal and mechanical properties of NR/poly(BA-*co*-3FMA) films with and without the addition of GNR.

1.3 Scope of the research work

The graft copolymerization of NR with poly(BA-*co*-3FMA) was carried out in the emulsion system initiated by KPS. The obtained GNR was used as the compatibilizer for the NR/poly(BA-*co*-3FMA) films. The mechanical, physical and thermal properties of the obtained films were investigated. The details of all experiments in this research were presented as followed:

1. Surveyed the previous literatures and prepared the materials and chemicals used for this research.
2. Prepared the NR-*graft*-poly(BA-*co*-3FMA) under nitrogen atmosphere. The effects of studied parameters on monomer conversion, grafting properties, grafting efficiency and fluorine content in the GNR were examined as followed:
    - BA/3FMA ratio (w/w): 100/0 – 0/100
    - Initiator concentration (phr): 0.5 - 2.0
    - Reaction temperature (C°): 50 – 80
    - Reaction time (h): 4 – 10
3. Characterized the chemical structure, latex morphology and particle size of the obtained GNR.

4. Casted the NR/poly(BA-*co*-3FMA) films (20/80 w/w) with or without the addition of GNR at various contents (0 – 20 wt% based on the amount of NR/poly(BA-*co*-3FMA)).
5. Characterized the properties of the obtained films as followed:
    - Compatibility testing: Molau test and atomic force microscope (AFM)
    - Water and oil repellence: Contact angle measured by using a microscope equipped with a Kruss (DSA 10 MK2, Germany)
    - T_g: Differential scanning calorimetry (DSC)
    - Mechanical properties: Universal testing machine
6. Summarized results and wrote thesis

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Natural rubber and its properties

Natural rubber (NR) is an important elastomer harvested from the latex of the *Hevea brasiliensis* tree. The chemical structure of NR has been known as *cis*-1,4-polyisoprene (C_5H_8) (ca. 93 – 95 wt%), which may be as 11,000 to 20,000 isoprene units in a polymer chain as shown in Figure 2.1 (Angnanon, Prasassarakich, and Hinchiranan 2011; Zhang, Man, et al. 2011). NR also shows the broad distribution with high average molecular weight (10,000 – 1,000,000 daltons) (Kongparakul, Prasassarakich, and Rempel 2008). Furthermore, NR is consisted of ca. 25-40% dry rubber content (DRC) and 5-10% non-rubber substances mainly composed with proteins, sugars, phospholipids and small amounts of mineral substances. NR can be used in a wide range of applications and products, either alone or in the combination with other materials since NR has excellent elastic properties such as high modulus, high flexibility and high fatigue resistance (Saramolee, Lopattananon, and Sahakaro 2014). Due to spontaneously crytallize at low temperature (glass transition temperature (T_g)~ -65 °C), this causes stiffness resulting in high tensile strength and resistance to cutting, tearing and abrasion. Although NR has improved properties after vulcanization, NR still has carbon-carbon double bonds (C=C) in the polymer chain (Angnanon, Prasassarakich, and Hinchiranan 2011; Aroonsingkarat and Hansupalak 2013) to induce the degradation by sunlight, ozone and long term heating. Moreover, NR is classified as non-polar rubber, which is susceptible to organic solvents, oil and fuels (Chumsamrong 2007; Hinchiranan et al. 2013).

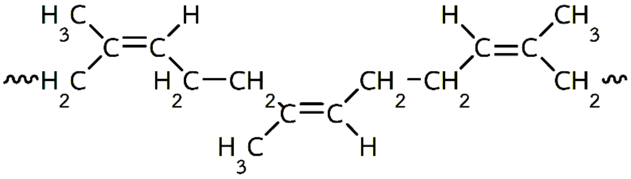


Figure 2.1 Natural rubber or *cis*-1,4-polyisoprene.

2.2 Chemical modifications of NR (Saramolee, Lopattananon, and Sahakaro 2014)

Chemical modifications of NR have been a subject of long interest. There are reviewed as shown below:

2.2.1 Cyclized natural rubber

Cyclized rubber, a hard brittle thermoplastic derivative of NR, is obtained by treating NR with acidic catalysts such as sulfuric acid, aromatic sulphonic acids and lewis acids (stannic chloride, titanium tetrachloride and boron trifluoride). Cyclized rubber can be applied as adhesives, bonding agents, paints, shoe soles, hard mouldings, industrial rollers etc. and as a reinforcing resin.

2.2.2 Hydrogenation (Kohiya and Ikedo 2014)

The NR hydrogenation can be carried out by using catalysts in the presence of hydrogen gas and organic solvents. Catalyst systems may be conveniently classified into four groups: metal and supported metal catalysts, noble metal catalysts, organometallic systems and diimide generators. Hydrogenated NR (HNR) is more crystalline and has slightly higher T_g than that of NR. The HNR valcanizates with high hydrogenation degree also show higher ozone resistance.

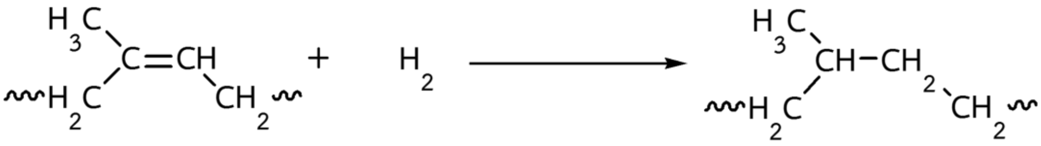


Figure 2.2 Hydrogenation of NR (Charles et al., 1986)

2.2.3 **Halogenation** (Odian 2004)

Chlorination, one of halogenated rubber types, has been extensively studied. The reaction is complex and may include addition, substitution, cyclization, crosslink and degradation. Chlorinated rubber is not flammable and has high resistance to organic chemicals. A fully chlorinated product is more stable than a partially chlorinated one. It can be applied in printing inks, chemicals and heat resistant surface coating.

2.2.4 **Epoxidization** (Charles et al., 1986).

NR can be epoxidized by peracids. The epoxidation process rapidly occurs via opening the strained epoxy ring as shown in Figure 2.3. This ring opening reation is carried out in the presence of hydrogen ions under high reaction temperature. The epoxidized NR (ENR) is an elastic material with higher density than NR. After epoxidation, the T_g of ENR linearly increased by 1 °C for every mole percentage of epoxidation resulting the reduction of resilience and air permeability with higher hysteresis. However, the wet traction of ENR is better. The epoxy groups also increases the polarity to enhance the hydrocarbon oil resistance. ENR can be potentially applied in engineering components, inner liners of tubeless tires, oil seals and tire treads.

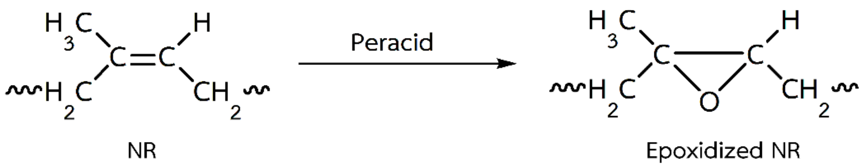
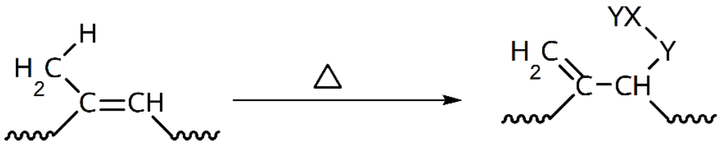


Figure 2.3 Epoxidation of NR (Charles et al., 1986).

2.2.5 Ene reaction

The general ene reaction with NR is presented in Figure 2.4. This is not related to active species such as ions and free radicals which act as intermediates. The ene reaction applied to NR leads the concept of rubber-bound antioxidants. The initial stage of the ene reaction involves the reaction between the rubber and a nitroso compound. Nitrosoarenes give a hydroxylamine as a main product. Such antioxidants are not leached during washing or solvent treatment. Thus, it may be useful for a rubber tread for garments. However, this process has not been exploited because of the formation of coloured by-products.



(X = Y cab be –N=O, -N=N-, >C=O, >C=C< and >C=S.)

Figure 2.4 Scheme of ene reaction of NR (Bhowmick and Stephene, 2001).

2.2.6 Graft copolymerization (Kohiya and Ikedo 2014)

Graft copolymerization of NR and vinyl polymers is prepared by polymerization of monomers initiated by free radicals or attachment of a polymer to the rubber backbone. The backbone and the branches polymers may be homopolymer or copolymers with different chemical nature or composition. The example of graft copolymerization of NR with MMA can be shown in Figure 2.5.

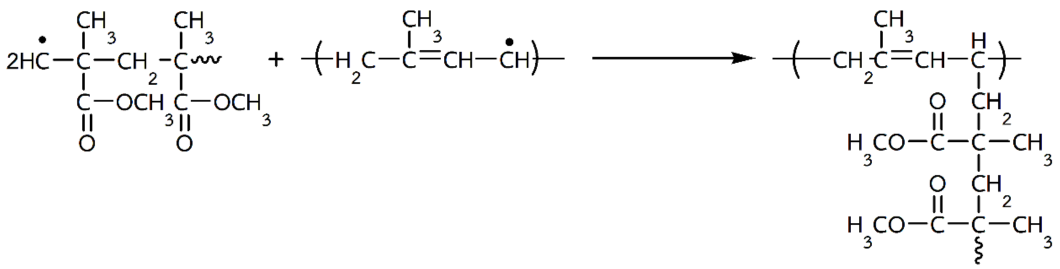


Figure 2.5 Graft polymerization of NR with MMA (Wang et al., 2011).

2.3 Graft copolymerization

2.3.1 Grafting processes (Bhattacharya and Misra 2004b; Angnanon, Prasassarakich, and Hinchiranan 2011; Shi et al. 2013).

The graft copolymers can be prepared by three main methods as shown in Figure 2.6:

(a) Grafting ‘‘from’’: polymerization of a second monomer is initiated by sites located on the main polymer chain.

(b) Grafting ‘‘to’’: the functional groups attached on the side chain of polymer react with reactive polymer.

(c) Grafting ‘‘through’’: macromonomer is copolymerized with a small molecule of comonomer defined as side chains.

Normally, there are two methods to synthesize graft copolymers (Chansook, 2001):

1. The side chain polymer can be directly linked by a suitable chemical reaction to the polymer backbone.

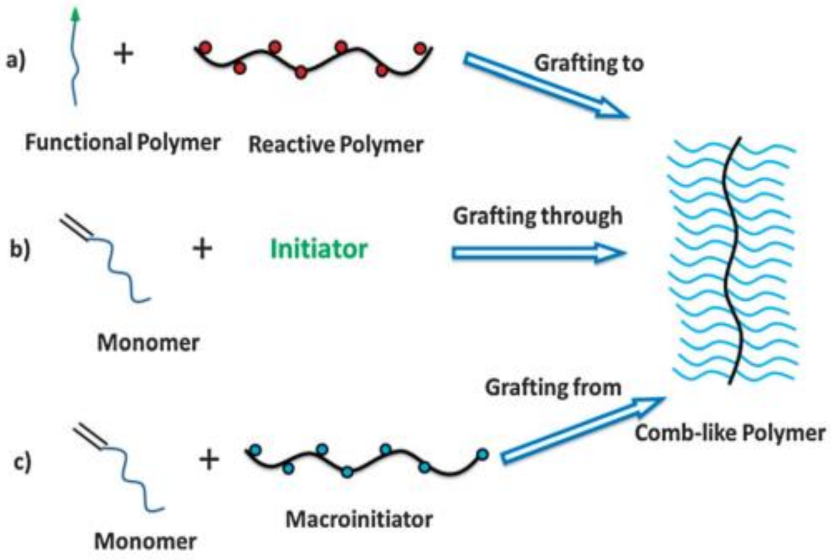


Figure 2.6 Synthetic methods for preparing comb-like polymers by (a) grafting to, (b) grafting through and (c) grafting from (Shi et al. 2013).

2. The backbone of polymer can be initiated to produce active sites such as free radicals or ions to be used for polymerization of suitable monomers resulting the side chain polymer.

2.3.2 Initiators of grafting

The different initiator systems have been extensively used to prepare graft copolymerization of vinyl monomers onto NR in recent years as follows:

(a) Thermal decomposition of initiators (Odian 2004)

The thermal or hemolytic dissociations are widely used to generate radicals to initiate polymerization for both commercial process and theoretical studies. The number of different chemicals used as thermal initiators is rather limited. Normally, the thermal initiators should have bond dissociation energies in the range of 100-170 kJ/mol. Several different types of peroxy compounds are widely used. There are acyl peroxides (eg. acetyl and benzoyl peroxides), alkyl peroxides (eg. cumyl and *tert*-butyl peroxides), hydroperoxides (eg. *tert*-butyl and cumyl hydroperoxides) and persters (eg. *tert*-butyl perbenzoate). Moreover, the azo compounds such as 2,2´azobisisobutyronitrile (AIBN) is most important member of this initiators class used for radical polymerization.

(b) Persulphate initiator system

In aqueous solutions, the persulphate ion is known as a strong oxidizing agent. It can be used either alone or with activators. The reaction proceeds via a free radical mechanism involving the decomposition of persulphate by using heat or reducing agents to produce sulphate radical.

(c) Redox initiator system (Odian 2004)

Redox initiator is an efficient method for graft polymerization. The redox reaction relates to both inorganic and organic components. An advantage of redox initiation is that radical production occurs at reasonable rate for wider range of temperature (273 - 323 K), which is depended on the particular redox systems. The redox initiations is normally used for graft copolymerization such as:

- Peroxide with combination of a reducing agent is a common source of radicals.
- The combination of various inorganic reductants and inorganic oxidizing agents to promote the radical polymerization

(d) Ionizing radiation

The ionizing radiation has been widely used to produce chemically active polymers for adsorption and separation processes. The irradiation of NR in the presence of vinyl monomers primarily leads a synthesis of graft copolymers, but some block copolymers are always occured. The ionizing radiation can be carried out in solution, emulsion or suspension. The monomers used in this process can be applied as liquid with or without a diluent or as vapor. The rubber may be pre-irradiated in the absence of air to produce free radicals for later monomer addition. However, the life of these radicals is short. Irradiation at very low temperature makes a possibility to use the trapped radicals technique for a variety of natural and synthetic rubbers. The graft polymer in the latex form is generally favored due to its simplicity. Thus, it can be seen that the graft copolymerization of vinyl monomers such as MMA, styrene (ST), acrylonitrile (ACN) and vinyl chloride (PVC) onto NR has been done in this way. The irradiation of organic macromolecules predominantly leads the formation of free radicals. The two available radiation sources are Co-60, which is commonly used in the radiation plants, and Cs 137. The Co-60 sources is relatively cheaper with 5.25 years of useful half lile.

2.3.3 Co-monomers

In polymer chemistry, a co-monomer refers a polymerizable precursor to a copolymer aside from the principal monomer to improve the properties and plastification of polymeric materials. Due to the different polarity of grafted polymer and main chain polymer, it causes the phase separation resulting in the difficulty of direct grafting. Thus, the use of co-monomer is required to promote the higher phase compatibility and grafting efficiency. There are some literatures studying the use of co-monomer for graft copolymerization. Sari et al., (2015) reported that the use of ST as the co-monomer for the graft copolymerization of ACN onto deproteinized natural rubber (DPNR) by free-radical emulsion polymerization to increases oil resistance. Without the addition of ST or ST content was lower than 1.5 wt% of total monomer, the latex coagulation was observed due to the imbalance of polarity in the latex. Therefore, the addition of ST higher than 1.5 wt% based on the total monomer content (DPNR/monomer = 70/30 (w/w)) provided the process stability. George et al. (2007) also grafted used ST and ACN onto the NR backbone using γ – ray initiation order to improve the percent grafting (PG) which was varied by change of NR/monomer (M) ratio in feed. The addition of ST could enhance the PG value decreasing the polarity difference between NR and ACN. Angnanon et al. (2011) was found that the ratio of ST/ACN at 3/1 (w/w) was a suitable ratio to increase the grafting efficiency for grafting on the NR backbone carried out in the solution state.

2.3.4 Applications of graft copolymerization

Graft copolymerization could be applied as the impact modifers or compatibilizers. The examples of graft copolymer are given below:

Hinchiranan et al. (2007) studied properties of modified acrylic sheet improved by the addition of graft NR (GNR) prepared by graft copolymerization of poly(MMA-*co*-ST) in the emulsion state initiated by potassium persulfate. The results showed that the impact resistance, tensile strength and elongation at break of the modified acrylic sheet increased from 34.6 to 107.6 kJ/m^2, 45 MPa to 62 MPa and 6% - 23%, respectively with increasing the amount of graft NR in the range of 0.5–4.0 parts. From the stress–strain behavior, the characteristics of the modified acrylic sheet shifted from brittle to ductile materials when the amount of graft NR increased.

Sookprasert and Hinchiranan (2015) investigated the Preparation of NR-graft-poly(lactic acid) (PLA) used as a compatibilizer for PLA/NR Blends. There were prepare two step, the first was NR was functionalized by various maleic anhydride (MAH) contents (5-20 phr) to produce NR-MAH and then NR-MAH was grafted with PLA.

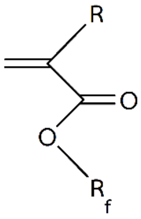
From the research found that The NR-MAH/PLA wt ratio at 1/1 provided the highest grafted PLA at 51%.

2.4 Fluorinated polymers and its properties

Fluorinate polymers are the polymer containing fluorine atoms in their backbone or side chain. The bond energy of C-F bond (131 kcal/mol) is higher than that of the C-H bond (99 kcal/mol) leading the greater thermal stability. The small van der Waals radius of fluorine atom promotes the strong C-F bonds with high electronegativity (He et al. 2011). Fluorinated polymers have many useful with interesting properties such as high thermal stability and weather resistance (Xu et al. 2013; Xiao and Wang 2009). They also have low surface free energy and the small dipole moment of C-F bond providing high contact angle for both water and oil (Jones 2008; Yang, Zhu, and Chen 2014). In addition, they have self-cleaning property, good permeability of oxygen gas, low values of dielectric constant and reflective index, low flammability with excellent inertness to solvent, hydrocarbons, acids and alkalies including low moisture adsorption (Zhang, Zhao, et al. 2011; Yao, Li, and Huang 2014). Thus, they have been widely used to improve the strength and thermal stability of other polymers. Generally, fluorinated polymers are derived from copolymer or homopolymer of fluorinated acrylate to improve the surface property due to trifluoromethyl (CF_3) cover on surface the substrate (Xu et al. 2013; Han et al. 2013; Chang et al. 2014).

Currently, fluorinated poly(meth) acrylates are used for various applications such as coating for chemical and water resistance, antifouling of coating and non-corrosive materials. Generally, they are classified as 2 types (Yao, Li, and Huang 2014):

1. Fluorinated alkyl (meth)acrylates: they are consisted of (meth)acrylates substituted with fluorinated alkyl groups as show in Figure 2.7.



R = H or CH_3

R_f = $(CH_2)_nCF_3$

$(CH_2)_n(CF_3)_{m-1}CF(CF_3)_2$

$(CH_2)_2X(CH_2)_m(CF_2)_nCF_3$ x = O, S

$(CH_2)_2NH(CH_2)_m(CF_2)_nCF_3$

$(CH_2)_2N(OH)(CH_2)_m(CF_2)_nCF_3$

Figure 2.7 Commercially available fluorinate alkyl (meth)acrylates (Yao, Li, and Huang 2014)

2. Fluorinated aryl (meth)acrylates: the monomers often contain an activated ester group with one or more fluorine substituents in aromatic ring, represented as pentafluorophenyl acrylate and methacrylate as presented in Figure 2.8.

Among the fluorinated polymers, 2,2,2-trifluoroethyl methacrylate (3FMA) is one of fluorinated polymers. Its chemical structure is shown in Figure 2.9. 3FMA is synthesized and formed as core-shell morphology by copolymerized with other monomers such as MMA and butyl acrylate (BA) (Chang et al. 2014; Boschet et al. 2010). The most literatures reported that fluorine-containing acrylic copolymer emulsions are water-borne latex with environmental friendly property and they can be applied in coating or adhesive industries (Han et al. 2013; Xu et al. 2013).

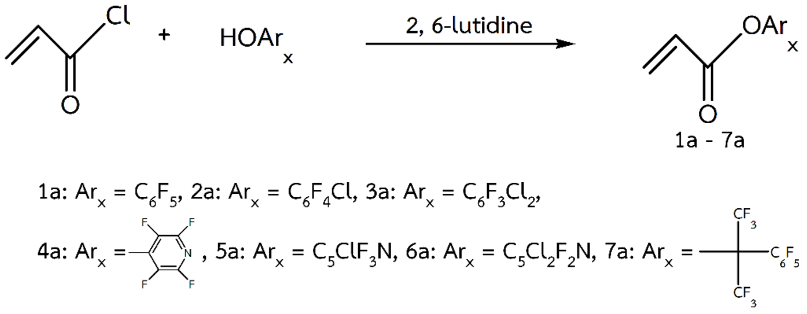


Figure 2.8 Fluorinated aryl (meth)acrylate (Yao, Li, and Huang 2014).

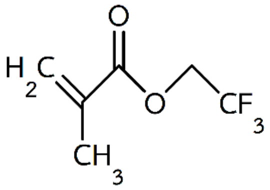


Figure 2.9 The structure of 2,2,2-trifluoroethyl methacrylate (3FMA).

Nevertheless, fluorinated polymers have limited since they are expensive and they have poor mechanical properties such as low flexibility, poor film formation due to its high brittleness (Zhang, Zhao, et al. 2011; Ozbay and Erbil 2014; Xu et al. 2016; Wang et al. 2015).

The copolymerization of fluorinated acrylates with other monomers and blending fluorine-containing acrylate polymers with fluorine-free acrylate polymers (Wang et al., 2015) is an appropriate way to overcome these disadvantages. The copolymerization of fluorinated acrylate with other cheaper monomer such as MMA, BA and methyl acrylate (MA) were achieved by block copolymerization, graft copolymerization (Tan et al. 2015), random copolymerization (Xu et al. 2016) and core-shell copolymerization (Yang, Zhu, and Chen 2014; Wei et al. 2011).

2.5 **Compatibilization** (Utracki 1998; Shonaike and Simon 1999)

Compatibilizers are usually required for promote the compatibilization of blends containing immiscible polymeric constituents the interfacial energy between their phases and leading the creation of a polymer alloys with enhanced their properties performance. The compatibilizers normally applied into the incompatible blends are random copolymer, diblock copolymer, triblock copolymer or graft copolymer (De Guzman et al. 2011) show as Figure 2.10.

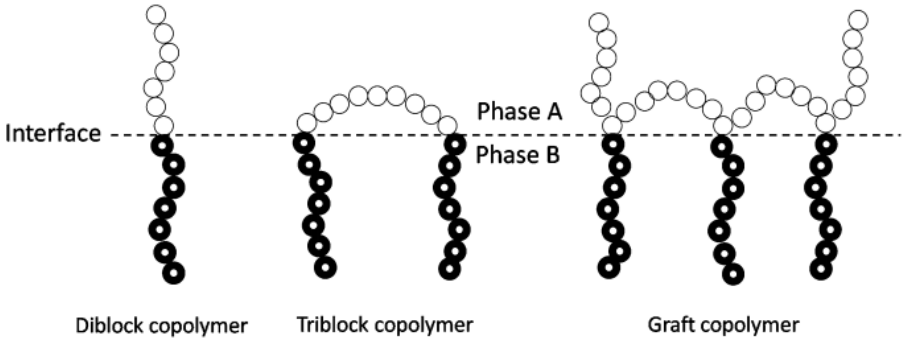


Figure 2.10 Ideal location of diblock, triblock, and graft copolymers at the interface of an immiscible A/B polymer blend (Zeng, Li, and Du 2015).

The compatibilizer possibly affects the properties of final products as followed (Angnanon, Prasassarakich, and Hinchiranan 2011):

1. Reduction of the interfacial tension resulting in the formation of finer dispersed phase.

2. Increase in the adhesion at phase boundaries giving the improved interface in the solid state.

3. Stabilization of the dispersed phase by reducing the rate of domain coalescence during melts processing and annealing.

The method of compatibilization has been proposed as followed (Folkes 1993):

1. Thermodynamic miscibility is the method using a balance of enthalpic and entropic contributions to the free energy of mixing. It is a main idea to produce commercial blends.

2. Addition of block or graft copolymers is popular technique to enhance the compatibilization of blends. The block and graft copolymers contain chemically identical segments to the blend components. Thus, they can be applied as compatibilizers to increase the miscibility between the copolymer segments and the corresponding blend components. The mechanical properties of the compatibilized

blends were improved resulting from the higher degree of dispersion and adhesion between the polymeric component phases in the blends.

3. Addition of functional polymers having the reactive units for increasing the affinity for other components is also the technique to increase the compatibility of the blends. The modification via functionalization may be achieved in a reactor or during an extrusion-modification process. Functionalized polymers (usually maleic anhydride or acrylic acid grafted polyolefins) are commercially available with acceptable cost for using as the compatibilizers for the polymer blends.

4. Reactive blendingis the method to blend the polymers having reactive sites to form crosslink during melt mixing process without the addition of another compatibilizer. The example materials used in the reactive blending process are graft or block copolymers to generate the *in situ* crosslink formation.

The use of graft copolymers is another possible route for the control of the phase morphology and the mechanical properties of immiscible polymer blends. The addition of a compatibilizer is an alternative method to improve toughness of the final product because it can react with one phase and physically interact with another phase resulting the improvement of adhesion between the rubber and plastic phases in the production of thermoplastic elastomers.

2.6 Literature Reviews

Wang et al. (2000) modified the NR latex films surface via graft copolymerization of 2,2,3,3,4,4,4-heptaflurobutyl acrylate (HFA) via UV – induced method to enhance the film hydrophobicity (water contact angle of modified film = 109°).

Liu et al. (2010) modified the ramie fibers via reversible addition- fragmentation chain transfer (RAFT) with graft copolymerization of 3FMA in supercritical carbon dioxide ($scCO_2$). The hydrophobicity of the modified ramie fibers was increased as seen from the larger water contact angles from 135°to 149°. Size exclusion chromatography also showed that the grafted poly(3FMA) (P3FMA) exhibited the narrow polydispersity (PDI = 1.28).

Guo et al. (2010) studied the graft copolymerization of P3FMA onto silicone rubber (MVQ-*g*-3FMA) for using as the compatibilizer for fluororubber (FKM) and silicone rubber (MVQ) (FKM/MVQ) blends. From the dynamic mechanical analysis (DMA), it was found that the addition of 6 phr MVQ-*g*-P3FMA could improve the phase separation be enhancing interfacial interaction of polymeric phases in the blends. It was observed that the mechanical properties of FKM/MVQ blend (50/50 (w/w)) having 6 phr MVQ-*g*-P3FMA were better than those of one without the addition of compatibilizer. The tensile strength, elongation at break and tear strength of compatibilized blends were 8.8 MPa, 410% and 20.9 kN/m, respectively which were higher than those of uncompatibilized ones having 5.4 MPa tensile strength and to 347% elongation at break with 14.6 kN/m tear strength due to the improved interfacial interaction of blend. Moreover, heat aging properties, oil resistance, low temperature properties and rubber–filler interaction of fumed silica - flled FKM/MVQ blends were also improved by the addition of MVQ-*g*-P3FMA.

Liang et.al (2010) synthesized fluorinate acrylate copolymer core - shell latexes by emulsion polymerization. This research focused on three fluorinate acrylate monomers such as 3FMA, hexafluorobutyl methacrylate (HFBM) and dodecafluoroheptyl methacrylate (DFHM). The result showed that the monomer having higher content of fluorine atom provide the final polymer with better thermal stability. Moreover, the contact angle of films product produced from the monomer with high amount of fluorine atom was higher reflecting the greater hydrophobicity.

Hinchiranan et al. (2013) investigated graft copolymerization of P3FMA onto NR backbone via melt – mixing process without the assistance of co-monomer. The obtained graft product was applied as the compatibilizer for NR/fluoroelastomer vulcanizates. Although this technique was easy for commercialization, the high reaction temperature was required (> 80 °C), which could promote the high level of gel formation (gel content = ca. 20 – 90%) in the obtained graft product with only 1.34% maximum grafting efficiency.

Wang et al. (2015) studied the surface wettability of fluorinated (FA) and non-fluorinated polyacrylate (NFA) latex blend films. The perfluoroalkyl ethyl methacrylate was used as a fluorinated acrylate monomer. MMA, BA and n-methylol acrylamide (N-MA) were used as non-fluorinated acrylate monomers. The latex were prepared by emulsion polymerization. FA with various number of fluorine atom and NFA latex were blended with various wt ratios to form the blend film. The water and oil contact angles of the obtained film were in the range of 85.4° - 116.7° and 29.0° - 92.8°, respectively. It was found that the increase in the contents of FA in the mixed latex provide the film with higher water and oil contact angles. This indicated that the surface wettability of the films decreased with increasing the amount of fluorine monomer.

Tan et al. (2016) studied the preparation of waterborne UV-curable comb-shape acrylate graft copolymer containing long fluorinated side chain. This system was performed by conventional radical graft copolymerization of mono-methacryloyloxy terminated fluorinated macromonomer (PHFA-GMA) onto (meth)acrylate copolymer backbone. It was found that the surface energy of the grafted film drastically decreased from initially 37 (mN/m) to 31 (mN/m) when the content of PHFA-GMA was 0.125 wt%.

Qu and He (2013) studied the synthesis and properties of silane- fluoroacrylate grafted with starch performed in the emulsion state. The first step of graft copolymerization was the grafting of vinyltrimethoxysilane (VTMS) onto starch to form VTMS - starch. Then, the graft product was mixed MMA, BA and 3FMA at ratio of 3/4/3. MMA/BA/3FMA to form core – shell latex. It was observed that the VTMS – starch acted as a core of the particles, while the poly(MMA/BA/3FMA) was the shell phases. The result showed that the obtained latex had the narrow particle size distribution. After casting, the film product had both hydrophobicity and lipophobicity with high water contact angle (107°) and cetane contact angle (25.0°), respectively. Moreover, low this film had surface energy (25.19 mN/m) with high thermal stability (330 – 440 °C).

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

High ammonia preserved natural rubber latex (NR) containing 60% dry rubber content (DRC) was purchased from Rubber Research Institute, (Bangkok, Thailand). 2,2,2-Trifluoroethyl methacrylate (3FMA) monomer with 99% purity was obtained from Sigma Aldrich (USA) and used as received. Butyl acrylate (BA) monomer (99% purity, Merck, USA) was purified with 10% sodium hydroxide (NaOH, QREC, New Zealand) to remove inhibitor. Sodium dodecyl persulfate (SDS) and isopropanol (IPA) were purchased from QREC (New Zealand). Potassium hydroxide (KOH) and potassium persulfate (KPS) used as the buffer and initiator, respectively for graft copolymerization were received from Ajax Finechem (Australia). Toluene, acetone and light petroleum ether were obtained from Fisher Scientific (Leicestershire, UK). All chemicals used in this research were analytical grade. Nitrogen gas (commercial grade with 95% purity) was manufactured by Prexair, Inc. (Thailand).

3.2 Graft copolymerization of poly(BA-*co*-3FMA) onto NR Latex

Graft copolymerization of NR with poly(BA-*co*-3FMA) in the latex stage was carried out in a 100 mL three-necked round-bottle flask. NR latex was diluted by using distilled water to achieve 30% DRC. The NR solution was then mixed with 0.25 parts per hundred of rubber (phr) KOH and 0.1 phr SDS. The mixture was stirred under nitrogen atmosphere at room temperature. After 15 min, 10 phr IPA was added as the stabilizer under stirring for 30 min. Then, 100 phr BA/3FMA monomer mixture at various BA/3FMA wt ratios was charged into the system under stirring followed by heating the system to desired reaction temperature (50 – 80 °C). The graft copolymerization was than initiated by introducing KPS at given concentrations (0.5 – 2.0 phr). The reaction was allowed for 4 -10 h. After the completion of grafting, the graft product in the latex form was casted on the glass mold (10 × 10 × 0.3 cm^3) and left in a vacuum oven at 40 °C for drying. Then, the casted graft NR were washed with distilled water to remove the unreacted monomers and dried at 40 °C in the vacuum oven until the constant weight of the casted graft product was reached. The components of the dry casted product such as free NR, ungraft copolymer and NR grafted with poly(BA-*co*-3FMA) (NR-*g*-poly(BA-*co*-3FMA)) sections were distinguished by using soxhlet extraction technique. The ungraft NR and copolymer portions were removed by using light petroleum ether and acetone, respectively for 24 h and then dried at 40 °C in a vacuum oven for each extraction step until a constant weight was received. The final product, NR-*g*-poly(BA-*co*-3FMA), would be obtained.

3.3 Synthesis of poly(BA-*co*-3FMA) latex

To compare the chemical structure of the grafted poly(BA-*co*-3FMA) in the graft NR, the poly(BA-*co*-3FMA) was also synthesized via emulsion copolymerization. Under nitrogen atmosphere, the system was conducted in a 100 mL round bottle containing 0.09 g KOH, 0.036 g SDS and 0.36 g IPA dissolved in the distilled water (18 mL). The 30/70 (w/w) BA/3FMA monomer mixture (3.6 g) was gradually dropped into the system under stirring. The amount of all chemicals used in this section was similar to the Section 3.2. When the reaction temperature reached to 60 °C, the reaction was initiated by charging 0.054 g KPS and allowed for 8 h to complete the reaction. The obtained copolymer latex was then casted on the glass mold (10 × 10 × 0.3 cm^3) and dried under vacuum at 40 °C for 24 h (yield = 92.3%).

3.4 Preparation of NR/poly(BA-*co*-3FMA) films with the addition of graft NR

The NR latex containing 30% DRC was mixed with the of poly(BA-*co*-3FMA) latex and graft NR. The ratio of NR/poly(BA-*co*-3FMA) was kept constant at 20/80 (w/w), while the amount of graft NR was varied in the range of 0 – 20 wt% based on the NR/poly(BA-*co*-3FMA) content. The latex mixture was then directly casted on the glass mold (10 × 10 × 0.3 cm^3) without the use of any solvents and drided under vacuum at 40 °C for 24 h or until weight constant was received. The thickness of the obtained film was ca 0.2 ± 0.0061 cm.

3.5 Characterizations

3.5.1 Structural characterization and evaluation of grafting efficiency

The chemical structure of NR and graft NR obtained after soxhlet extraction was characterized by using attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) recorded from the wavelength of 500 cm^{-1} to 4,000 cm^{-1} (Nicolet Magna 750 FT-IR spectrometer equipped with a liquid-nitrogen-cooled mercury-cadmium-telluride (MCT) detector).

According to avoidance of gel formation affecting the calculation of grafting properties, the mole and weight percentages of 3FMA and BA in the graft NR obtained from the soxhlet extraction were evaluated from fluorine-19 (^{19}F-NMR) and proton (^{1}H-NMR) nuclear magnetic resonance spectroscopy (Bruker:Avance III HD 500 MHz, USA) which the peak areas of ^{1}H NMR spectra for the olefinic proton of NR at 5.05 ppm (Saramolee, Lopattananon, and Sahakaro 2014), methylene proton of 3FMA at 4.28 ppm and methylene proton of BA at 3.94 ppm (Zhang, Zhao, et al. 2011) following Eq. 3.1–3.6, which were adapt from the previous literatures (Hinchiranan et al. 2013; Saramolee, Lopattananon, and Sahakaro 2014):

$$C_{3FMA} = \frac{(S_1/2)}{S_0 + (S_1/2) + (S_2/2)} \times 100 \qquad (3.1)$$

$$C_{BA} = \frac{(S_2/2)}{S_0 + (S_2/2) + (S_1/2)} \times 100 \qquad (3.2)$$

$$C'_{3FMA} = \frac{(M_{3FMA} \times C_{3FMA})}{(M_{3FMA} \times C_{3FMA}) + (M_{BA} \times C_{BA}) + M_{NR}(100 - C_{3FMA} - C_{BA})} \times 100 \qquad (3.3)$$

$$C'_{BA} = \frac{(M_{BA} \times C_{BA})}{(M_{3FMA} \times C_{3FMA}) + (M_{BA} \times C_{BA}) + M_{NR}(100 - C_{3FMA} - C_{BA})} \times 100 \qquad (3.4)$$

where C and C' are mol% and wt%, respectively of 3FMA and BA in the graft NR. M is defined as the molecular weight of the repeating unit of polymeric composition in the graft copolymer (M_{NR} = 68 g/mol, M_{3FMA} = 168.11 g/mol and M_{BA} = 128.17 g/mol). The S_0, S_1 and S_2 are integrated peak areas in the ^{1}H NMR spectra of the olefinic proton of NR at 5.05 ppm, methylene proton of 3FMA at 4.28 ppm and methylene proton of BA at 3.94 ppm, respectively.

The monomer conversion could be calculated following Eq. 3.5. The total content of the poly(BA-*co*-3FMA) formed was then applied for calculation of %GE as shown in Eq. 3.6 (Zhang, Man, et al. 2011)

$$\%Conversion = \frac{\text{Weight of total polymer fromed}}{\text{Weight of monomer charged}} \times 100 \qquad (3.5)$$

$$\%GE = \frac{\text{Weight of grafted poly(BA-}co\text{-3FMA)}}{\text{Weight of total poly(BA-}co\text{-3FMA) formed}} \times 100 \qquad (3.6)$$

3.5.2 Particle size distribution and morphology analysis of NR latex before and after graft copolymerization

The particle size distribution of NR and graft NR was comparatively measured by using a particle size analyzer (Nano track 252, USA). The latex samples (30% DRC) were diluted with deionized water (latex/deionized water = 1/10 (w/w)) in an appropriate container as indicated by instruments before analysis.

The morphology of NR particles before and after graft copolymerization was observed by using transmission electron microscope (TEM) (Model JEM–100CXII, Japan) with an acceleration voltage of 120 kV. One drop (ca. 1 mL) of the emulsion (30% DRC) was diluted by using 300 mL deionized water and placed on a carbon-coated copper grid. For the graft latex, it was stained with 1.0 wt% phosphatotungstic acid (PTA) (a negative stain), while the NR latex was stained with 1.0 wt% osmium tetroxide (OsO_4) (a positive stain). After staining, the samples were dried in air before observation (Chang et al. 2014; Wei et al. 2011).

3.5.3 Measurement of contact angle and calculation of surface energy of NR/poly(BA-*co*-3FMA) films with and without the addition of GNR

The water and hexadecane contact angle of the NR/poly(BA-*co*-3FMA) films containing various GNR contents (%GE = 69.4) obtained from Section 3.2 was measured by using a microscope equipped with a Kruss (DSA 10 MK2, Germany) at room temperature. The injection volume of deionized water or hexadecane represented as oil was controlled as 0.5 µL. The average of five readings on the different regions of each film was used as the final contact angle of each samples. The surface free energy (γ) of the samples was then calculated following Eq. 3.9 and 3.10 (Wei et al. 2011):

$$(1+\cos\theta)=2[(\gamma_L^d\gamma_S^d)^{1/2}+(\gamma_L^p\gamma_S^p)^{1/2}] \tag{3.7}$$

$$\gamma = \gamma_s^d + \gamma_s^p \tag{3.8}$$

where θ is the static contact angle of the liquid on the film surface; γ_L and γ_s are the surface tensions of the liquid and solid, respectively; γ_L^p and γ_s^p are the polar components of the liquid and solid surface tension, respectively; γ_L^d and γ_s^d are dispersive components of the liquid and solid surface tension, respectively. γ_s^d and γ_s^p are calculated from the contact angles, surface tension and dispersion and polar components of water (γ_L = 72.8 mN/m, γ_L^d = 21.8 mN/m and γ_L^p = 51.0 mN/m) and hexadecane (γ_L = 21.6 mN/m, γ_L^d = 27.6 mN/m and γ_L^p = 0 mN/m) (Wei et al. 2011).

3.5.4 Glass transition temperature of NR/poly(BA-*co*-3FMA) films with and without the addition of GNR

The glass transition temperature (T_g) of samples was measured by using differential scanning calorimetry (DSC) (Mettler Toledo, 822, Thailand Ltd.) under nitrogen atmosphere at a heating rate of 10 °C/min^{-1} from -100 to 100 °C. The T_g of each sample was determined from the mid-point of the base-line shift of the DSC thermogram.

3.5.5 Mechanical properties of NR/poly(BA-*co*-3FMA) films with and without the addition of GNR

The tensile properties of the NR/poly(BA-*co*-3FMA) films with and without the addition of graft NR were measured with an universal testing machine (INSTRON 3366). The sample was cut as dumbbell shape following ISO 37 (type 2) with 10 mm original gauge length in the chamber with a constant temperature at 25 °C. The crosshead speed was controlled as 50 mm/min (Suksawad, Yamamoto, and Kawahara 2011). The results of tensile properties of the obtained films were the compared with those of parafilm M® film normally used as the self–sealing film covering laboratory glassware.

3.5.6 Compatibility testing

The role of graft NR used as the compatibilizer for NR and poly(BA-*co*-3FMA) phases in the blended films was confirmed by using Molau testing technique and surface topology analyzed by atomic force microscope (AFM, Asylum research, USA)

For the Molau test, the film obtained from Section 3.2 (0.03 g) were dissolved in 6 mL acetone in test tubes at room temperature for 24 h. The turbidity reflecting the compatibilization of the resulting solution was then observed (Carone et al. 2000; Yang et al. 2012).

For the AFM measurement, the obtained NR/poly(BA-*co*-3FMA) films with and without compatibilization by GNR (from Section 3.4) in the dimension of 1 × 1 × 0.2 cm^3 were placed on the glass slides. The surface topology of the obtained films was measured by using Asylum research, UK and simultaneously captured under the tapping mode (scan side = 50 μm and scan rate = 0.3 Hz). The average roughness (R_a) of samples was then calculated (Wang 2000).

3.5.7 Oil resistance testing of films

For the oil resistance, the films obtained from Section 3.4 (2 × 2 × 0.2 cm^3) were immersed in 10 mL hexadecane at room temperature for 10 min. The characteristics of films after immersion were observed and also compared with Parafilm M®.

CHAPTER IV

RESULTS AND DISSCUSSION

4.1 Structural characterization of NR before and after graft copolymerization

After graft copolymerization, the obtain graft NR (GNR) latex. To evaluate the amount of each part in GNR, the extraction was applied to distinguish the graft part, free NR and free copolymer. The soxhlate extraction, the chemical structure of natural rubber (NR) grafted with poly(butyl acrylate (BA)-*co*-2,2,2-trifluoroethyl methacrylate (3FMA)) (NR-*g*-poly(BA-*co*-3FMA)) was characterized and compared with that of NR and poly(BA-*co*-3FMA) by using ATR-FTIR and NMR techniques. Figure 4.1. shows the ATR-FTIR spectra of NR, poly(BA-*co*-3FMA) and NR-*g*-poly(BA-*co*-3FMA). For the NR structure, Figure 4.1a exhibits the characteristic peaks of C-H streching at 2,849 - 2,967 cm^{-1}, -CH$_2$ distortion vibration at 1,446 cm^{-1}, C=C stretching peak at 1,684 and C=C bending at 833 cm^{-1} (Angnanon, Prasassarakich, and Hinchiranan 2011; Zhang, Man, et al. 2011; Xu et al. 2013).

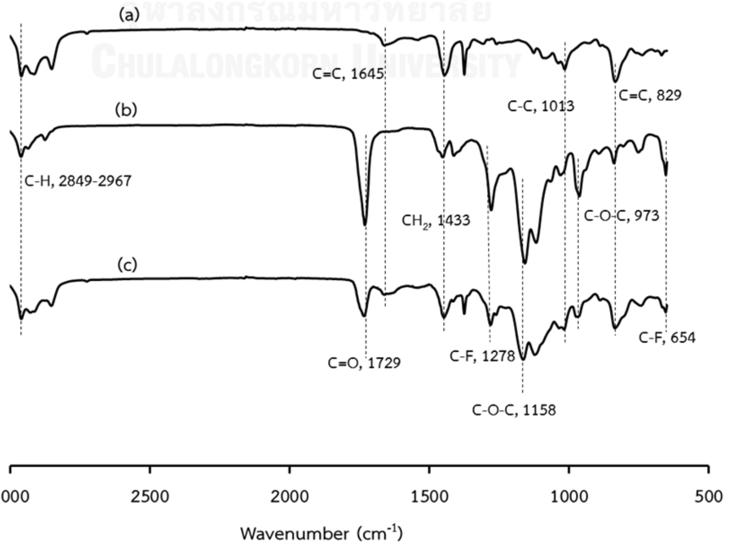


Figure 4.1 ATR-FTIR spectra of (a) NR, (b) poly(BA-*co*-3FMA) and (c) NR-*g*-poly(BA-*co*-3FMA) (68.5 %GE).

To consider the poly(BA-*co*-3FMA) spectrum, Figure 4.1b shows the strong peak absorptions at 1,731 cm^{-1} and 1,164 cm^{-1} attributed to the stretching vibration of carbonyl group (C=O) and the asymmetric stretching of C-O-C, respectively. Moreover the peaks at 1,281 cm^{-1} and 654 cm^{-1} corresponded to C-F group of 3FMA (He et al. 2011; Chang et al. 2014) and 973 cm^{-1} corresponded to C-O-C of BA structure (Hao et al. 2012; Qu and He 2013) were also observed. For the graft copolymer (NR-*g*-poly(BA-*co*-3FMA)), Figure 4.1c shows the strong fluorine peak C-F (-CF_3 group) stretching vibration band around 1,281-1,278 cm^{-1} and 654 cm^{-1}, which confirmed the presence of the 3FMA units in the structure of graft copolymer (Hao et al. 2012; Zhou, Zhang, and Ma 2013).

To confirm the ATR-FTIR result, the chemical structure of NR before and after graft copolymerization with poly(BA-*co*-3FMA) was analyzed by ^1H NMR and ^{13}F NMR spectroscopy. For ^1H NMR spectra, Figure 4.2a shows the chemical shifts of NR at 1.61 ppm, 1.97 ppm and 5.05 ppm, which were attributed to the unsaturated -CH_3 (c), unsaturated -CH_2 (b) and olefinic proton (a), respectively (Zhang, Man, et al. 2011; Saramolee, Lopattananon, and Sahakaro 2014). Whereas, the structure of poly(BA-*co*-3FMA) (Figure 4.2b) indicated the chemical shifts at 3.94 ppm (d) and 4.37-4.27 ppm (h), which were corresponded to -OCH_2 in BA (Xiao and Wang, 2009) and –OCH_2 in 3FMA (Boschet et al. 2010; Xu et al. 2016), respectively. Furthermore, the other characteristic peaks of –CH at 2.11 ppm (b), -CH_2 at 1.78 ppm (c) and 1.29 ppm (f) and -CH_3 at 1.52 ppm (c) and 0.86 ppm (g) were observed. For the chemical structure of NR-*g*-poly(BA-*co*-3FMA), Figure 4.2c indicates the chemical shifts at 5.05 ppm (a), 3.94 ppm (d) and 4.37-4.27 ppm (h), which were similar to those of NR and poly(BA-*co*-3FMA) structures.

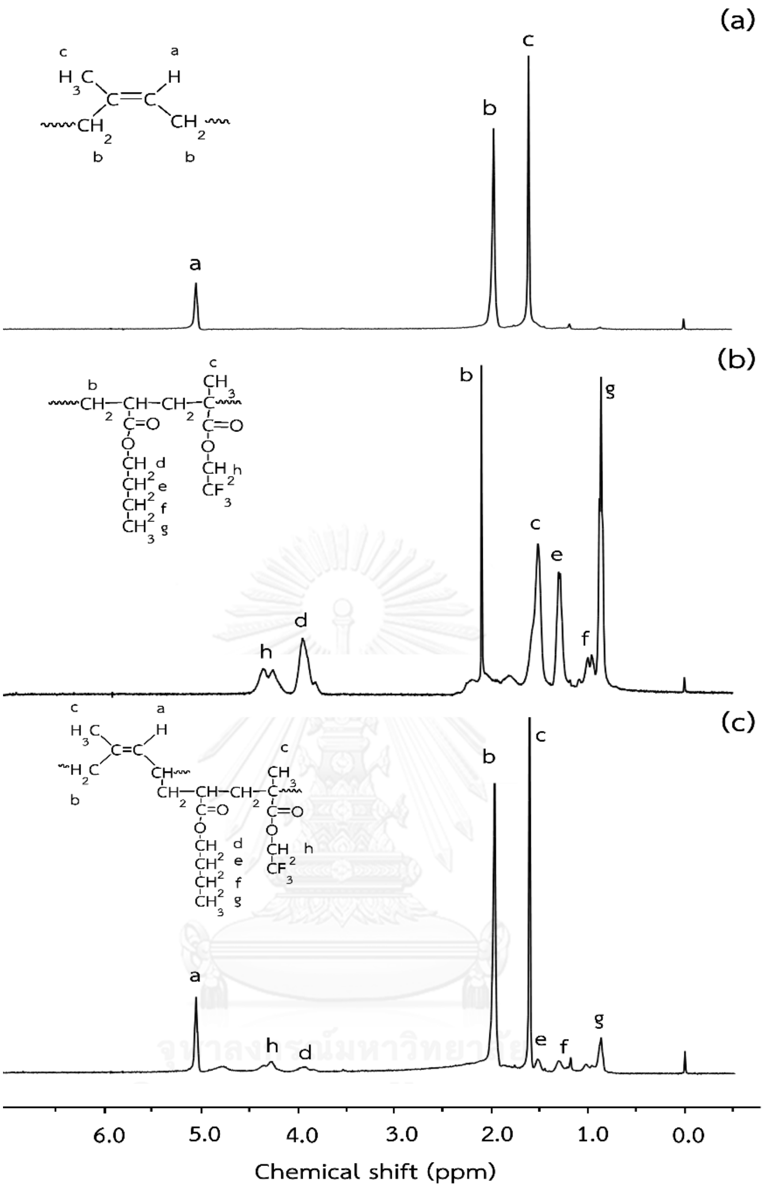


Figure 4.2 ^{1}H NMR spectra of (a) NR, (b) poly(BA-co-3FMA) and (c) NR-g-poly(BA-co-3FMA) (68.5 %GE)

Moreover, the ^{13}F NMR spectra as illustrated in Figure 4.3 exhibited the signal at -74.54 ppm corresponded to –CF_3 group in 3FMA structure (Zhang, Zhao, et al. 2011; Xu et al. 2016) for both poly(BA-*co*-3FMA) (Figure 4.3a) and NR-g-poly(BA-*co*-3FMA) (Figure 4.3b). These results confirmed that the poly(BA-*co*-3FMA) was successfully grafted onto the NR backbone.

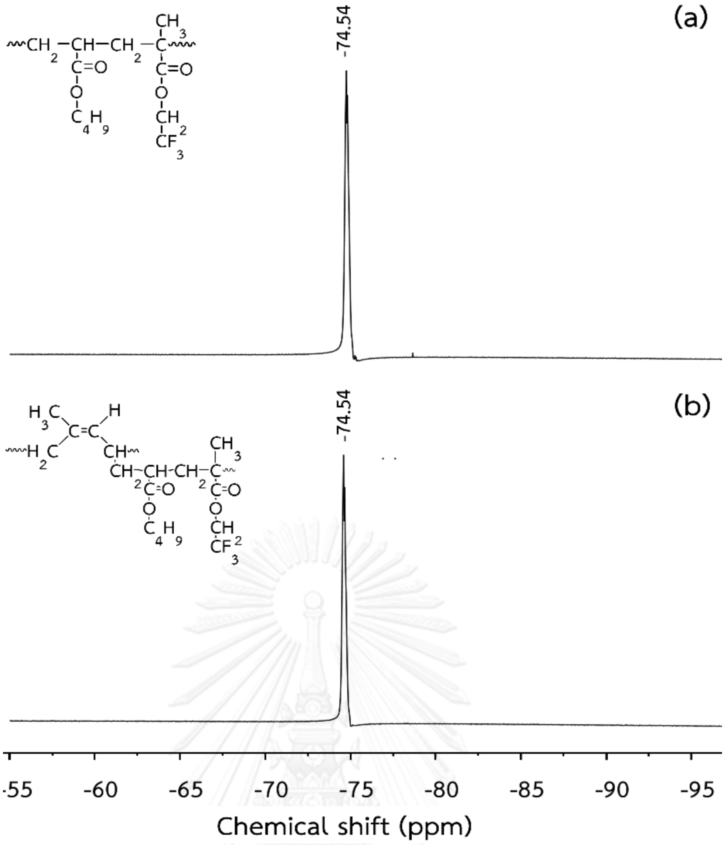


Figure 4.3 ^{13}F NMR spectra of (a) poly(BA-*co*-3FMA) and (b) NR-*g*-poly(BA-*co*-3FMA) (68.5 %GE).

4.2 Effect of reaction parameters on graft copolymerization of poly(BA-*co*-3FMA) onto NR backbone

3.2.1 BA/3FMA wt ratio

The effect of BA/3FMA wt ratio on the monomer conversion, grafting properties, GE and the contents of BA and 3FMA portions in the NR-*g*-poly(BA-*co*-3FMA) analyzed by ^{1}H NMR spectroscopy was presented in Figure. 4.4. The reaction condition was controlled at 1.5 phr initiator concentration and 100 phr monomer mixture at 60 °C for 8 h. Without the addition of BA, Figure 4.4a showed that the level of monomer conversion was ca. 60% with only 5.3% grafting effiency (GE). This implied that the

3FMA monomer was converted as homopolymer resulted in the high amounts of free copolymer (35.6 wt%) and free NR (45.1 wt%) as shown in Figure 4.4b. This was due to the effect of polarity difference between NR and 3FMA. For the 5.3 %GE, the content of grafted poly(3FMA) (P3FMA) in the NR-*g*-poly(BA-*co*-3FMA) was calculated as 14.5 mol%. To consider the use of only BA, Figure 4.4a showed the higher monomer conversion at 85.6% with high %GE (63.2%). This indicated that BA had higher reactivity to be grafted onto the NR backbone than 3FMA.

From the previous literature, Chang et al. (2013) reported that the BA and 3FMA copolymer could be successfully co-polymerized. Thus, it was possible to apply BA as a co-monomer for grafting 3FMA onto the NR structure. From the results presented in Figure 4.4a, it was observed that the increase in the BA content in the BA/3FMA monomer mixture from 10/90 to 30/70 (w/w) provided the higher levels of both monomer conversion and GE from 67.8% to 83.2% and 31.4% to 68.5%, respectively resulted from the enhancement of NR-*g*-poly(BA-*co*-3FMA) with the reduction of the ungrafted NR and free copolymer contents (Figure 4.4b). The amounts of 3FMA in the grafted portion also increased from 16.0 to 25.2 mol% (Figure 4.4c). This implied that the BA was initially grafted onto NR structure and 3FMA was then co-polymerized with the prior graft BA to form grafted poly(BA-*co*-3FMA).The use of co-monomer to increase the degree of grafting was also reported in the systems of grafting ‘‘from’’, grafting ‘‘onto’’ (Bhattacharya and Misra 2004a) and grafting ‘‘through’’(Shi et al. 2013) which the desired polymer could not be easily grafted onto the substrate possibly due to the polarity mismatch resulting in the phase separation of applied polymer and substrate backbone.

However, the increase in the BA content higher than 30/70 (w/w) BA/3FMA slightly decreased the level of monomer conversion (68.2%) with significant reduction of GE value to 36.5% when the ratio of BA/3FMA was 90/10 (w/w). This was due to the self-polymerization or chain transfer (Thiraphattaraphun et al. 2001;

Nakason et al. 2006; Wongthong et al. 2013) of excess BA monomer resulted in the higher content of ungrafted poly(BA) with the inhibition of poly(BA-*co*-3FMA) formation. Figure 4.4c also showed that the amount of 3FMA in the NR-*g*-poly(Ba-*co*-3FMA) portion decreased to 10.1 mol% at 90/10 (w/w) BA/3FMA ratio.

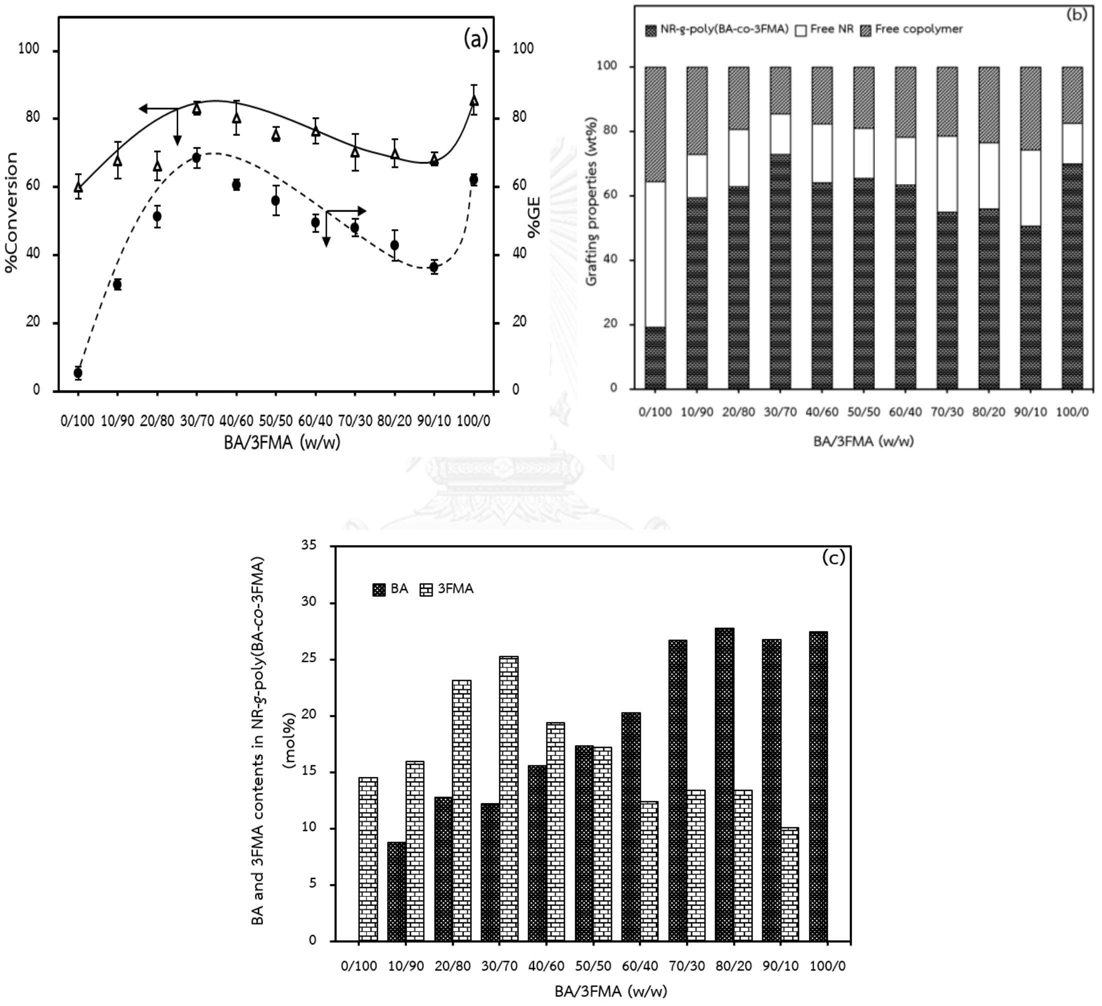


Figure 4.4 Effect of BA/3FMA monomer ratio on (a) % conversion and %GE, (b) grafting properties and (c) BA and 3FMA contents in the NR-*g*-poly(BA-*co*-3FMA) by using 1.5 phr KPS at 60 °C for 8h.

3.2.2 Effect of the initiator concentration

The effect of potassium persulphate (KPS) initiator on the monomer conversion, GE, grafting properties, portions of grafted BA and 3FMA in the NR-*g*-poly(BA-*co*-3FMA) was investigated as shown Figure 4.5.

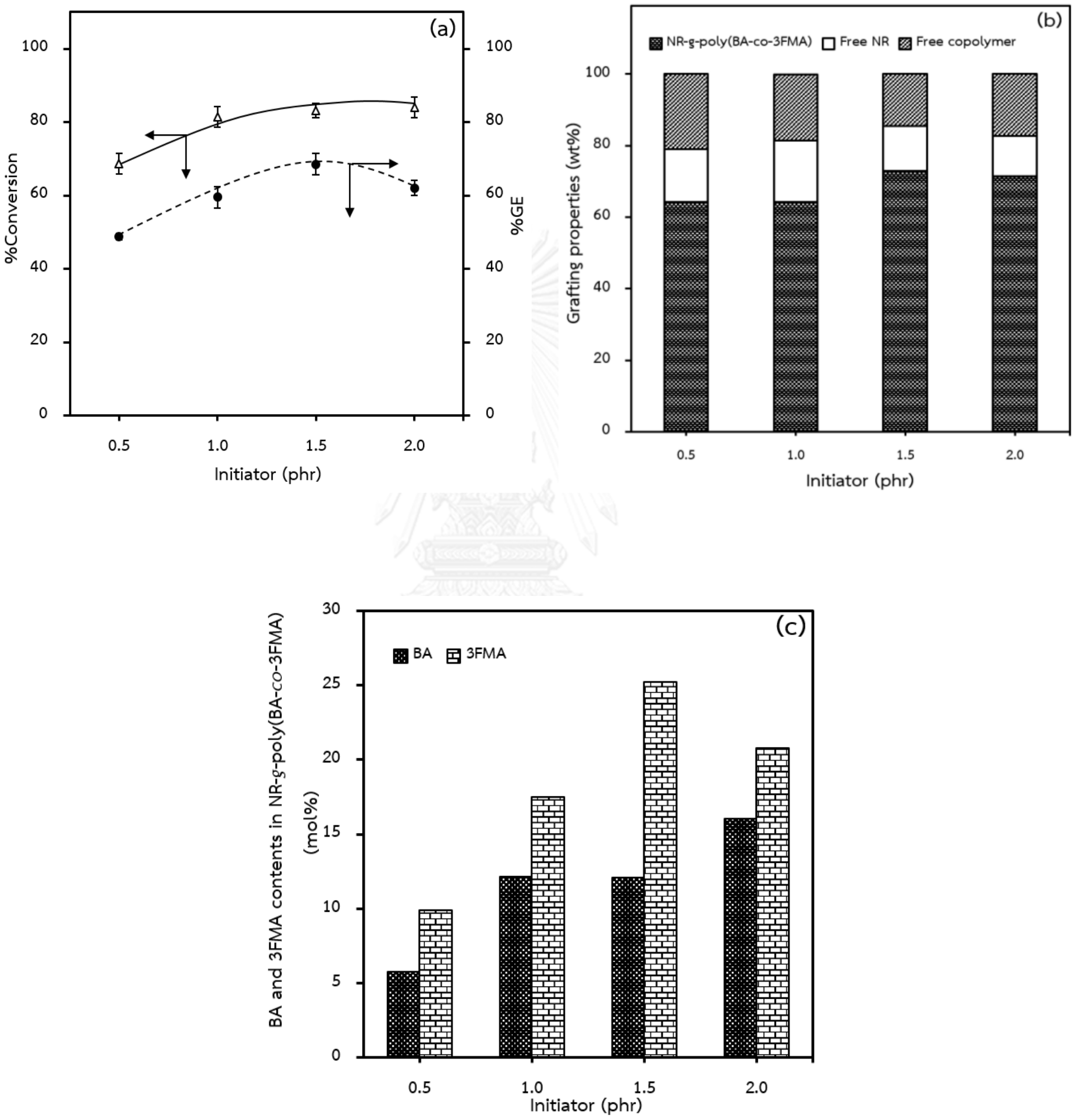


Figure 4.5 Effect of initiator concentration on (a) %conversion and %GE, (b) grafting properties and (c) BA and 3FMA contents in the NR-*g*-poly(BA-*co*-3FMA).

The concentration of KPS was varied in the range of 0.5 – 2.0 phr when the BA/3FMA ratio, reaction temperature and reaction time were kept content at 30/70 (w/w), 60 °C and 8h, respectively. Figure 4.5a showed that the increase in the initiator content from 0.5 to 2.0 phr increased the degree of conversion to 84%. It was observed that the maximum GE value at 68.5% was achieved when the initiator content at 1.5 phr was applied. Above this point, the GE decreased to 62.1% with the higher amount of free copolymer (Figure 4.5b). Moreover, the amount of 3FMA in the NR-*g*-poly(BA-*co*-3FMA) portion was maximized at 25.2 mol%. This could be explained that the sufficient amount of free radicals could enhance the rate of graft copolymerization (Angnanon, Prasassarakich, and Hinchiranan 2011; Kangwansupamonkon, Gilbert, and Kiatkamjornwong 2005; Arayapranee and Rempel 2008). However, the overdose of free radical generated from the high initiator content promoted the recombination resulting in the termination of grafting reaction. In addition, the excess free radicals provided the higher possibility to react with monomers and produce the free copolymer (Thiraphattaraphun et al. 2001; Kangwansupamonkon, Gilbert, and Kiatkamjornwong 2005).

3.2.3 Effect of the reaction temperature

The temperature is one of important factors that control the kinetics of graft copolymerization (Bhattacharya and Misra, 2004). The effect of reaction temperature on graft copolymerization of poly(BA-*co*-3FMA) onto NR was shown in Figure 4.6. The reaction temperature was varied in the range of 50 - 80°C. The BA/3FMA ratio was controlled as 30/70 (w/w) initiated by 1.5 phr KPS content for 8h. It could be seen that the increase in the reaction temperature to 80°C provided the highest monomer conversion ca. 86.1% (Figure 4.6a). Since the dissociation temperature of KPS was 50°C (Van herk and Monteiro, 2002; 30), the increase in the reaction temperature above this point could promote the high content of free radicals for grafting. At the 60°C, it was the suitable reaction temperature for providing the maximum 3FMA content in the grafted portion (25.2 mol%) (Figure 4.6c).

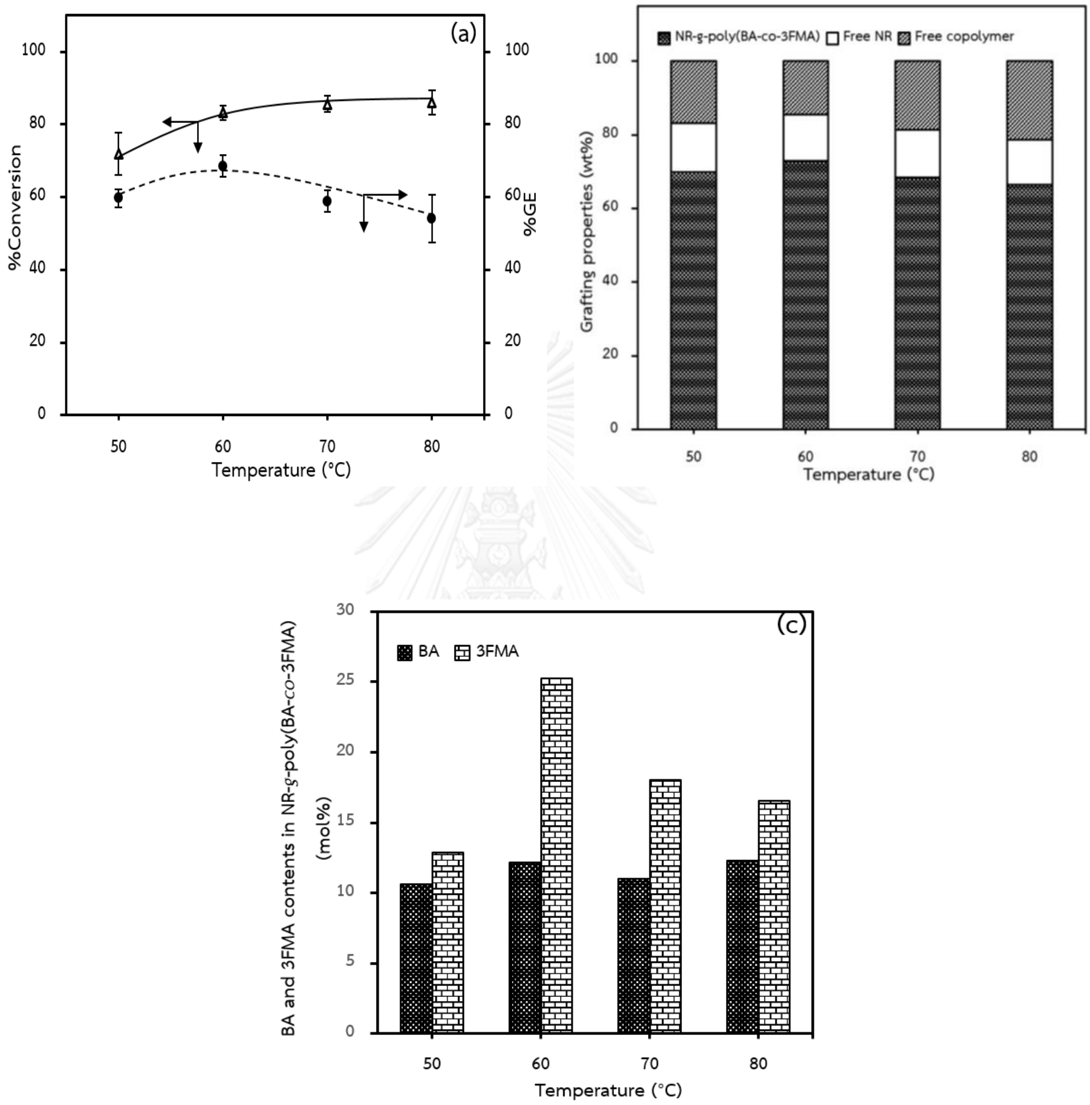


Figure 4.6 Effect of reaction temperature on (a) %conversion and %GE, (b) grafting properties and (c) BA and 3FMA contents in the NR-*g*-poly(BA-*co*-3FMA).

However, the GE value tended to be decreased 68.5% to 58.1% when the reaction temperature was increased from 60°C to 80°C (Figure 4.6a) with the higher content of free copolymer from 14.6 wt% to 21.3 wt% (Figure 4.6b). Moreover, the amount of 3FMA in the NR-*g*-poly(BA-*co*-3FMA) decreased to 16.5 mol% (Figure 4.6c). This could be explained that the use of high reaction temperature above the optimum point generated the excessive free radicals resulting in the chain transfer effect to promote the high free copolymer content. This phenomenon was also observed in the systems of graft copolymerization of ST and ACN onto NR (Kangwansupamonkon, Gilbert, and Kiatkamjornwong 2005; Angnanon, Prasassarakich, and Hinchiranan 2011).

3.2.4 Effect of the reaction time

The reaction time is one of role to determine graft copolymerization (Indah Sari et al. 2015). In this research, the reaction time was varied in from 4 to 10 h, which the BA/3FMA ratio, KPS content and reaction temperature were kept constant at 30/70 (w/w), 1.5 phr and 60°C, respectively. Generally, the levels of conversion increases with longer reaction time to a certain value. Figure 4.7a indicated that the degree of monomer conversion increased from 73.5% to 83.5% when the reaction time increased from 4 to 10 h. The maximum GE and 3FMA content in the NR-*g*-poly(BA-*co*-3FMA) were 68.5% and 25.3 mol% (Figure 4.7b and Figure 4.7c, respectively) at the reaction time of 8 h. Above this point, the GE and 3FMA content in the NR-*g*-poly(BA-*co*-3FMA) decreased to 51.6% and 18.7 mol% with the higher content of free copolymer (Figure 4.7b and Figure 4.7c, respectively). This was explained that the longer reaction time caused the higher steric hindrance of the NR particle by the prior grafted copolymer resulting in the inhibition of new coming monomers to the grafting sites and promoting the opportunity for self-polymerization to form free copolymer or crosslink reaction (Voronenkov and Musabekov 1968, Thiraphattaraphun et al. 2001, Khutoryanskiy and Staikos 2009, Lakshmi et al., 2011)

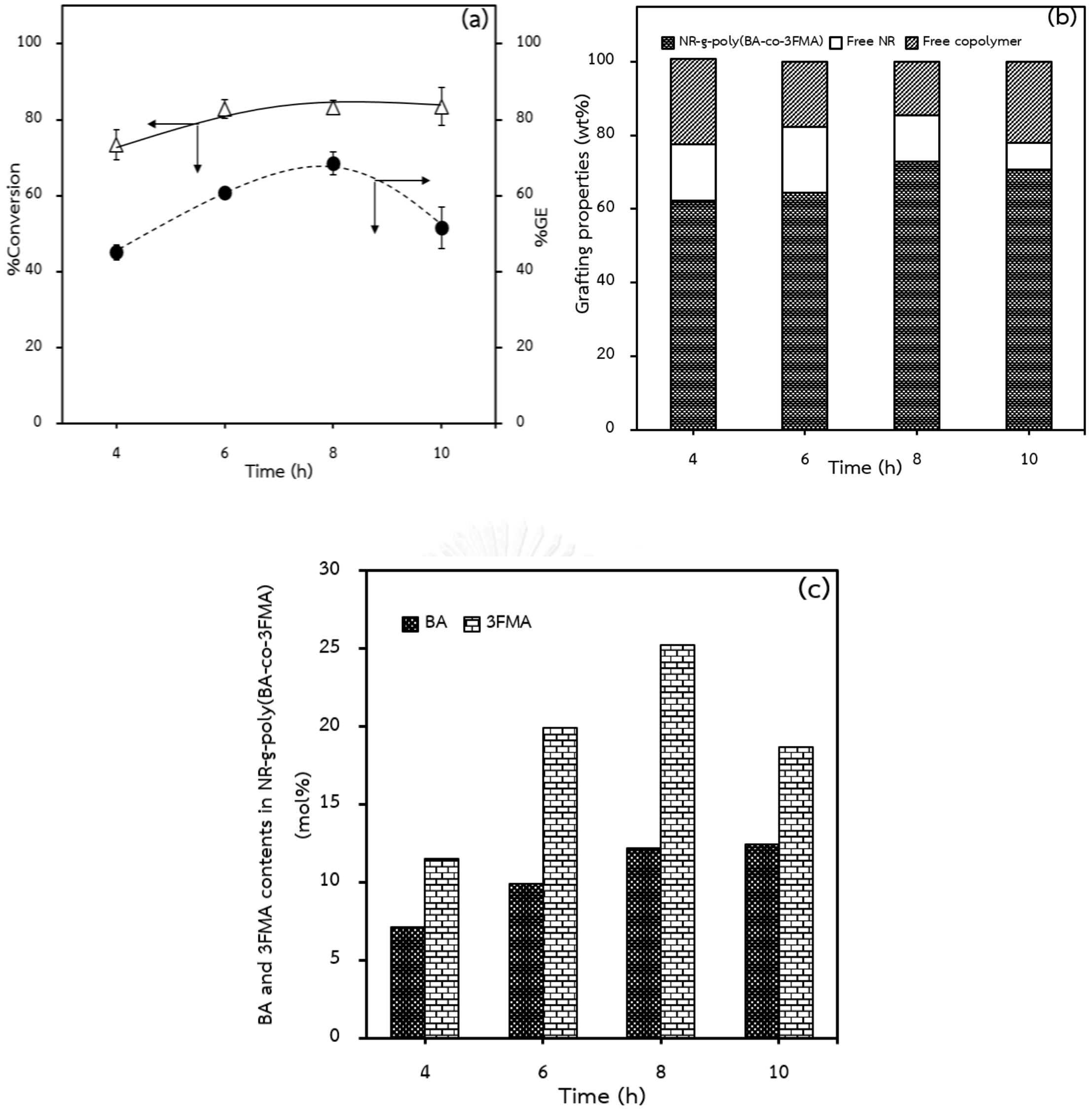


Figure 4.7 Effect of reaction time on (a) %conversion and %GE, (b) grafting properties and (c) BA and 3FMA contents in the NR-*g*-poly(BA-*co*-3FMA).

4.3 Morphology and particle size distribution of NR latex before and after graft copolymerization

Figure 4.8 illustrates the comparative TEM micrographs of NR before and after grafting with poly(BA-*co*-3FMA). Figure 4.8a shows the TEM image of NR latex particles indicating the back color due to the carbon-carbon double bonds in the NR structure

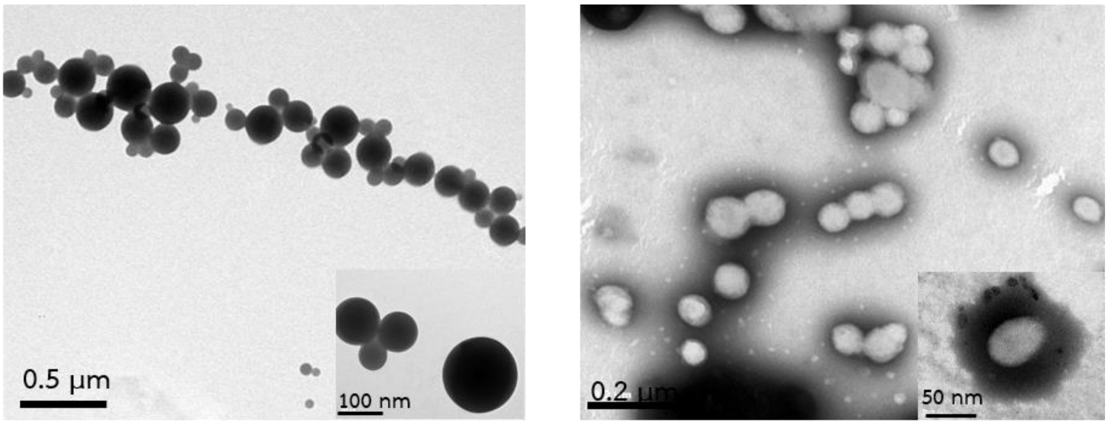


Figure 4.8 TEM micrographs of (a) NR particles stained by OsO_4 and (b) GNR particles (68.5 %GE) was stained by PTA.

which was easily stained by osmium tetroxide (OsO_4) (Kangwansupamonkon, Gilbert, and Kiatkamjornwong 2005). To enhance the phases of NR and graft copolymer in the grafted NR, the graft particles were stained by phosphotungstic acid (PTA) (Oliveira et al. 2005) to increase the resolution of the graft copolymer phase indicating as black color covering the light core, which was the NR phase. Thus, the results showed that the grafted NR particles were in the type of core-shell morphology (Han et al. 2013; Xu et al. 2013). The thickness of the grafted copolymer shell measured by SemAfore 5.2 software was ca. 56.3 ± 3.6 nm.

The particle size distribution of NR before and after graft copolymerization compared with poly(BA-*co*-3FMA) was also shown in Figure 4.9. The result indicated that NR particles had the large average diameter of 1,089 nm with broader particle size distribution (Figure 4.9a), whereas the particle size of poly(BA-*co*-3FMA) was ca. 53.9 nm as show in Figure 4.9b. When NR was grafted with poly(BA-*co*-3FMA), Figure 4.9c showed the bimodal particle size distribution with two average size as 378 nm (68.4%) and 1,492 nm (31.6%). This indicated that the graft product was consisted of 2 portions: grafted part and ungrafted part. This was possible that the grafted part was generated from the smaller particle size of NR, which might be easier to be grafted by poly(BA-*co*-3FMA).

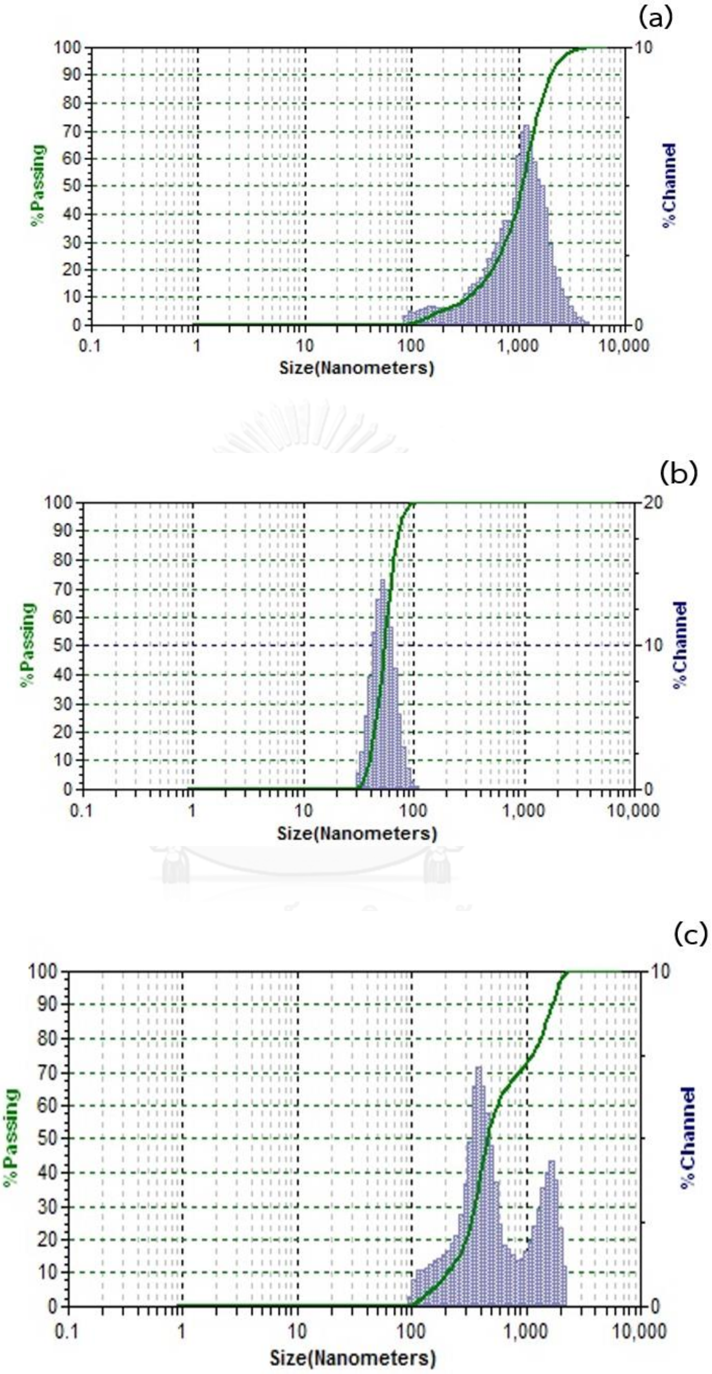
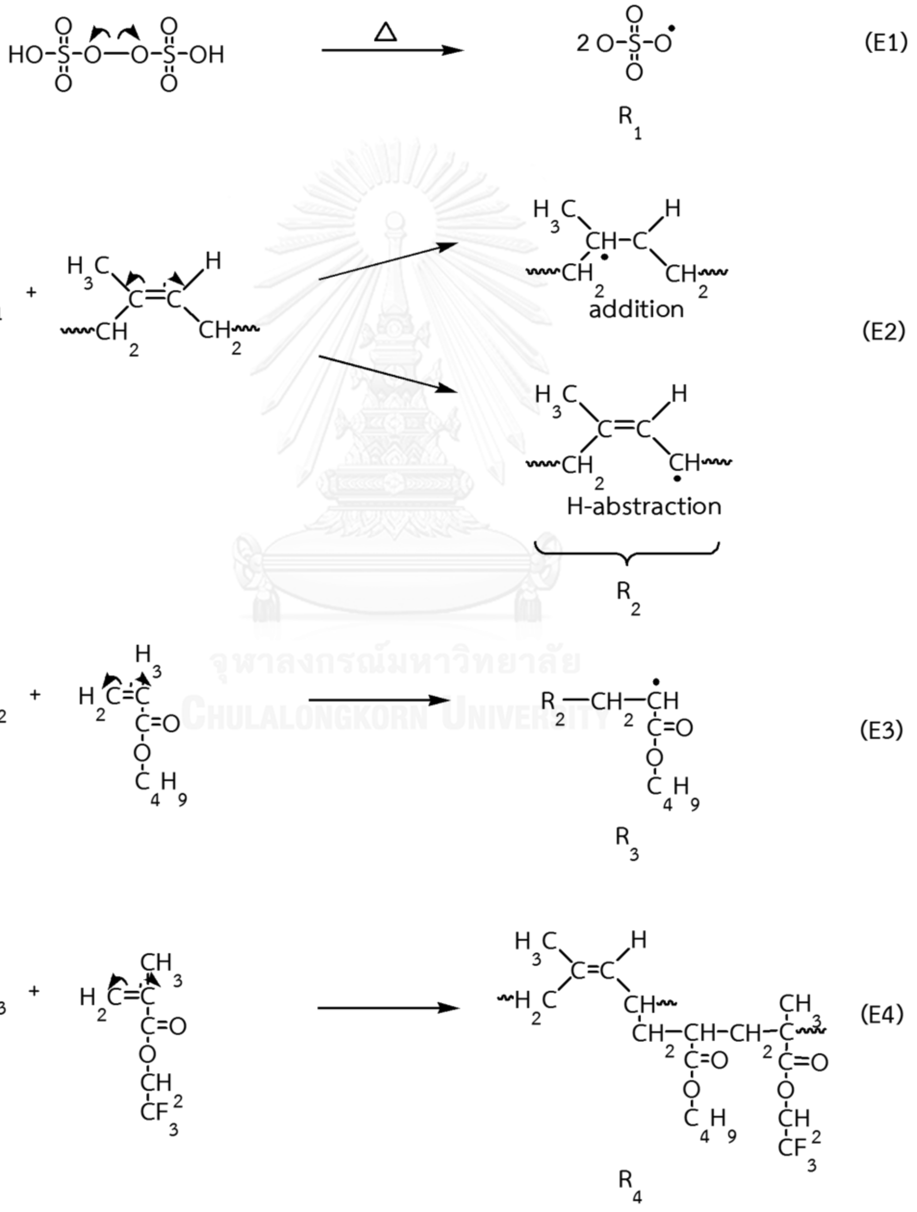


Figure 4.9 Particle size distribution of (a) NR, (b) poly(BA-*co*-3FMA) and (c) GNR (68.5 %GE).

From the structural characterization as explained above, the reaction mechanism of graft copolymerization of poly(3FMA-*co*-BA) onto NR via free radical method could be proposed as shown in Scheme 4.1. When the KPS initiator was thermally dissociated at 60 °C to generate KPS radical (E1) and then attacked to NR backbone to form the grafting sites (E2), it was possible that BA was the first monomer to react with the grafting sites located on the NR structure (E3).



Scheme 4.1 Proposed mechanism of graft copolymerization of poly(BA-*co*-3FMA) onto NR backbone.

According to the monomer reactivity ratios predicted from the Alfrey-Price Q and e parameters, the copolymerization behavior of BA (Q = 0.48, e = 0.67) (Funt and Ogryzlo 1957) and 3FMA (Q = 1.13, e = 0.98) (Boschet et al. 2009) indicates a tendency to from random copolymer with $r_{BA}•r_{3FMA}$ as 0.9. Moreover, NR was more compatible with BA than 3FMA since the solubility parameters of NR (16.8- 17.0 MPa$^{1/2}$) (Gelling et al., 1991), which was closer to that of BA (17.7 MPa$^{1/2}$) (Choi and Chung 2003) than PTFEMA (12.93 MPa$^{1/2}$) (Papadopoulou and Panayiotou, 2014). Then, 3FMA with lower reactivity for grafting would be polymerized at the grafted BA position to produce graft poly(BA-*co*-3FMA).

4.4 Molau test and AFM measurement of NR/poly(BA-*co*-3FMA) with and without the addition of GNR

The effect of the GNR on the compatibility between NR and poly(BA-*co*-3FMA) phases in the films prepared via direct casting of mixed NR and poly(BA-*co*-3FMA) latexs was investigated by using Molau test as shown in Figure 4.10. In the presence of acetone, NR could not be dissolved in this solvent due to the polarity difference (Figure 4.10a), whilst, poly(BA-*co*-3FMA) could be completely dissolved as exhibited in Figure 4.10b. However, the NR/poly(BA-*co*-3FMA) (Figure 4.10c) showed the phase separation, which NR portion in the film could not be dissolved. For the compatibilized samples, the NR/poly(BA-*co*-3FMA) films containing 5-10 wt% GNR showed the milky solution (Figure 4.10d and 4.10e). This indicated that graft NR could be acted as the emulsifying agent to enhance the compatibility of polymeric phases in the films (Yang et al. 2012). However, the overdose of graft NR (>10 wt%) in the composite films indicated the phase separation. This could be concluded that the 10 wt% GNR (Figure 4.10e) was the appropriated content to promote the phase compatibility.

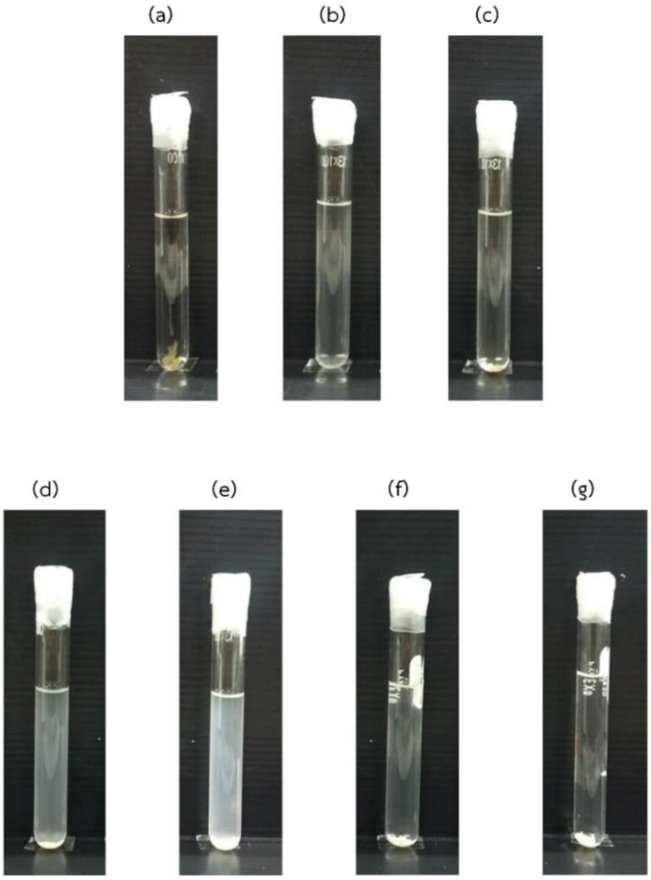


Figure 4.10 Molau test images: (a) NR, (b) poly(BA-*co*-3FMA), (c) NR/poly(BA-*co*-3FMA) (20/80 w/w) and NR/poly(BA-*co*-3FMA containing various GNR contents (d) 5 wt%, (e) 10 wt%, (f) 15 wt% and (g) 20 wt% (GNR contained 68.5 %GE)

AFM is a newly developed instrument which is widely used for detecting the morphology of polymer films on a nanometer scale. In Figure 4.11, the 2 and 3 diamension AFM images presented the average roughness (R_a) of the NR/poly(BA-*co*-3FMA (20/80 (w/w)) film with and without the addition of graft product. It could be seen that the uncompatibilized film had R_a as 72.7 nm. When the 5 wt% GNR was added into the film, the R_a value was increased to 180.3 nm and the black color representing the hole in the film was observed. When the amount of GNR was increased to 10 wt%, the white zone representing the poly(BA-*co*-3FMA) was homogeneneously dispersed throughout the film surface and the R_a value was decreased to 37.9 nm. However, the excessive content of GNR in the film provided the agglomeration of white zone indicating the less compatibility between the polymeric phases in the film resulted in the larger R_a again (as seen in Figure 4.11d and 4.11e) (Zeng, Li, and Du 2015).

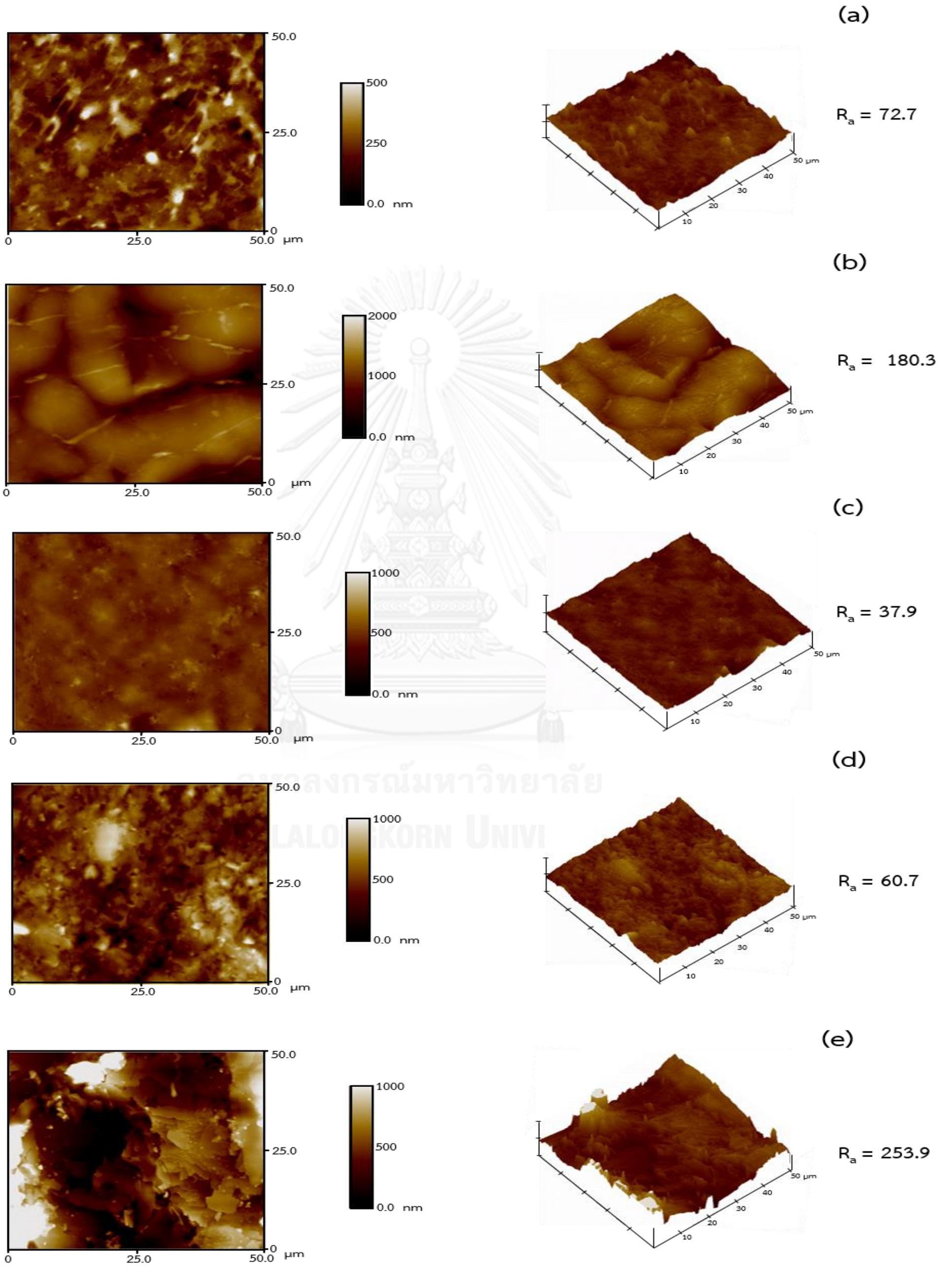
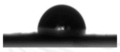
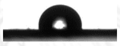
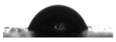
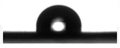
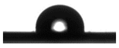


Figure 4.11 AFM images: (a) NR/poly(BA-*co*-3FMA) (20/80 (w/w)) and NR/poly(BA-*co*-3FMA) containing various GNR contents as (b) 5 wt%, (c) 10 wt%, (d) 15 wt% and (e) 20 wt% (GNR contained 68.5 %GE).

4.5 Contact angle and surface energy of composite films with and without the addition of GNR

The hydrophobicity and oleophobicity of the obtained films could be estimated in a term of contact angle by deposition of water and oil drops on the film surfaces. The films exhibit the hydrophobic property when the contact angle of water droplet is greater than 90° (Hao et al. 2012). Table 4.1 shows the contact angles of water and hexadecane (representative of oil) droplets on the surfaces of NR/poly(BA-*co*-3FMA) films containing various amount of GNR (68.5 %GE). It was observed that NR had water and hexadecane contact angle of 86° and 25.8°, respectively with high surface energy as 20.8 mN/m. To consider the poly(BA-*co*-3FMA) film, it had water and hexadecane contact angles as 103° and 31.1°, respectively indicating the higher hydrophobicity and oleophobicity than NR film. However, the film obtained from the mixture of NR and poly(BA-*co*-3FMA) latex (NR/poly(BA-*co*-3FMA) =20/80 (w/w)) showed the slightly lower water contact angle (101°) and hexadecane contact angle (31.1°). When the GNR (68.5 %GE) was introduced into the NR/poly(BA-*co*-3FMA) in the range of 5–10 wt% based on the film weight, the contact angle of water and hexadecane were higher to 110° and 54.1°, respectively reflecting the improvement of both hydrophobicity and olephobicity of the obtained films. Morever, the surface energy was decreased to the minimum value as 8.04 mN/m. However, the overdose of graft NR (15-20 wt%) provided the heterogeneity of the films similar to one without the addition of graft NR. These films exhibited the higher surface energy (10–12 mN/m) with the lower contact angles of water (ca. 100°) and hexadecane (ca. 43°).

Table 4.1 The contact angle of water and hexadecane droplets on the surfaces of NR/poly(BA-*co*-3FMA) films containing various amounts of GNR.

Sample	GNR content (wt %)	Contact engles (°)		Surface energy (mN/m)
		Water	Hexadecane	
NR	-	 86.0 ± 3.03	 25.8 ± 1.25	20.8
poly(BA-*co*-3FMA)	-	 103.2 ± 1.06	 39.5 ± 0.61	11.3
NR/poly(BA-*co*-3FMA)	-	 101 ± 1.21	 31.1 ± 0.66	11.9
	5	 105 ± 1.89	 45.3 ± 4.07	10.1
	10	 109 ± 0.86	 54.1 ± 2.4	8.4
	15	 103 ± 1.47	 46.2 ± 2.92	10.8
	20	 100 ± 1.94	 43.1 ± 2.65	12.3

[a] NR/poly(BA-*co*-3FMA) = 20/80 (w/w).

[b] %GE = 68.5

4.6 Glass transition temperatures of NR/poly(BA-*co*-3FMA) films with and without the addition of graft NR

The DSC technique was employed to determine the glass transition temperature (T_g) of polymeric matrix as shown in Figure 4.12. It was found that the single T_g of NR appeared at -67.8°C (Figure 4.12a). In the case of poly(BA-*co*-3FMA) (Figure 4.12b), its T_g showed the broad peak at 31.9°C possibly due to the overall or partial interaction between polymeric components in the copolymer (Jaisankar and Radhakrishnan 2000). Without the addition of graft product (68.5 %GE), the NR/poly(BA-*co*-3FMA) film exhibited two T_gs at -67.4 and 27.5 °C. The lower T_g belonged to the NR phase while the higher T_g was the poly(BA-*co*-3FMA) phase in the film, which was lower than the pure poly(BA-*co*-3FMA) due to the effect of the soft segment of NR matrix (Dahlan, Khairul zaman, and Ibrahim 2000). For the films compatibilized by using the graft NR, it was observed that the T_g of NR phase was slightly shifted toward the higher temperature to -66.1 °C, while the T_g of poly(BA-*co*-3FMA) decreased to the lower value (21.9 °C) when the amount of graft NR added into the blend film was 10 wt% as shown in Figure 4.12e. This phenomenon indicated the partial miscibility resulted from the graft product acting as the interfacial agent to decrease the interfacial tension between the polymeric compositions in the film (Angnanon, Prasassarakich, and Hinchiranan 2011). The use of graft NR higher than 10 wt% provided the higher T_g of NR phase to ca. -64 °C, whereas the T_g of the poly(BA-*co*-3FMA) portion increased to 24-26 °C. This was due to the high T_g of graft product reflecting the rigid material (Jaisankar and Radhakrishnan 2000).

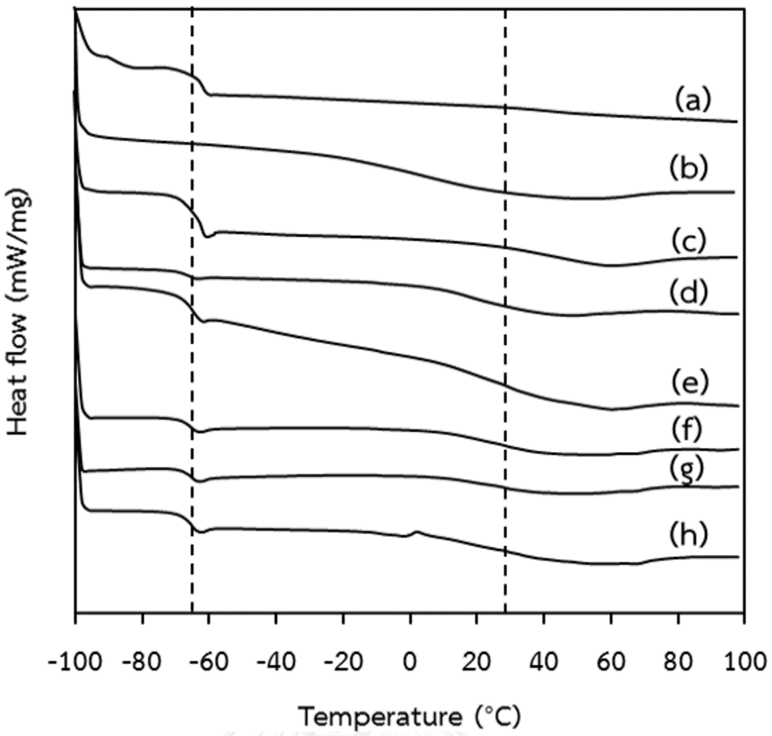


Figure 4.11 DSC curves of (a) NR, (b) poly(BA-*co*-3FMA), (c) GNR, (d) NR/poly(BA-*co*-3FMA) (20/80 w/w) and NR/poly(BA-*co*-3FMA containing various GNR contents (e) 5 wt%, (f) 10 wt%, (g) 15 wt% and (h) 20 wt% (GE of GNR = 68.5%)

Table 4.2 Glass transition temperature of the NR/poly(BA-co-3FMA) films with and without the addition of graft NR

samples	GNR contant (wt%)[a]	T_g (°C)	
		NR phase	poly(BA-*co*-3FMA) phase
NR	-	-67.8	-
poly(BA-*co*-3FMA)	-	-	31.9
GNR	-	-64.0	44.7
NR/poly(BA-*co*-3FMA)	-	-67.4	27.5
	5	-66.9	23.6
	10	-66.1	21.9
	15	-64.6	23.9
	20	-64.1	26.0

[a] GE = 68.5%

4.7 Mechnical properties of NR/poly(BA-*co*-3FMA) films with and without the addition of GNR

Table 4.3 illustrates the tensile strength and elongation at break of NR/poly(BA-*co*-3FMA) films with and without the addition of GNR and also compared to the Parafilm M®. The thickness of the Parafilm M® measured by Dial Thickness gages was ca. 0.13 ± 0 mm. It was observed that poly(BA-*co*-3FMA) (thickness = 0.32 ± 0.04 mm.) had tensile strength as 4.6 MPa with very low elongation at break as 7% indicating the brittle film. When NR latex was blended with poly(BA-*co*-3FMA) latex at 20/80 (w/w) NR/poly(BA-*co*-3FMA) with or without the addition of GNR (%GE = 68.5%), the tensile strength of the obtained film was in the range of 4-5 MPa. However, the addition of 5-10 wt% GNR provided the higher elongation at break from 180% to 242-297% indicating the higher toughness film. This was possible that the GNR promoted the higher compatibility between NR and poly(BA-*co*-3FMA) phases in the films. Above 10 wt% GNR, the elongation at break of the obtained film decreased to 231% when the 20 wt% GNR was applied in the NR/poly(BA-*co*-3FMA) film possibly due to the phase separation resulting from the over saturation of the interface of polymer constituents in the films (Jaisankar and Radhakrishnan 2000). This result was also agree with the T_g values and the Molau test. To compare with the Parafilm M®, it could be seen that the compatibilized NR/poly(BA-*co*-3FMA) with 10 wt% GNR had similar elongation at break to Parafilm M® reflecting the similar toughness. However, the tensile strength of the obtained film was slightly higher. To consider at 100% modulus of films, the addition as 5-15 wt% GNR could decrease 100% modulus of the obtained films indicating that the obtained film had higher flexibility.

Table 4.3 Tensile properties of the NR/poly(BA-*co*-3FMA) films with and without the addition of GNR.

samples	GNR contant (wt%)	Tensile strength (MPa)	Elongation at break (%)	100% Modulus (MPa)
Poly(BA-*co*-3FMA)	-	4.6 ± 0.3	7 ± 0	-
NR/poly(BA-*co*-3FMA)	-	4.6 ± 0.1	180 ± 6	4.39 ± 0.49
	5	3.9 ± 0.6	242 ± 6	3.75 ± 0.66
	10	5.1 ± 0.4	297 ± 9	3.80 ± 0.20
	15	3.7 ± 0.2	289 ± 40	2.73 ± 0.07
	20	4.5 ± 0.6	231 ± 7	3.85 ± 0.45
Parafilm M®	-	2.9 ± 0.2	279 ± 3	3.17± 0.34

4.8 Oil resistance testing of films

Table 4.4 shows the oil resistance of NR/poly(BA-*co*-3FMA) with and without the addition of GNR by immersing for 10 min and compared to Parafilm M®. It was found that Parafilm M® was easily dissolved in oil or non-polar solvents with 66.5% wt loss. To compare with the NR/poly(BA-*co*-3FMA) film, the weight loss of this film decreased to 33.6%. Moreover, the NR/poly(BA-*co*-3FMA) compatibilized by 10 wt% GNR provided the highest oil resistance with lowest weight loss after immersion (17.2%). Above this point, the oil resistance of the compatibilized film was similar to the uncompatibilized one indicating the phase separation (Angnanon, Prasassarakich, and Hinchiranan 2011; Hinchiranan et al. 2013).

Table 4.4 Oil resistence of NR/poly(BA-co-3FMA) films with and without the addition of GNR.

Samples	GNR contant (wt%)^a	% Swelling
Parafilms	-	66.5 ± 0.98
poly(BA-*co*-3FMA)	-	1.20 ± 0.75
NR/poly(BA-*co*-3FMA)	-	33.6 ± 1.36
	5	35.8 ± 3.68
	10	17.2 ± 2.17
	15	32.6 ± 12.0
	20	35.3 ± 2.19

^{a}%GE = 68.5%

Thus, it could be concluded that the NR/poly(BA-*co*-3FMA) film compatibilized by 10 wt% GNR had better mechanical properties with oil resistance than Parafilm M®. Figure 4.12 also confirmed that the NR/poly(BA-*co*-3FMA) compatibilized by 10 wt% GNR could replace Parafilm M® for using as the self-sealing film.

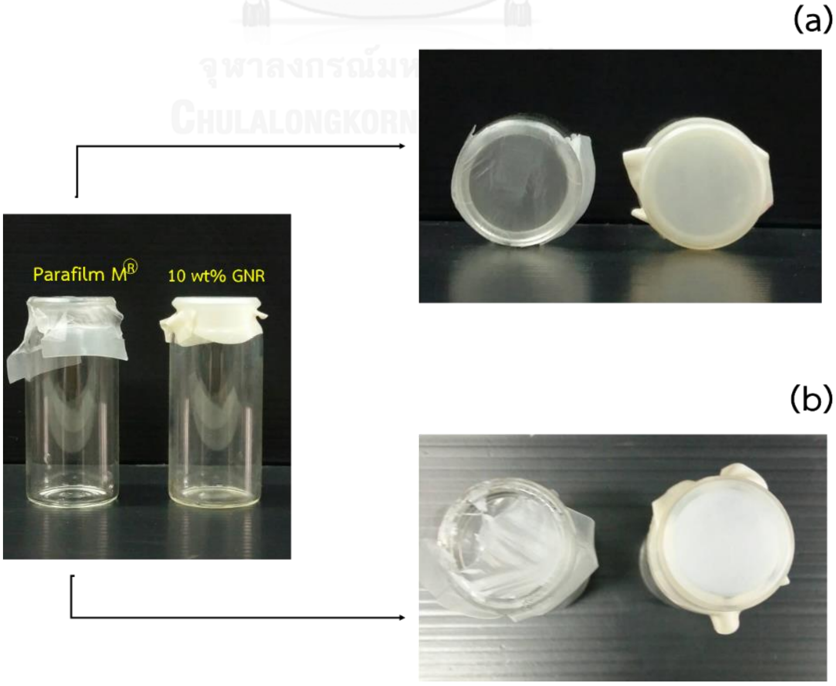


Figure 4.12 Application of before (a) and after (b) contact with hexadecane

CHAPTER V

CONCLUSIONS AND RECOMMENDATION

5.1 Conclusions

This research focused on the graft copolymerization of 2,2,2-trifluoroethyl methacrylate (P3FMA) onto the natural rubber (NR) backbone in the emulsion system by using potassium persulphate (KPS) as an initiator. Since the polarity difference of NR and 3FMA monomer obstructed the direct grafting of P3FMA onto NR structure, BA was selected as a co-monomer to enhance the grafting efficiency (GE) of this system. The effects of BA/3FMA wt ratio, initiator concentration, reaction temperature and reaction time on the monomer conversion, grafting properties and GE of the graft product were investigated. The graft natural rubber (GNR) was also used as a compatibilizer for NR/poly(BA-*co*-3FMA) blends (20/80 (w/w)). The compatibility, mechanical properties, oil resistance and application of the blends were also investigated.

5.1.1 Effect of reaction parameters on the graft copolymerization of poly(BA-*co*-3FMA) onto NR

The wt ratio of BA/3FMA used in this system was varied in the range of 0/100 - 100/0. The results indicated that the use of BA/3FMA at 30/70 (w/w) provided the highest level of monomer conversion at 83.2% with the highest GE value and grafted 3FMA content in the graft NR as 68.5% and 25.3 mol%, respectively when the reaction was initiated by 1.5 phr KPS at 60 °C for 8 h.

The morphology of GNR latex obtained from transmission electron microscopy (TEM) showed the core-shell type, which NR acted as the core and grafted poly(BA-*co*-3FMA) covering the NR core was the shell of the obtained grafted particles.

Moreover, the obtained latex showed the bimodal particle size distribution suggesting that the smaller NR particles would be easier grafted by poly(BA-*co*-3FMA).

5.1.2 Effect of GNR on the phase compatibility and properties of the NR/poly(BA-co-3FMA) films.

The addition of GNR (%GE=68.5%) into the NR/poly(BA-*co*-3FMA) film (20/80 (w/w)) was varied in the range of 5-20 wt%. From the Molau test, it was observed that the NR/poly(BA-*co*-3FMA) containing 10 wt% GNR showed the milky solution in acetone. Moreover, the topology obtained from AFM measurement of this samples showed the less roughness indicating the improved compatibility between NR and poly(BA-*co*-3FMA) phases in the film. The contact angles of water and hexadecane of this film composition were highest indicating that this film had both hydrophobicity and oleophobicity.

In the part of the thermal properties, it was noticed that the uncompatibilized NR/poly(BA-*co*-3FMA) films exhibited 2 glass transition temperatures (T_g). The lower T_g value for NR was not changed from -67 °C, while the T_g of the poly(BA-*co*-3FMA) phase was slightly lower from 31.9 °C to 27.5 °C possibly due to the soft NR portion, which was partially compatible with BA in the polymer phase. The addition of 10 wt% GNR slightly increased T_g of NR phase to -66 °C with significantly decreasing T_g value of poly(BA-*co*-3FMA) to 21.9 °C. Above this point, the over saturation at interface in the films was observed resulting in the similar T_g values of both phases to the uncompatibilized film.

The mechanical properties in terms of tensile strength and elongation at break of compatibilized NR/poly(BA-*co*-3FMA) films were higher than those of uncompatibilized one and Parafilm M® used in laboratory. In addition, the oil resistance of the compatibilized film using 10 wt% GNR was highest and it could be applied as self-sealing film similar to Parafilm M®.

5.2 Recommendation

A further study of the graft copolymerization and polymer blend should be concerned with the following aspects:

1. Graft copolymerization of other fluorine containing monomers onto NR should be explored to obtained the graft copolymer with superhydrophobicity or superoleophobicity.

2. Application of graft product as the coating materials should be further investigated.

REFERENCES

Abu Bakar, R., Fauzi, M.S. 'Natural Rubber-Grafted-Poly (Methyl Methacrylate): Influence of Coagulating Agents on Properties and Appearances', Chemical Engineering Journal, 6(2012): 962-66.

Angnanon, S., Prasassarakich, P., and Hinchiranan, N. 'Styrene/Acrylonitrile Graft Natural Rubber as Compatibilizer in Rubber Blends', Polymer-Plastics Technology and Engineering, 50(2011): 1170-78.

Arayapranee, W., Prasassarakich, P., and Rempel, G.L. 'Blends of poly(vinyl chloride) (PVC)/natural rubber-*g*-(styrene-*co*-methyl methacrylate) for improved impact resistance of PVC', Journal of Applied Polymer Science, 93(2004): 1666-72.

Arayapranee, W., and Rempel, G. L. 'Preparation of a natural rubber core/polymer shell in a nanomatrix by graft copolymerization', Journal of Applied Polymer Science, 110(2008): 2475-82.

Aroonsingkarat, K., and Hansupalak, N. 'Prediction of styrene conversion of polystyrene/natural rubber graft copolymerization using reaction conditions: Central composite design versus artificial neural networks', Journal of Applied Polymer Science, 128(2013): 2283-90.

Bhattacharya, A., and Misra, B.N. 'Grafting: a versatile means to modify polymers: techniques, factors and applications', Progress in Polymer Science, 29(2004): 767-814.

Boschet, F., Kostov, G., Ameduri, B., Yoshida, T., and Kawada, K. 'Kinetics of the radical copolymerization of 2,2,2-trifluoroethyl methacrylate withtert-butyl α-trifluoromethacrylate', Journal of Polymer Science Part A: Polymer Chemistry, 48(2010): 1029-37.

Carone, E., Kopcak, U., Gonçalves, M. C., and. Nunes, S. P. 'In situ compatibilization of polyamide 6/natural rubber blends with maleic anhydride', Polymer, 41(2000): 5929-35.

Chang, G., He, L., Liang, J., Wang, N., Cao, R., and Zhao, X. 'Polysiloxane/poly(fluorinated acrylate) core–shell latexes and surface wettability of films', Journal of Fluorine Chemistry, 158(2014): 21-28.

Chumsamrong, P., and Monprasit, O. 'preparation, adhesive performance and Stability of natural rubber latex grafted with N-butyl acrylate (BA) and methyl methacrylate (MMA)', suranaree journal of science and technology, 14(2007): 269-76.

Dahlan, H. M., Khairul zaman, M. D., and Ibrahim, A. 'Liquid Natural Rubber (LNR) as a Compatibilizer in NR/LLDPE Blends', Applied Polymer Science, 78(2000): 1776–82

De Guzman, M., Liu, P.Y., Chen, J.T., Tung, K.L., Lee, K.R., and Lai, J.Y. 'Effect of compatibilizer on compatibility and pervaporation performance of PC/PHEMA blend membranes', Journal of Membrane Science, 378(2011): 503-11.

Folkes, M.L., and Hope, P.S. Polymer Blends and Alloys, 1993.

George, B., Maiti, S. N., and Varma, I. K. 'Impact modification of SAN using NR-*g*-SAN copolymers', Journal of materials science, 42(2007): 8262-70.

Guo, J., Zeng, X., Li, H., and Luo, Q. 'Compatibilization of Fluororubber/ Silicone Rubber Blends by the Incorporation of 2,2,2-Trifluoroethyl Methacrylate Grafted Silicone Rubber', Journal of Elastomers & Plastics, 42(2010): 539-60.

Han, D., Zhu, L., Chen, Y., Li, W., and Feng, L. 'Synthesis and characterization of acrylic latex: Effects of fluorine and silicon components on properties of the latex copolymers', Journal of Fluorine Chemistry, 156(2013): 38-44.

Hao, L., An, Q., Xu, W., and Huang, L. 'Synthesis, film morphology and hydrophobicity of novel fluorinated polyacrylate emulsion and solution on silicon wafer', Colloids and Surfaces A: Physicochemical and Engineering Aspects, 396(2012): 83-89.

He, G., Zhang, G., Hu, J., Sun, J., Hu, S., Li, Y., Liu, F., Xiao, D., Zou, H., and Liu, G. 'Low-fluorinated homopolymer from heterogeneous ATRP of 2,2,2-trifluoroethyl methacrylate mediated by copper complex with nitrogen-based ligand', Journal of Fluorine Chemistry, 132(2011): 562-72.

Hinchiranan, N, Suppaibulsuk, B., Promprayoon, S., and Prasassarakich, P. 'Improving properties of modified acrylic sheet via addition of graft natural rubber', Materials Letters, 61(2007): 3951-55.

Hinchiranan, N., Wannako, P., Paosawatyanyong, B., and Prasassarakich, P. '2,2,2-Trifluoroethyl methacrylate-graft-natural rubber: Synthesis and application as compatibilizer in natural rubber/fluoroelastomer blends', Materials Chemistry and Physics, 139(20130: 689-98.

Indah Sari, T., Handaya Saputra, A., Bismo, S., Maspanger, D.R., and Cifriadi, A. 'The Effect of Styrene Monomer in the Graft Copolymerization of Arcylonitrile onto Deproteinized Natural Rubber', International Journal of Technology, 6(20150: 1164.

Jaisankar, S. N., and Radhakrishnan, G. 'Effect of Compatibilizer on Morphology and Mechanical Properties of TPUBAN Blends', Polymer engineering and science, 40(2000): 620-26.

Jones, B. Technical Director, Halocarbon Products Corporation. 'Fluoropolymers', JCT CoatingsTech magazine, 2008.

Juntuek, P., Ruksakulpiwat, C., Chumsamrong, P., and Ruksakulpiwat, Y. 'Glycidyl methacrylate grafted natural rubber: Synthesis, characterization, and mechanical property', Journal of Applied Polymer Science, 122(2011): 3152-59.

Kangwansupamonkon, W., Gilbert, R.G., and Kiatkamjornwong, S. 'Modification of Natural Rubber by Grafting with Hydrophilic Vinyl Monomers', Macromolecular Chemistry and Physics, 206(2005): 2450-60.

Kohiya, S., and Ikedo, Y.. Chemistry, Manufacure and Applications od Natural rubber, 2014.

Kongparakul, S., Prasassarakich, P., and Rempel, G.L. 'Catalytic hydrogenation of methyl methacrylate-g-natural rubber (MMA-*g*-NR) in the presence of $OsHCl(CO)(O_2)(PCy_3)_2$', Applied Catalysis A: General, 344(2008): 88-97.

Li, G., Xu, A., Geng, B., Yang, S., Wu, G., and Zhang, S. 'Synthesis and characterization of fluorinated diblock copolymer of 2,2,2-trifluoroethyl methacrylate and methyl methacrylate based on RAFT polymerzation', Journal of Fluorine Chemistry, 165(2014): 132-37.

Liu, X., Chen, J., Sun, P., Liu, Z.W., and Liu, Z.T. 'Grafting modification of ramie fibers with poly(2,2,2-trifluoroethyl methacrylate) via reversible addition–fragmentation chain transfer (RAFT) polymerization in supercritical carbon dioxide', Reactive and Functional Polymers, 70(2010): 972-79.

Nakason, C., Saiwaree, S., Tatun, S., and Kaesaman, A. 'Rheological, thermal and morphological properties of maleated natural rubber and its reactive blending with poly(methyl methacrylate)', Polymer Testing, 25(2006): 656-67.

Odian, G. Principles of Polymerization, Wiley & Sons, Inc., Hoboken, New Jersey, 2004.

Oliveira, P.C., de Oliveira, A.M., Garcia, A., de Souza Barboza, J.C., de Carvalho Zavaglia, C.A., and dos Santos, A.M. 'Modification of natural rubber: A study by 1H NMR to assess the degree of graftization of polyDMAEMA or polyMMA onto rubber particles under latex form in the presence of a redox couple initiator', European Polymer Journal, 41(2005): 1883-92.

Oommen, Z., and Thomas, S. 'Compatibility studies of natural rubber/poly(methyl methacrylate) blends by viscometry and phase separation techniques', Journal of materials science, 32(1997): 6085 — 94.

Ozbay, S., and Erbil, H. Y. 'Solution copolymerization of perfluoroalkyl ethyl methacrylate with methyl methacrylate and butyl acrylate: Synthesis and surface properties', Colloids and Surfaces A: Physicochemical and Engineering Aspects, 452(2014): 9-17.

Qu, J., and He, L. 'Synthesis and properties of silane-fluoroacrylate grafted starch', Carbohydrate Polymers, 98(2013): 1056-64.

Rosli, N.A., Ahmad, I., Anuar, F.H., and Abdullah, I. 'Mechanical and thermal properties of natural rubber-modified poly(lactic acid) compatibilized with telechelic liquid natural rubber', Polymer Testing, 54(2016): 196-202.

Saramolee, P., Lopattananon, N., and Sahakaro, K. 'Preparation and some properties of modified natural rubber bearing grafted poly(methyl methacrylate) and epoxide groups', European Polymer Journal, 56(2014): 1-10.

Shi, H., Zhao, Y., Dong, X., Zhou, Y., and Wang, D. 'Frustrated crystallisation and hierarchical self-assembly behaviour of comb-like polymers', Chemical Society Reviews, 42(2013): 2075-99.

Shonaike, G.O., and Simon, G.P. Polymer Blend and Alloys, 1999.

Sookprasert, P., and Hinchiranan, N. 'Preparation of Natural Rubber-graft-Poly(lactic acid) Used as a Compatibilizer for Poly(lactic acid)/NR Blends', Macromolecular Symposia, 354(2015): 125-30.

Suksawad, P., Yamamoto, Y., and Kawahara, S. 'Preparation of thermoplastic elastomer from natural rubber grafted with polystyrene', European Polymer Journal, 47(2011): 330-37.

Tan, L., Su, Q., Zhang, S., and Huang, H. 'Preparing thermoplastic polyurethane/thermoplastic starch with high mechanical and biodegradable properties', RSC Adv., 5(2015): 80884-92.

Thiraphattaraphun, L. , Kiatkamjornwong, S., Prasassarakich, P., and Damronglerd, S. 'Natural Rubber-*g*-Methyl Methacrylate/Poly(methyl methacrylate) Blends', Journal of Applied Polymer Science, 81(2001): 428–39.

Utracki, L.A. Commercial Polymer Blends, 1998.

Wang, P., Tan, K.L., Ho, C.C., Khew, M.C., and Kang, E.T. 'Surface modification of natural rubber latex films by graft copolymerization', European Polymer Journal, 36(2000): 1323–31.

Wang, X. , Xu, G., Liang, Y., and JIAN HU, Y. 'Surface Wettability of Fluorinated and NonFluorinated Polyacrylate Latex Blend Films', Journal of Polymeric Materials, 32(2015): 329-36.

Wei, Z., Ling, H., Junyan, L., Gang, C., and Na, W. 'Preparation and properties of core-shell nanosilica/poly(methyl methacrylate-butyl acrylate-2,2,2-trifluoroethyl methacrylate) latex', Journal of Applied Polymer Science, 120(20110: 1152-61.

Wongthong, P., Nakason, C., Pan, Q., Rempel, G.L., and Kiatkamjornwong, S. 'Modification of deproteinized natural rubber via grafting polymerization with maleic anhydride', European Polymer Journal, 49(2013): 4035-46.

Xiao, X., and Wang, Y. 'Emulsion copolymerization of fluorinated acrylate in the presence of a polymerizable emulsifier', Colloids and Surfaces A: Physicochemical and Engineering Aspects, 348(2009): 151-56.

Xu, A.h., Zhang, L.q., Ma, J.c., Ma, Y., Geng, B., and Zhang, S. 'Preparation and surface properties of poly(2,2,2-trifluoroethyl methacrylate) coatings modified with methyl acrylate', Journal of Coatings Technology and Research, 13(2016): 795-804.

Xu, W., An, Q., Hao, L., Zhang, D., and Zhang, M. 'Synthesis and characterization of self-crosslinking fluorinated polyacrylate soap-free latices with core–shell structure', Applied Surface Science, 268(20130: 373-80.

Yang, H., Cao, X., Ma, Y., An, J., Ke, Y., Liu, X., and Wang, F. 'Effect of maleic anhydride grafted polybutadiene on the compatibility of polyamide 66/acrylonitrile-butadiene-styrene copolymer blend', Polymer Engineering & Science, 52(2012): 481-88.

Yang, W., Zhu, L., and Chen, Y. 'Synthesis and characterization of core–shell latex: Effect of fluorinated acrylic monomer on properties of polyacrylates', Journal of Fluorine Chemistry, 157(2014): 35-40.

Yao, W., Li, Y., and Huang, X. 'Fluorinated poly(meth)acrylate: Synthesis and properties', Polymer, 55(2014): 6197-211.

Zeng, J.B., Li, K.A., and Du, A.K. 'Compatibilization strategies in poly(lactic acid)-based blends', RSC advances, 5(2015): 32546-65.

Zhang, C., Man, C., Pan, Y., Wang, W., Jiang, L., and Dan, Y. 'Toughening of polylactide with natural rubber grafted with poly(butyl acrylate)', Polymer International, 60(2011): 1548-55.

Zhang, S., Zhao, J., Chu, G., Zhang, L., Xu, A., Li, H., and Geng, B. 'Synthesis, characterization and properties of a novel fluorinated methacrylate polymer', Journal of Fluorine Chemistry, 132(2011): 915-19.

Zhou, J., Zhang, L., and Ma, J. 'Fluorinated polyacrylate emulsifier-free emulsion mediated by poly(acrylic acid)-b-poly(hexafluorobutyl acrylate) trithiocarbonate via ab initio RAFT emulsion polymerization', Chemical Engineering Journal, 223(2013): 8-17.

APPENDICES

APPENDIX A

Overall composition of natural rubber and monomers

Table A1 Properties of natural rubber latex

Properties	Content (%)
Total solid content (TSC)	61.50
Dry rubber content (DRC)	60.00
Non-rubber solids	2.00
Ammonia content on total weight	0.60
pH value	10.50
KOH number	1.00
Volatile fatty acid number	0.20
Mechanical stability @ 55%	650 sec.
Coagulum	0.1
Sludge	0.1

Table A2 Properties of 2,2,2-trifluoroethyl methacrylate (3FMA)

Properties	Reported values
Molecular weight (g/mol)	168.11
Boiling point (°C)	102
Density at 25 °C (g/ml)	1.181
Flash point in closed cup (°C)	17

Table A3 Properties of butyl acrylate (BA)

Properties	Reported values
Molecular weight (g/mol)	128.17
Boiling point (°C)	145
Density at 25 °C (g/ml)	0.89
Flash point in closed cup (°C)	39

APPENDIX B

CALCULATION

B1 Calculation of grafted 3FMA and BA monomer content

The molar compositions of 3FMA and BA in the GNR can be determined by using the ^{1}H-NMR spectroscopy of GNR as shown in Figure B1. The molar compositions of 3FMA and BA in the GNR was calculated by the flowing equations, which was adapted from the previous literature (Hinchiranan et al., 2013).

$$\%\text{mol of graft 3FMA in GNR } (C_{3FMA}) = \frac{(S_1/2)}{S_0 + (S_1/2) + (S_2/2)} \times 100$$

$$\%\text{mol of graft BA in GNR } (C_{BA}) = \frac{(S_2/2)}{S_0 + (S_1/2) + (S_2/2)} \times 100$$

Integrated peak area at 5.05 ppm of olefinic proton of NR = S_0.

Integrated peak area at 4.28 ppm of methylene proton of TFEMA = S_1.

Integrated peak area at 3.53 ppm of methoxy proton of BA = S_2.

For example: S_0 = 1.00, S_1 = 0.79 and S_2 = 0.44

$$\%\text{mol of graft 3FMA in GNR } (C_{3FMA}) = \frac{(0.79/2)}{1.00 + (0.79/2) + (0.44/2)} \times 100$$

$$= 24.46\%$$

$$\%\text{mol of graft BA in GNR } (C_{BA}) = \frac{(0.44/2)}{1.00 + (0.79/2) + (0.44/2)} \times 100$$

$$= 13.62\%$$

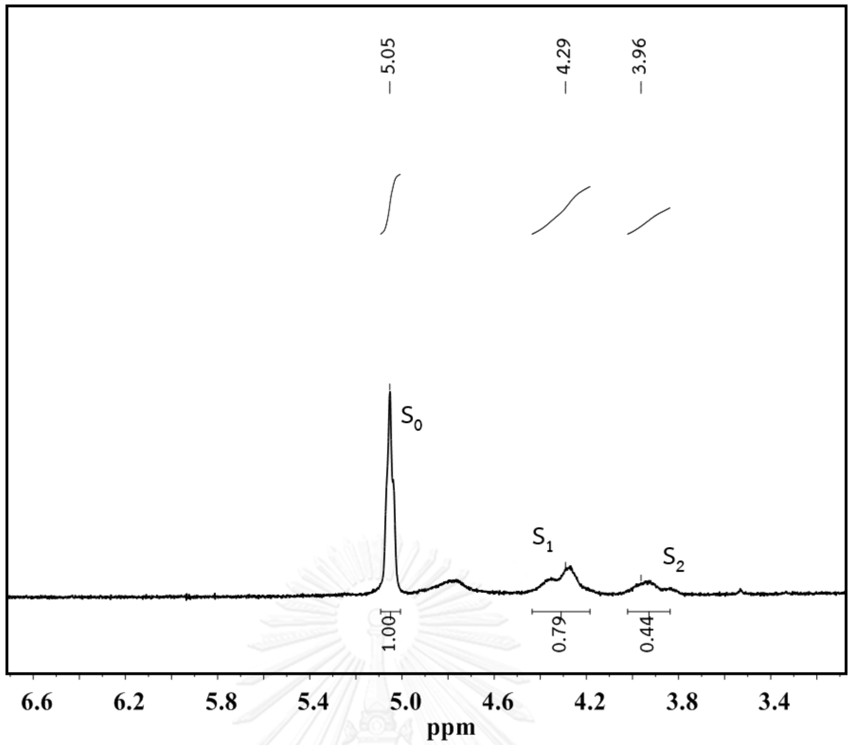


Figure B-1 ^{1}H-NMR spectra of GNR (condition: monomers content = 100 phr, 3FMA/BA = 30/70 (w/w), Initiator = 1.5 phr, T = 60 °C, t = 8 h).

B2 Calculation of grafting properties and %GE

For example: all obtained data from GNR (condition: monomers content = 100 phr, 3FMA/BA = 30/70 (w/w), Initiator = 1.5 phr, T = 60 °C, t = 8 h).

Weight of NR (A) = 3.61 g
Weight of monomer charged (B) = 3.63 g
Weight of obtained product (C) = 6.68 g
Weight of sample (D) = 0.71 g
Weight of sample after extraction with PE (E) = 0.61 g
Weight of sample after extraction with acetone (F) = 0.51 g

%Conversion

%Conversion = (C-A)/B × 100

= (6.68 – 3.61)/3.63 × 100

= 84.72

Graft natural rubber, GNR

%GNR = F/D × 100

= 0.51/0.71 × 100

= 71.90

%Free NR

%Free NR = (D-E)/D × 100

= (0.71 – 0.61)/0.71 × 100

= 14.56

%Free copolymer

%Free copolymer = (E-F)/D × 100

= (0.61 – 0.51)/0.71 × 100

= 13.51

%Grafting efficiency (%GE)

Weight total polymer formed = C– A

= 6.68 – 3.61

= 3.07 g

Weight of free copolymer = (%free copolymer × C)/100

= (13.51 × 6.68)/100

= 0.90 g

Weight of copolymer grafted

= weight total polymer formed - weight of free copolymer

= 3.07 – 0.90

= 2.17 g

%GE = (2.17/3.07) × 100

= 70.68

B3 Calculation of surface energy

For example: all obtained data from poly(BA-*co*-3FMA) film

Contact angle of hexadecane on the poly(BA-*co*-3FMA) film surface (θ_H) = 54.1°

Surface tensions of hexadecane (γ_H) = 27.6 mN/m

Dispersive parameters of hexadecane surface tension (γ^d_H) = 27.6 mN/m

Polar parameters of hexadecane surface tension (γ^p_H) = 0.0 mN/m

Contact angle of water on the poly(BA-*co*-3FMA) film surface (θ_W) = 108.6.0°

Surface tensions of water (γ_W) = 72.8 mN/m

Dispersive parameters of water surface tension (γ^d_W) = 21.8 mN/m

Polar parameters of water surface tension (γ^p_W) = 51.0 mN/m

1. Dispersive parameters of poly(BA-*co*-3FMA) film surface tension (γ^d_F)

$$\gamma_H(1 + \cos\theta) = 2\left[(\gamma^d_H \cdot \gamma^d_F)^{1/2} + (\gamma^p_H \cdot \gamma^p_F)^{1/2}\right]$$

$$27.6(1 + \cos 63) = 2\left[(27.6 \cdot \gamma^d_F)^{1/2} + (0.0 \bullet \gamma^p_F)^{1/2}\right]$$

$$((27.6\gamma^d_F)^{1/2})^2 = (27.6(1 + \cos 54.1)/2)^2$$

$$\gamma^d_F = 479.3/27.6$$

$$\gamma^{d}_{F} = 17.36\ \text{mN/m}$$

2. Polar parameters of PTFEMA film surface tension (γ^{p}_{F})

$$\gamma_{w}(1 + \cos\theta) = 2\left[(\gamma^{d}_{W}\,\gamma^{d}_{F})^{1/2} + (\gamma^{p}_{W}\,\gamma^{p}_{F})^{1/2}\right]$$

$$72.8(1 + \cos 108.6) = 2\left[(21.8 \text{ X } 17.36)^{1/2} + (49.6\gamma^{p}_{F})^{1/2}\right]$$

$$((49.6\gamma^{p}_{F})^{1/2})^{2} = ((72.8(1 + \cos 108.6)/2) + (21.8 \text{ X } 17.36)^{1/2})^{2}$$

$$49.6\gamma^{p}_{F} = 28.52$$

$$\gamma^{p}_{F} = 0.575\ \text{mN/m}$$

3. Surface tensions of 3FMA film (γ_{F})

$$\gamma_{F} = \gamma^{d}_{F} + \gamma^{p}_{F}$$

$$= 17.36 + 0.575$$

$$= 17.94\ \text{mN/m}$$

APPENDIX C

Data of graft copolymerization

Table C1 Raw data of %conversion, %GE and components in copolymer of graft NR

BA/3FMA wt ratio	Conversion (%)	Grafting properties (wt%)			%GE	Components in graft copolymer	
		%free NR	%free copolymer	NR-*g*-poly(BA-*co*-3FMA) (%)		BA	3FMA
0/100	61.11	45.21	36.24	18.55	4.46	-	12.3
	56.11	43.48	34.55	21.97	3.87	-	14.9
10/90	63.13	12.21	26.99	60.80	29.9	12.0	15.7
	66.79	18.13	26.79	55.07	32.9	4.52	13.4
20/80	63.13	17.01	17.93	65.05	53.6	14.9	24.1
	69.23	18.36	20.84	60.80	49.2	11.3	22.5
30/70	81.07	10.36	15.77	73.87	64.7	9.6	26.0
	83.84	12.80	14.46	72.74	68.3	13.6	24.5
40/60	75.07	16.08	16.70	67.22	61.075	15.7	19.0
	84.86	22.13	17.56	60.32	61.862	18.4	18.3
50/50	77.95	17.29	20.89	61.82	52.404	17.3	16.3
	73.95	17.37	16.66	65.96	60.813	19.3	18.6

Table C1 Cont.

Exp.	Conversion (%)	Grafting properties (wt%)			%GE	Components in graft copolymer (mol%)	
		%free NR	%free co	NR-*g*-poly(BA-*co*-3FMA)		BA	3FMA
60/40	74.44	18.33	21.91	59.76	48.5	23.2	9.97
	79.62	8.05	22.97	68.98	47.5	20.1	13.9
70/30	76.40	20.82	23.37	55.81	45.5	24.9	12.2
	68.16	22.85	20.12	57.02	50.5	25.3	11.6
80/20	74.65	23.92	25.07	51.01	41.3	30.4	15.6
	66.80	21.72	24.25	54.03	39.26	28.1	12.7
90/10	68.48	21.41	24.91	53.69	38.5	26.9	11.6
	69.94	25.83	26.92	47.24	34.5	29.4	8.4
100/0	89.94	14.81	17.12	68.07	64.0	27.3	-
	84.75	16.08	17.93	65.99	60.9	26.2	-

Table C2 Raw data of initiator concentration, reaction temperature and reaction time in copolymer of graft NR

KPS (phr)	Temp. (°C)	Time (h)	Conversion (%)	Grafting properties (wt%)			GE (%)	Components in graft copolymer (mol%)	
				free NR (%)	free copolymer (%)	NR-*g*-poly(BA-*co*-3FMA (%)		BA	3FMA
0.5	60	8	66.00	15.33	20.85	63.82	47.76	4.70	9.83
0.5	60	8	68.55	17.33	20.66	62.01	49.24	7.05	10.13
1.0	60	8	81.28	15.44	19.27	65.30	57.19	16.12	18.09
1.0	60	8	85.17	18.31	17.58	64.11	61.79	12.17	16.35
1.5	60	8	81.07	10.36	15.77	73.87	64.72	9.61	25.97
1.5	60	8	83.84	12.80	14.46	72.74	68.29	13.62	24.46
2.0	60	8	80.79	7.78	17.16	75.06	61.65	16.13	19.35
2.0	60	8	85.12	13.77	18.32	67.91	60.29	13.31	23.05
1.5	50	8	77.99	14.99	17.85	67.14	59.29	9.20	20.80
1.5	50	8	71.60	13.11	15.79	71.10	62.29	11.40	15.07
1.5	60	8	81.07	10.36	15.77	73.87	64.72	9.61	25.97
1.5	60	8	83.84	12.80	14.46	72.74	68.29	13.62	24.46

Table C2 Cont.

KPS (phr)	Temp. (°C)	Time (h)	Conversion (%)	Grafting properties (wt%)			GE (%)	Components in graft copolymer (mol%)	
				free NR (%)	free copolymer (%)	NR-*g*-poly(BA-*co*-3FMA (%)		BA	3FMA
1.5	70	8	88.10	11.37	19.11	69.52	59.27	8.16	20.92
1.5	70	8	83.78	13.95	16.98	69.06	62.87	12.00	15.27
1.5	80	8	87.67	11.78	20.24	67.97	56.61	13.85	18.58
1.5	80	8	82.33	13.58	18.54	67.87	58.93	11.23	16.30
1.5	60	4	75.89	12.80	24.57	62.63	42.86	6.64	10.37
1.5	60	4	75.60	19.57	22.80	57.62	46.75	7.69	12.67
1.5	60	6	80.86	19.79	17.77	62.44	60.26	9.89	19.43
1.5	60	6	82.23	19.85	18.03	62.12	59.99	9.71	18.35
1.5	60	8	81.07	10.36	15.77	73.87	64.72	9.61	25.97
1.5	60	8	83.84	12.80	14.46	72.74	68.29	13.62	24.46
1.5	60	10	78.49	7.58	19.96	72.46	54.36	16.18	20.88
1.5	60	10	88.51	6.70	25.62	67.67	45.25	8.17	17.93

APPENDIX D

Mechanical properties

Table D1 Tensile test of the parafilm, NR/poly(B-*co*-3FMA) films with and without the addition of GNR (68.5 %GE).

samples	Graft NR content (wt %)	Tensile strength (MPa)				
		1	2	3	Ave.	S.D.
Parafilms		3.08	2.69	2.93	2.9	0.2
poly(BA-*co*-3FMA)		4.90	4.50	4.30	4.6	0.3
NR/poly(BA-*co*-3FMA)	0	4.60	4.60	4.50	4.6	0.1
	5	4.19	4.23	3.23	3.9	0.6
	10	4.80	5.50	5.10	5.1	0.4
	15	3.50	3.60	3.90	3.7	0.2
	20	5.10	4.00	4.40	4.5	0.6

Table D2 Elongation at break of the parafilm, NR/poly(B-*co*-3FMA) films with and without the addition of GNR (68.5 %GE)..

samples	Graft NR content (wt %)	Elongation at break (%)				
		1	2	3	Ave.	S.D.
Parafilms		283	278	277	279	3
poly(BA-*co*-3FMA)		7	7	7	7	0
NR/poly(BA-*co*-3FMA)	0	186	174	180	180	6
	5	244	246	235	242	6
	10	297	307	289	297	9
	15	253	283	332	289	40
	20	222	237	233	231	7

VITA

Miss Kotchamon Yimmut was born on February 22, 1991 in Phatthalung, Thailand. She graduated a Bachelor's Degree of Science from Department of Polymer Science, Prince of Songkla University, Songkhla, Thailand. She has continued her study in Master's Degree in Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University since 2014 and finished her study in 2017.

Presentation:

2016 "Preparation and Properties of Natural Rubber Grafted with Poly(Butyl Acrylate-co-Fluorinated Acrylate)", 8 - 11 August, Advances in Functional Materals conference 2016 (AFM 2016) at ICC, Jeju Island, South Korea.

2016 "Synthesis and Properties of Poly(Butyl Acrylate-co-Fluorinated Acrylate)-Graft-Natural Rubber", 26 - 28 October, The 6th TiChE International Conference 2016 (ITiChE 2016), Bangkok, Thailand.