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สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2559
ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

GRAFT COPOLYMERIZATION OF FLUORINATED ACRYLATE MONOMER ONTO
NATURAL RUBBER LATEX

Miss Kritiya Homchoo



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กฤติยา หอมชู : กราฟต์โคพอลิเมอร์ไอโซไซยานูเรทของมอนอเมอร์ฟลูออรีเนเตดอะครีเลตบนลาเท็กซ์ยางธรรมชาติ (GRAFT COPOLYMERIZATION OF FLUORINATED ACRYLATE MONOMER ONTO NATURAL RUBBER LATEX) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร.นพิตา วิทยุธีระนันท์, 90 หน้า.

ความไม่เข้ากันและการแยกวัฏภาคของของผสมฟลูออรีเนเตดอะครีเลต/ยางธรรมชาติเกิดขึ้นเนื่องจากสภาพขั้วที่ต่างกันของพอลิเมอร์ผสม เพื่อลดการแยกวัฏภาคในคอมพอลิเมชัน กราฟต์โคพอลิเมอร์ไอโซไซยานูเรทเป็นวิธีที่นิยมใช้ในการเพิ่มความเข้ากันได้ของของผสม ในการศึกษาครั้งนี้ 2,2,2-ไตรฟลูออโรเอทิลเมทาครีเลตถูกกราฟต์ลงบนโครงสร้างของยางธรรมชาติ โดยเมทิลเมทาครีเลตถูกใช้เป็นมอนอเมอร์ร่วมเพื่อเพิ่มประสิทธิภาพในการกราฟต์ การกราฟต์โคพอลิเมอร์ไอโซไซยานูเรทเตรียมจากกระบวนการอิมัลชันผ่านอนุมูลอิสระโดยใช้โพแทสเซียมเปอร์ซัลเฟตเป็นตัวริเริ่มปฏิกิริยา ศึกษาสมบัติการกราฟต์ซึ่งเป็นผลจากความเข้มข้นของตัวริเริ่มปฏิกิริยา สัดส่วนโดยน้ำหนักระหว่างเมทิลเมทาครีเลต/2,2,2-ไตรฟลูออโรเอทิลเมทาครีเลต อุณหภูมิในการทำปฏิกิริยา และเวลาในการทำปฏิกิริยา พบว่าภายใต้ภาวะที่เหมาะสม (50/50 โดยน้ำหนักของเมทิลเมทาครีเลต/2,2,2-ไตรฟลูออโรเอทิลเมทาครีเลต 0.75 ส่วนในยางธรรมชาติ 100 ส่วน ของโพแทสเซียมเปอร์ซัลเฟตที่อุณหภูมิ 60 องศาเซลเซียสเป็นเวลา 4 ชั่วโมง) ยางธรรมชาติกราฟต์ที่ได้ มีประสิทธิภาพการกราฟต์และปริมาณไตรฟลูออโรเอทิลเมทาครีเลตสูงสุด 23.6% และ 7.3% โดยโมล ตามลำดับ และมีปริมาณเจล 3.8% วิเคราะห์โครงสร้างทางเคมีของยางธรรมชาติกราฟต์ด้วยเทคนิคเอทเทนนูเอทโทพัลรีเฟลกแทนซ์อินฟราเรดสเปกโตรสโคปี และนิวเคลียร์แมกเนติกเรโซแนนซ์สเปกโตรสโคปี สันฐานวิทยาของลาเท็กซ์ของยางธรรมชาติกราฟต์วิเคราะห์ด้วยกล้องจุลทรรศน์อิเล็กตรอนแบบส่องผ่านแสดงให้เห็นเป็นแบบแกน-เปลือก ยางธรรมชาติกราฟต์ถูกนำไปผสมกับพอลิ(2,2,2-ไตรฟลูออโรเอทิลเมทาครีเลต)เพื่อทำเป็นฟิล์มพอลิ(2,2,2-ไตรฟลูออโรเอทิลเมทาครีเลต)ตัดแปรร การทดสอบความเข้ากันได้ระหว่างพอลิเมอร์ที่เป็นองค์ประกอบในฟิล์มใช้เทคนิคการทดสอบแบบโมดู และกล้องจุลทรรศน์แรงอะตอม ค่ามุมสัมผัสของน้ำและเฮกซะเดคเคน พลังงานพื้นผิว และการวิเคราะห์สมบัติเชิงกลและสมบัติทางความร้อนของฟิล์มที่ได้ยังถูกทดสอบอีกด้วย สังเกตได้ว่าการเติมยางธรรมชาติกราฟต์ช่วยให้ฟิล์มมีสมบัติทางพื้นผิวและสมบัติเชิงกลที่ดีกว่าการเติมยางธรรมชาติที่ไม่ผ่านการกราฟต์

สาขาวิชา ปีโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต

ปีการศึกษา 2559

ลายมือชื่อ อ.ที่ปรึกษาหลัก

5671909123 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE

KEYWORDS: FLUORINATED ACRYLATE / GRAFT COPOLYMERIZATION / NATURAL RUBBER / SURFACE PROPERTIES

KRITIYA HOMCHOO: GRAFT COPOLYMERIZATION OF FLUORINATED ACRYLATE MONOMER ONTO NATURAL RUBBER LATEX. ADVISOR: ASSOC. PROF. NAPIDA HINCHIRANAN, Ph.D., 90 pp.

The incompatibility and phase separation of fluorinated acrylate polymer/natural rubber (NR) blend was obtained due to polarity mismatch of polymeric constituents in the blend. To decrease the phase separation in the composite, the graft copolymerization was a favorite method to enhance the compatibility of the blends. In this study, 2,2,2-trifluoroethyl methacrylate (TFEMA) was grafted onto NR backbone, which was assisted by methyl methacrylate (MMA) acting as a co-monomer for enhancing the grafting efficiency (GE). The graft copolymerization was carried out by emulsion-grafting process via free radical using potassium persulphate (KPS) as an initiator. The grafting properties were investigated as a functions of initiator concentration, MMA/TFEMA wt ratio, reaction temperature and reaction time. Under the optimum conditions (condition: 50/50 (w/w) of MMA/TFEMA, 0.75 phr of KPS at 60 °C for 4 h) the obtained gross graft NR (GNR) contained the maximum %GE and grafted TFEMA content as 23.6% and 7.3 mol%, respectively, with 3.8% gel content. The chemical structure of GNR after soxhlet extraction was analyzed by using attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) and nuclear magnetic resonance spectroscopy (NMR). The morphology of GNR latex characterized by using transmission electron microscopy (TEM) was core-shell type. The graft product was then blended with PTFEMA to form modified PTFEMA films. The compatibility testing between polymeric constituents in the films was observed via Molau test and atomic force microscope (AFM). Water and hexadecane contact angles, surface energy and analysis of mechanical and thermal properties of the obtained films were also examined. It was observed that the addition of GNR provided the better surface and mechanical properties of the modified PTFEMA films than that of non-grafted NR.

Field of Study: Petrochemistry and Polymer Student's Signature
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CHAPTER I

INTRODUCTION

1.1 The statement of problem

2,2,2-Trifluoroethyl methacrylate (TFEMA) belongs to a family of fluorinated acrylate monomers with low fluorine content (34%) (Chen et al. 2006). It exhibits unique properties such as high thermal stability with high resistance to chemicals and weather. The low surface energy of these fluorinated acrylate polymer provides hydrophobic and oleophobic characteristics. The presence of fluorinated moiety in C-F bonds in the polymer provides the superior properties than C-H bonds (Yao, Li, and Huang 2014). Poly (2,2,2-trifluoroethyl methacrylate) (PTFEMA) is employed for various applications, especially in surface coatings and modification of surface properties for electrode materials (Wang et al. 2016), automotive industry (Alyamac and Soucek 2011), ramie fiber etc. (Liu et al. 2010). However, PTFEMA is expensive and has high glass transition temperature (T_g) as ca. 79 °C (Papadopoulou and Panayiotou 2014) resulting in the poor film-forming property (Xu et al. 2016).

To consider the elastomeric materials, natural rubber (NR) or *cis*-1,4-polyisoprene is one of green materials with outstanding mechanical properties and its price is cheaper than the conventional petroleum-based elastomers. It has low T_g (-62.3°C) (Kongparakul, Prasassarakich, and Rempel 2008) with excellent elasticity and it can be formed as flexible films (Phinyocheep 2014). It is normally applied as thin film for various applications such as gloves, dental dam, condoms, balloons and catheters (Yip and Cacioli 2002) including a film former for pharmaceutical coating applications (Panrat et al. 2012). Moreover, NR can be used as the impact modifier to improve the mechanical properties of brittle polymers. However, the use of NR is

limited due to its high level of unsaturation resulting the low resistance to thermal and oxidative degradation. In addition, NR is deteriorated by non-polar chemicals since it is classified as a non-polar rubber (Phinyocheep 2014).

In order to improve the disadvantage of PTFEMA and NR with reducing the production cost for using only PTFEMA, the blending of PTFEMA with NR is expected to give the desirable properties with reasonable price. However, NR is incompatible with PTFEMA due to the polarity mismatch of polymeric constituents in the blend. To decrease the phase separation in the composite, the graft copolymerization is an attractive method to enhance the compatibility among composition in the blends. Unfortunately, it is difficult to directly graft PTFEMA onto NR structure due to their polarity difference. The introduction of appropriate co-monomer could enhance the grafting efficiency (GE) in some systems. Wongthong et al. (2014) reported that the addition of styrene (ST) as the co-monomer could enhance the GE value of maleic anhydride (MA) onto deproteinized natural rubber (DPNR). Okieimen and Urhoghide (2002) studied the graft copolymerization of acrylonitrile (AN) and methyl methacrylate (MMA) monomer mixtures onto crumb natural rubber. The results showed that the increase in the MMA content in the monomer mixture from 38 to 50 mol% could increase the level of grafting from 35 to 60%. Normally, the graft copolymerization of vinyl monomers onto NR could be performed in the molten state (Hinchiranan et al. 2013), solution form (Angnanon, Prasassarakich, and Hinchiranan 2011) and emulsion process (Kongparakul, Prasassarakich, and Rempel 2008). However, the emulsion graft copolymerization operated at milder condition is expected to inhibit the gel formation during grafting reaction and this process is easier to handle with economical efficiency due to low viscosity and no use of the toxic solvents (Ebewele 2000; Guo et al. 2007). Moreover, NR in the latex form is available and lower price than the solid rubber. Thus, the graft copolymerization in the emulsion state is suitable for further industrial scale production.

The aim of this research was to prepare the graft copolymerization of PTFEMA onto NR latex assisted by methyl methacrylate (MMA) as the co-monomer in the emulsion system. The chemical structure of the obtained gross graft NR (GNR) after Soxhlet extraction was analyzed by using attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) and nuclear magnetic resonance spectroscopy (NMR). The grafting properties were investigated as functions of MMA/TFEMA wt ratio, initiator concentration, reaction temperature and reaction time. The morphology of GNR latex was characterized by using transmission electron microscopy (TEM). The graft product was then blended with PTFEMA to form the modified PTFEMA films. The compatibility testing between polymeric constituents in the films was observed via Molau test and atomic force microscope (AFM). The contact angle, surface energy and analysis of mechanical and thermal properties of the obtained films were also reported.

1.2 Objectives of the research work

The objectives of this research are stated as followed:

1. To prepare the graft copolymer of poly(TFEMA-co-MMA) onto NR via emulsion graft copolymerization. The effects of MMA/TFEMA wt ratio, initiator concentration, reaction temperature and reaction time on the grafting properties were investigated.
2. To characterize the chemical structure of graft copolymer by using ATR-FTIR, $^1\text{H-NMR}$ and $^{19}\text{F-NMR}$ spectroscopy. The morphology of graft latex was also characterized by using TEM.
3. To study the effect of GNR on compatibility, thermal properties, surface properties and mechanical properties of the modified PTFEMA films.

1.3 Scope of the research work

The details of experimental procedure for this research were presented as followed:

1. Survey previous literatures and related research works.
2. Prepare the graft copolymer of poly(TFEMA-co-MMA) onto NR via emulsion process initiated by potassium persulphate (KPS).
3. Characterize the structure of graft copolymer after soxhlet extraction by using ATR-FTIR, $^1\text{H-NMR}$ and $^{19}\text{F-NMR}$ spectroscopy.
4. Determine the grafting properties and gel content of GNR and the morphology of GNR latex was also characterized by using TEM.
5. Prepare the modified PTFEMA films containing various contents of GNR.
6. Determine the compatibility, surface properties, thermal properties and mechanical properties of the modified PTFEMA films.
7. Summarize the results and write the thesis

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Fluorinated acrylate polymers (Yao, Li, and Huang 2014)

The fluorinated (meth)acrylates belong to a family of fluoropolymers that are consisted of acrylate which one or more fluorine atoms substitute in hydrogen atom. The presence of fluorinated moiety in the polymer provides outstanding properties including high resistance to thermal, chemical, aging, and weather degradation. They also have low level of dielectric constant, refractive index, surface energy and flammability. Moreover, they are excellent inertness to solvents, hydrocarbons, acids, alkalis, and moisture adsorption as well as oil and water repellency due to strong C-F bond (131 kcal/mol) in comparison with C-H bond (99 kcal/mol). This indicates that C-F bond is the most stable. In addition, fluorinated (meth)acrylates have good reactivity with other monomers or polymer segments and they are more conveniently synthesized than other fluoropolymers. Therefore, it can be used for various applications; especially, coating for water and chemical resistance and antifouling coatings. Fluorinated (meth)acrylates can be divided into two types:

1. Fluorinated alkyl acrylates that are consisted of (meth)acrylates substituted with fluorinated alkyl groups as shown in Figure 2.1. Their homopolymers are sparsely soluble in organic solvents. In particular, polymers with a fluorinated carbon ($\text{CF}_3(\text{CF}_2)_m$) having 8 or higher fluorine atoms are generally insoluble in organic solvents.

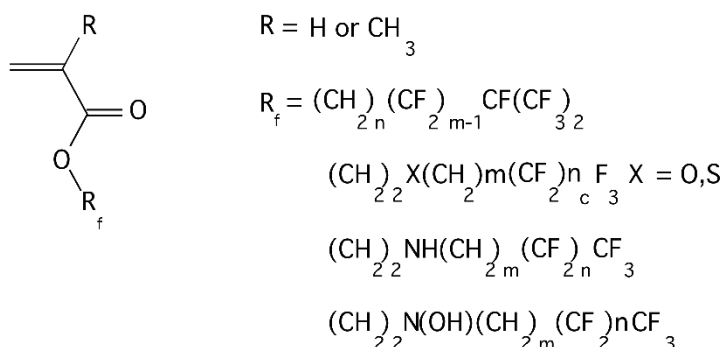


Figure 2.1 Fluorinated alkyl (meth)acrylates (Yao, Li, and Huang 2014)

2. Fluorinated aryl (meth)acrylates contain an activated ester group with one or more fluorine substituents in the aromatic ring as shown in Figure 2.2

However, the application of the fluorinated acrylate polymers for coating is very limited because of low adhesion, high price (Wang et al. 2015), poor film formation (Xu et al. 2016) and lack of elasticity. To overcome these disadvantages, 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. The fluorinated acrylate copolymers can be synthesized by block copolymerization (Zhao et al. 2011), graft copolymerization (Tan, Liu, and Wang 2016), random copolymerization (Xu et al. 2016) and core-shell copolymerization (Li, Zeng, et al. 2014).

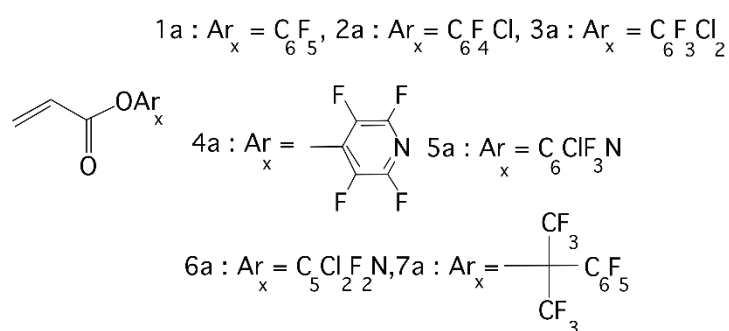


Figure 2.2 Fluorinated aryl (meth)acrylate (Yao, Li, and Huang 2014)

Zhao et.al. (2011) studied the pH-responsive and fouling-release properties of polyethersulfone (PES) ultrafiltration membranes modified by multi-functional block-like copolymers. The PES membrane was blended with block copolymer prepared by poly(butyl methacrylate)-*b*-poly(methacrylic acid)-*b*-poly(hexafluorobutyl methacrylate) (PBMA-*b*-PMAA-*b*-PHFBM) via free radical polymerization. The membranes exhibited desirable fouling release property with the highest and stable cleaning efficiency above 57% due to the presence of fluorine-containing segments; whereas, the membranes without fluorine-containing portion exhibited the drastic protein fouling.

Li et al. (2014a) studied the preparation of superhydrophobic fluorinated-polyacrylate/silica hybrid coating. The core-shell fluorinated-polyacrylate (PFA) emulsion was synthesized through emulsion polymerization. Methyl methacrylate (MMA), butyl acrylate (BA), acrylic acid (AA) and hydroxy-propyl acrylate (HPA) were used as a core phase, while dodecafluoroheptyl methacrylate (DFMA) was applied as a shell phase. It was found that the water contact angle of the PFA film enlarged from 85° to 104° with increasing DFMA content in the shell phase from 0 to 31.8 wt%. Moreover, PFA/SiO₂ hybrid coating showed the resistance to acid and base and it also provided the weather resistance ability and thermal stability.

Xu et al. (2016) studied the preparation and surface property of poly(2,2,2-trifluoroethyl methacrylate) (FMA) coatings, which was modified with methyl acrylate (MA). Series of copolymers of FMA and MA with different copolymer compositions were synthesized by solution polymerization. It was found that the copolymer with ca. 50 mol% MA exhibited comparable hydrophobic property and thermal stability to the PFMA homopolymer. The glass transition temperature of the copolymers could be decreased to room temperature resulting in the good film-forming property.

It could be observed that the fluorinated poly(meth)acrylate-based copolymers provided unique properties such as low surface energy, chemical resistance, thermal

stability and weather resistance. These advantages were obtained from the fluorinated acrylate monomer with low fluorine monomer content.

2.2 Natural rubber (Phinyocheep 2014; MatadorRubber 2007)

Natural rubber (NR) are derived from tapping based on cutting of the *Hevea brasiliensis* bark belonging to *Euphorbiaceae* family. The obtained product is colloid having the rubber particles with the spherical form dispersed in water. Latex particle size is varying approximately from 0.05 to 3 μm . The chemical structure of NR is consisted of *cis*-1,4-polyisoprene as shown in Figure 2.3. In the fresh latex, it contains approximately 25-40% dry rubber content (DRC) and 5-10% non-rubber components such as proteins, carbohydrates and other organic and inorganic constituents.

Macromolecule of NR is regularly long, flexible and practically linear. Thus, it has very good elasticity with spontaneous crystallization under influence of deformation forces at relative prolongation as higher than 80%. It also has excellent strength characteristics and T_g about $-70\text{ }^\circ\text{C}$. Moreover, NR is also claimed as the low cost material with availability in tropical countries. The type of NR product is classified as two major types: latex concentrate (NR latex) and solid dry rubber. The NR latex is consisted of 60% (V/V) rubber content (polyisoprene) and it is preserved with ammonia. The NR latex can be used in various applications; especially, in the form of thin film such as gloves, condoms, dental dam (Yip and Cacioli 2002) and coating application (Panrat et al. 2012) since it has good film forming properties (Panrat et al. 2012; Phinyocheep 2014). NR has unsaturated C=C bonds, which are easily degraded by ozone, oxygen and sunlight. In addition, NR cannot be used in the presence of non-polar chemicals since the chemical structure of NR is claimed as non-polarity.

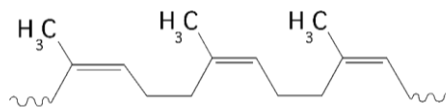


Figure 2.3 cis-1,4-polyisoprene (Phinyocheep 2014)

2.3 Properties improvement of NR

Due to the drawback and excellent properties of NR, many efforts have been applied to improve NR properties or to introduce NR into new polymeric materials for specific applications. There are two important methods for improving the properties of NR: blending of NR with other polymers and chemical modification of NR structure.

2.3.1 Blending of NR

NR blends are mixtures of NR and one or more polymers without the formation of new chemical bonds. This technique can enhance the polymer performance with advantageous properties of each polymeric components (Bahrami et al. 2017) The polymer blending is the economic method, easy manufacture and less time consumption. Thus, the blending is suitable for industrial-scale production. The NR blends can be classified as two types: rubber/rubber and plastic/rubber blends (Patel and Shin 2011). The rubber /rubber blends is normally used in the composite structures such as tires, hoses, conveyer or belts. The compounds have many unique characteristics such as high elasticity, abrasion resistance and dampening properties (Rodgers and Halasa 2011). In the case of the plastic/rubber blends, they offer several interesting possibilities to serve in various applications. These blends also provide the product with variety of properties from soft elastic rubbery to ductile materials depended on the relative proportions of the components (Patel and Shin 2011). Generally, blending of NR had been use to improve mechanical properties of brittle polymers.

Mina et al. (2004) investigated the hardness of both PMMA and PMMA/NR blends prepared by the solution method. The PMMA/NR ratio was varied in the range 100/0–95/5 (w/w). The microhardness (H) of the blends had been investigated by means of the microindentation technique. The microhardness and T_g of PMMA/NR blends were lower than that of PMMA from 180 to 140 MPa and 352 to 347 K, respectively. In addition, the mechanical deformation of the blends was much higher than that of PMMA at higher draw ratios due to the elongated rubber particles acting as the fibers in a reinforced composite materials for which the material becomes stronger in the direction of the ellipsoid.

Neoh and Hashim (2004) studied the mechanical, morphological and aging properties of polystyrene (PS) toughening by grafted polystyrene-modified NR (SNR). It was found that the mechanical properties of PS/NR and PS/SNR blends were greater than those of pure PS. For example, the tensile strength of PS/NR and PS/SNR blends containing 5 vol% rubber loading were 28.6 and 31.0 MPa, respectively, which was higher than that of PS (27.5 MPa). The impact strength of the rubber-toughened samples was also higher than that of the pure PS approximately 0.5–2.5 times for PS/NR blends and 2.4–11.7 times for PS/SNR blends.

Benmesli and Riahi (2014) studied flow properties, thermal properties, mechanical properties and morphology of polyamide 6/liquid NR blends prepared by melt mixing. The addition of NR in polyamide 6 from 0 to 20 wt% decreased the hardness shore D from 110 to 60 with increasing the elongation at break from 84 to 209.5%.

From the previous literatures, it was observed that the obtained blends exhibited the homogeneously miscible or immiscible depended on the relative polarity (Patel and Shin 2011). In the case of immiscible blends, their morphology was varied. Normally, the observed morphologies can be divided as (i) a dispersion of one polymer in the matrix of the other polymer and (ii) a co-continuous two-phase

morphology. The factors relate to the morphology type is the nature of the blend components, the viscosity and the viscosity ratio of both polymers at the blending temperature and the blend composition (Koning et al. 1998).

Since the most of the plastic/NR blends shows the immiscibility resulting in poor physical and mechanical properties, the addition of compatibilizer is necessary. Usually, the phase separation of polymer blends is readily occurred because the monomer units in the polymer chains are covalently bonded to each others. This limits the arrangement of the polymer chains and leads poor interface and adhesion between the components resulted in the poor performance of the polymer blends (Covas et al. 2016; Datta 2013). In order to modify the interfacial tension between the separated phases, the addition of compatibilizer is expected to enhance the interaction of polymeric constituents in the blends (Satyanarayana, Bhowmick, and Dinesh Kumar 2016). The role of the compatibilizer is the reduction of the interfacial energy to improve the adhesion between phases. The finer dispersion can be achieved during mixing and the stable fine dispersion can against agglomeration during processing and throughout the product life (Datta 2013). Figure 2.4 shows an idealized compatibilizer which one segment of comptibilizer is miscible with one component of the blend, while the other segment is miscible with the other component of the blend (Patel and Shin 2011). The compatibilization of plastic/rubber blends can be prepared by epoxidation and grafting of NR such as NR-*graft*-MMA/poly(methyl methacrylate) (PMMA) blend (Thiraphattaraphun et al. 2001), maleated NR/PMMA blend (Nakason et al. 2006) and epoxidize NR/poly(vinyl chloride) (PVC) blend (Radhakrishnan Nair et al. 2009).

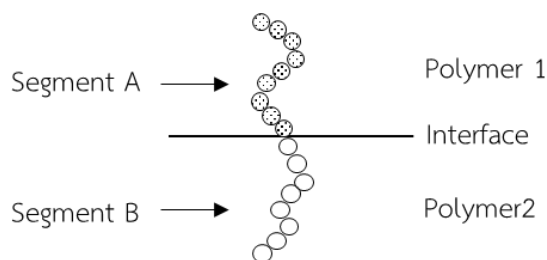


Figure 2.4 Idealized compatibilizing block copolymer (Patel and Shin 2011)

2.3.2 Epoxidation (Phinyocheep 2014)

Epoxidation is the chemical reaction that can convert the C=C bonds as oxiranes (epoxides) using a variety of reagents including air oxidation, hypochlorous acid, hydrogen peroxide, and organic peracid. The procedure of epoxidation is shown in Figure 2.5. The epoxidized NR (ENR) has a wide range of properties depending on the degree of epoxidation. The higher epoxidation levels increased the hardness of the rubber. It was found that ENR with less than 50% epoxidation is still elastic material with an off-white colour. The oxidative stability of ENR is better than that of NR since ENR contains the less unsaturation. When the epoxidation level is increased, the polarity of the rubber is also increased and therefore solubility in polar solvent is increased and solubility in nonpolar solvent is decreased. Consequently, ENR shows the better oil resistance than NR. In addition, the air permeability is similar to butyl rubber. The tensile strength of ENR remains high as it undergoes strain crystallisation as NR. The blending of ENR with other polymers has been widely studied. The epoxide group in ENR can act as a proton acceptor which offers potential interaction with polar atoms in other polymers.

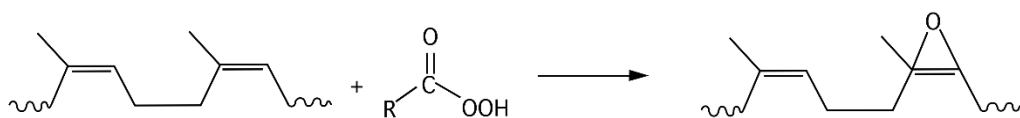


Figure 2.5 Scheme of epoxidation of NR (Phinyocheep 2014)

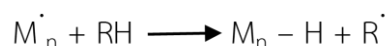
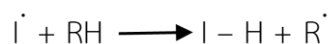
2.3.3. Graft copolymerization (Phinyocheep 2014)

The graft copolymerization of vinyl monomers onto NR has been widely used as a thermoplastic elastomers or as a compatibilizer for various blending systems. The graft copolymers contain segments with identical structures or with specific reactive interactions that can promote the interfacial adhesion and reduce the interfacial tension among the immiscible rubber components in the blends (Hinchiranan et al. 2013). The graft copolymerization of NR is the incorporation of vinyl monomers on the NR backbone at the active sites. The mechanism of graft copolymerization by a free radical process may be divided as two main types: (i) addition of a radical initiator (I^\cdot) or polymer radicals (M_n^\cdot) derived from the homopolymerization of monomers in the system onto the C=C bonds in the rubber molecule (RH) and (ii) abstraction of a labile hydrogen atom from the RH by I^\cdot or M_n^\cdot as shown below:

1. Addition of radicals to the C=C bonds in RH:



2. Hydrogen abstraction from RH:



The molecular structure of the graft copolymer is preferably represented by grafting at the allylic position of the NR molecule as shown in Figure 2.6.

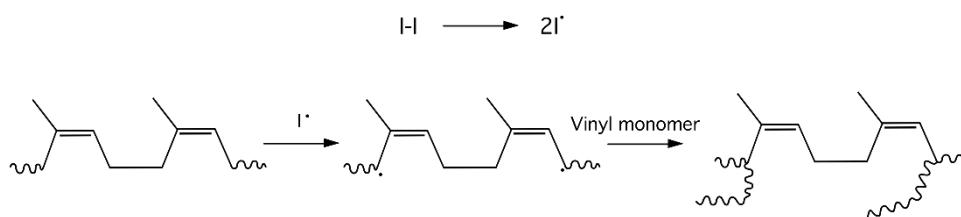


Figure 2.6 Graft copolymerization of vinyl monomer onto NR backbone via radical polymerization (Phinyocheep 2014).

The graft copolymers can be prepared via three procedures: grafting onto, grafting from and grafting through (O'dian 2004).

- Grafting onto involves the functional groups between two different polymers. It is the least useful method since the reaction occurred between polymers are slow and there are relatively limited numbers of polymers with functional groups those are able to react with each other. However, this procedure provides high grafting density depended on the content of functional group on the polymer backbone. The grafting onto can be shown in Figure 2.7a.

- Grafting from involves a polymer with functional groups that initiate polymerization of monomer. This method is useful since many polymers can be used together with a range of reaction conditions (radical and ionic). Besides, the higher grafting density is depended on the amount of functional group on the polymer backbone. The grafting from reaction is shown in Figure 2.7b.

- Grafting through involves the polymerization (or copolymerization) of a macromonomers, usually a vinyl macromonomers. Grafting through is convenient procedure, but this technique requires the synthesis of the macromonomers. The grafting density derived from this process is controlled by the ratio of macromonomer to comonomer. The grafting through reaction is exhibited in Figure 2.7c.

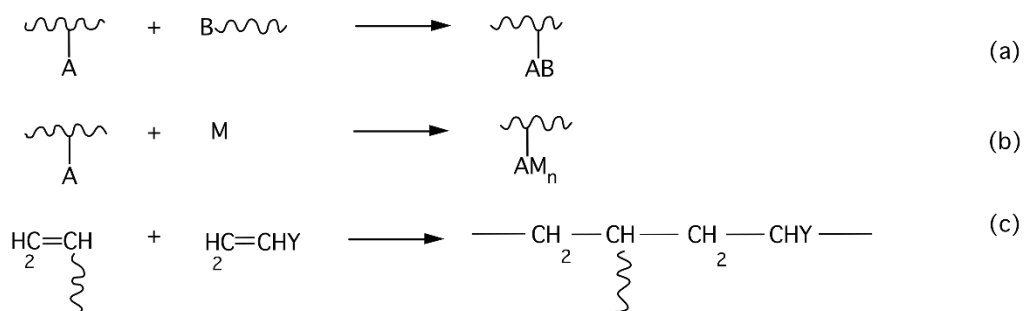


Figure 2.7 The methods for synthesizing graft copolymers: (a) grafting onto, (b) grafting from and (c) grafting through (Odiان 2004).

2.4 Initiation of free radical

Radicals can be produced by a variety of thermal, high-energy radiation, photochemical process and redox methods.

2.4.1 Thermal decomposition (Odiان 2004)

The thermal or homolytic dissociation of initiators is the most widely used process to generate radicals for initiating the polymerization. The compounds having O-O, S-S, N-O and peroxides are used in this method. Especially, peroxy compounds are favorite to be used as radical sources such as acyl peroxides, alkyl peroxides, hydroperoxides, peresters, acyl alkylsulfonyl peroxides, dialkyl peroxydicarbonates, diperoxyketals, and ketone peroxides. The dissociation of peroxy compounds is shown in Figure 2.8

In addition, the azo compounds can be applied in this method. The member of this class such as 2,2'-Azobisisobutyronitrile, 2,2'-azobis(2,4-dimethylpentanenitrile), 4,4'-azobis(4-cyanovaleric acid) and 1,1'-azobis(cyclohexanecarbonitrile). The dissociation of azo compounds is indicated in Figure 2.9

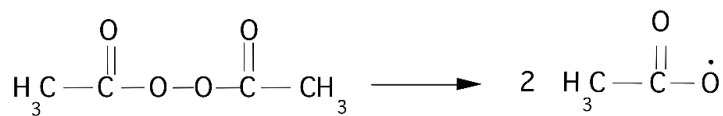


Figure 2.8 The thermal dissociation of acetyl peroxides (Odian 2004)

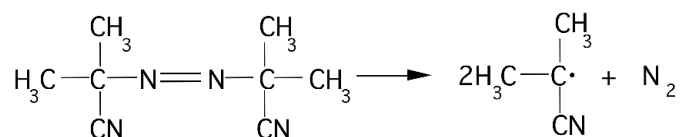


Figure 2.9 The thermal dissociation of 2,2'-Azobisisobutyronitrile (Odian 2004).

2.4.2. Redox polymerization (Halasa, Massie, and Ceresa 2013)

Redox polymerizations are among the most popular techniques for grafting reactions. The possible initiator systems such as ferrous ion oxidation and those based on ceric ion reduction are widely used. At the same time of the addition of monomer, a hydroperoxide or similar group is reduced to a free radical plus an anion, while the metal ion is oxidized to a higher valency state. When the reducible group is attached to a polymeric chain, the free radical grafting sites are formed on the macromolecular backbone acting as the initiators for graft copolymerization as shown in Figure 2.10. The redox initiation usually provides grafting with a minimum homopolymerization since only the polymeric radical is formed. However, it is limited to polymers containing the necessary functional group (Odian 2004).

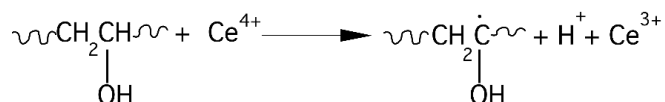


Figure 2.10 Redox reaction with ceric ion (Odian 2004).

2.4.3 High-energy radiation techniques

Polymer radicals can also be produced by the irradiation of main-chain. Much of the irradiation energy is adsorbed by the removal of hydrogen atoms in the main-chain to generate radicals on the polymeric backbone which is used as the active sites for initiating the graft copolymerization (Halasa, Massie, and Ceresa 2013). This technique proceeds in three different ways (Bhattacharya and Misra 2004).

- **pre-irradiation**

The polymer backbone is first irradiated in vacuum or in the presence of an inert gas to form free radicals. The irradiated polymer substrate is then treated with the monomer in liquid or vapor state or as a solution in a suitable solvent. However, the decided disadvantage of the pre-irradiation technique is a scission of the base polymer due to its direct irradiation, which can result in the formation of block co-polymers.

- **peroxidation**

In the peroxidation grafting method, the trunk polymer is subjected to high-energy radiation in the presence of air or oxygen to form hydroperoxides or diperoxides, depended on the nature of the polymeric backbone and the irradiation conditions. The stable peroxy products are then treated with the monomer at higher temperature, whereas the peroxides undergo decomposition as radicals, which then initiate grafting. The advantage of this technique is that the intermediate peroxy products can be stored for long periods before performing the grafting step.

- **mutual irradiation technique**

This process, the polymers and monomers are simultaneously irradiated to form free radicals and subsequent addition. Since the monomers are not exposed to radiation in the pre-irradiation technique, the obvious advantage is that this method does not produce high content of homopolymer.

These processes are represented through simple mechanisms as described in Figure 2.11.

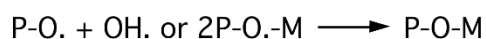
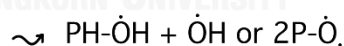
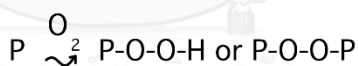
2.4.4 Photochemical synthesis (Bhattacharya and Misra 2004)

Photolytic grafting is similar to radiation grafting, except the depth of penetration by UV which is less than by ionizing radiation (Odian 2004). In case of grafting without the addition of a sensitizer, a chromophore on a macromolecule absorbs light and dissociate as reactive free-radicals via bond breaking. This mechanism involves the generation of free radicals on the backbone and these free radicals then react with the free radicals generated from monomer to form the grafted co-polymer as shown in Figure 2.12.

(a) Per-irradiation



(b) Peroxidation



(c) Mutual irradiation

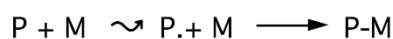


Figure 2.11 Different ways occur during high-energy radiation techniques (Bhattacharya and Misra 2004)

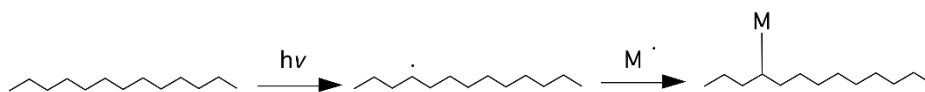


Figure 2.12 Photolytic grafting without using a sensitizer (Bhattacharya and Misra 2004).

Normally, the photochemical synthesis is often performed in the presence of a photosensitizer such as benzophenone or benzoin. The sensitizer forms free radicals, which can undergo diffusion, so that they abstract hydrogen atoms from the base polymer and the radical sites required for grafting are then produced as shown in Figure 2.13.

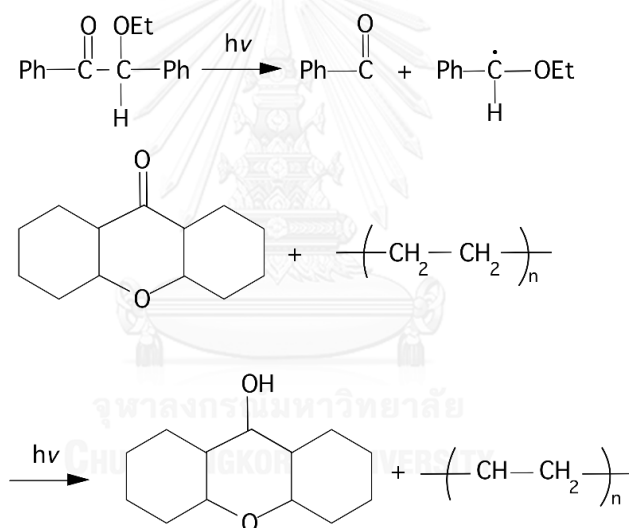


Figure 2.13 Photolytic grafting using a sensitizer (Bhattacharya and Misra 2004)

2.5 Literature reviews

Mielczarski et al. (2010) studied the surface-segregation of fluorinated copolymer/poly(dimethylsiloxane) (PDMS) blend films. The fluorinated copolymer was synthesized via free radicals in the solution process. The copolymer solution was then mixed with the bis(silanol)-terminated PDMS, the ES40 cross-linker and the DBTDA catalyst in the presence of xylene to form the blend film. The results from X-ray

photoelectron spectroscopy (XPS) revealed that the amount of fluorine atoms at the outer surface of the blend film was higher than that of the theoretical value. This was attributed to the surface segregation that could induce the fluorinated chain segments of the copolymer in the blend films.

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 (NMA) 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 blend 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 latex blend and the fluorinated acrylate monomer in the FA latex increased the water and oil contact angles. This indicated that the surface wettability of the blend film decreased with increasing the consumption 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 drastically decreased from initially 37 (mN/m) to 31 (mN/m) with the content of PHFA-GMA as 0.125 wt%.

Wang et al. (2000) studied the surface modification of NR latex films by graft copolymerization with either acrylamide (AAm) or 2,2,3,3,4,4,4 heptafluorobutyl acrylate (HFA). The graft copolymerization was carried out by UV-induced graft copolymerization. The water contact angle of the obtained film increased from 80 ° for ungraft NR film to 109 ° when HFA grafted onto the NR surface due to the hydrophobic nature of the fluoropolymer.

Hinchiranan et al. (2013) studied the preparation of graft copolymerization of 2,2,2-trifluoroethyl methacrylate (TFEM) onto NR via melt-mixing process. The obtained graft NR (GNR) was then applied as the compatibilizer for NR/fluoroelastomer (FKM) vulcanizates. The addition of GNR as 15 parts per hundred of rubber (phr) enhanced the compatibility between the NR and FKM phases with a highest homogeneity of the vulcanizates. Moreover, the tensile strength of compatibilized vulcanizates was also higher than that of the incompatibilized ones because of the higher degree of homogeneity of compatibilized blend. The reason of compatibility was that the CF_3 bonds in GNR might reduce the interfacial tension resulting in the improvement of the adhesion between the constituent phases in the rubber blends.

Thiraphattaraphun et al. (2001) studied the mechanical properties and the fractural behavior of NR-g-MMA (GNR)/PMMA blends. The GNR were prepared via emulsion graft copolymerization initiated by potassium persulphate (KPS). The GNR/PMMA blends were then formed via melt-mixing method. The properties of the GNR/PMMA blends were evaluated as a functions of the graft copolymer composition and the blend ratio. The tensile fractural surface examined by scanning electron microscopy (SEM) revealed that the GNR/PMMA blends containing GNR with high level of grafting efficiency (GE) provided the smoother fractural surface. This observation indicated that the graft copolymer acted as an interfacial agent to give a good adhesion between the two phases of the blend.

Nakason et al. (2006) studied the rheological, thermal and morphological properties of the maleated NR (MNR) and its blending with PMMA. MNR were prepared by grafting with maleic anhydride (MAH) onto NR via melt-mixing at 135 °C. The SEM micrograph showed that the cavity of the MNR/PMMA blends decreased with increasing the levels of MAH in MNR. Furthermore, the PMMA was more finely dispersed with the increase in the MAH concentration. This indicated that MNR could be used as an

interfacial agent to reduce the size of the dispersed phase by increasing the interaction with polar groups in the PMMA.

Okieimen and Urhohide (2002) studied the characteristics of NR graft with acrylonitrile (AN) and MMA monomer mixtures and the miscibility of the graft product with PVC. The graft copolymerization was conducted in the presence of solvent. The degree of grafting increased from 35 to 66% with increasing MMA content from 38 to 50 mol%. Moreover, the obtained graft product could provide the semimiscible blends with PVC.

Wongthong et al. (2014) studied the grafting of MAH onto deproteinized natural rubber (DPNR) with the addition of styrene (ST) used as the co-monomer in order to increase the GE value of MAH. The graft copolymerization was carried out using a microemulsion polymerization technique. It was found that the grafting system in the presence of styrene showed the higher GE value than the system in the absence of the solvent. Moreover, the GE increased with an increase in the ratio of ST/MA. This attributed to an improvement of GE for styrene-assisted grafting reaction.

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

High ammonia preserved natural rubber (NR) latex containing ca. 60% dry rubber content (DRC) was purchased from Rubber Research Institute of Thailand (Bangkok, Thailand). The gel content of NR latex was observed as 50 wt%. The detail for gel testing will be explained in the Section 3.6. Methyl methacrylate (MMA) and 2,2,2-trifluoroethyl methacrylate (TFEMA) were supplied by Sigma-Aldrich (USA). The chemical structures of both MMA and TFEMA were shown in Figure 3.1. Before use, MMA was purified by washing with 10 wt% sodium hydroxide and deionized water until neutral. Then, the purified MMA was dried over sodium sulphate anhydrous. The dried MMA monomer was then distilled under reduced pressure (50-60 °C/200 mmHg) and stored in a refrigerator (Arayapranee, Prasassarakich, and Rempel 2002). Whereas, TFEMA was used as received without further purification. Potassium hydroxide (KOH) was purchased from QReCTM (New Zealand). Sodium dodecyl sulphate (SDS) and potassium persulphate (KPS) were supplied by Ajax Finechem (Australia). The deuterated chloroform (CDCl_3) was also obtained from Cambridge Isotope Laboratories (USA). Tetrahydrofuran (THF) was purchased from QReCTM (New Zealand).

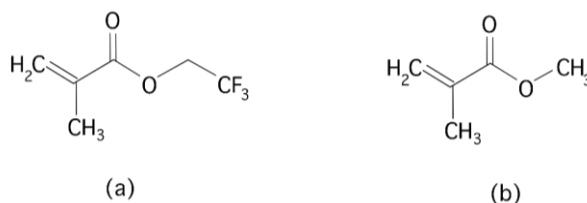


Figure 3.1 Chemical structures of (a) 2,2,2-trifluoroethyl methacrylate (TFEMA) and (b) methyl methacrylate (MMA).

3.2 Graft copolymerization of poly(TFEMA-co-MMA) onto NR particles

Dilute NR latex with 30%DRC (14 g) was charged into 100 mL three neck flask having 20 mL distilled water containing 0.25 part per hundred of rubber (phr) KOH and 1 phr SDS used as a buffer and emulsifier, respectively under stirring in nitrogen atmosphere at room temperature. The 100 phr MMA/TFEMA monomer mixture (0/100, 30/70, 50/50, 60/40, 70/30 and 100/0 (w/w)) was gradually dropped into the system. The mixture was then heated up to desired temperature (50-80 °C). KPS initiator (0.5-2 phr) was then charged into the reaction mixture. The reaction was allowed for 2-8 h under stirring. When the reaction was ceased, 20 g (total solid content = 23 wt%) obtained gross graft NR (GNR) latex was casted on the petri dish ($\varnothing = 90$ mm) at room temperature to form a film with 0.62 ± 0.06 mm thickness. When the dry GNR film was peeled off from the petri dish, it was washed out by distilled water and then dried in a vacuum oven at 40 °C until the weight of film was constant.

3.3 Synthesis of poly(TFEMA-co-MMA) and PTFEMA latex

Poly(TFEMA-co-MMA) (MMA/TFEMA = 50/50 (w/w)) and PTFEMA were synthesized following the similar method for grafting without the addition of NR latex. The amount of monomers, KPS, KOH and SDS were kept constant at 8 g, 0.03 g, 0.01 g and 0.04 g, respectively. The reaction was allowed for 8 h under stirring in the nitrogen atmosphere at 60°C. The total solid content of the poly(TFEMA-co-MMA) was ca 23%. The gel content of poly(TFEMA-co-MMA) and PTFEMA were 0.2 and 98 wt%, respectively.

3.4 Structural characterization and determination of grafting properties

The GNR film was consisted of three main fractions: NR-g-poly(TFEMA-co-MMA) (graft NR), free NR (unreacted NR) and free copolymer (ungrafted copolymer). The free

NR in the graft product film obtained from the Section 3.2 was removed by using soxhlet extraction with petroleum ether for 24 h and then dried before extracting with acetone for another 24 h to remove the free copolymer. The content of each part of each step was determined from the different weight of sample before and after extraction. The percentage of grafting efficiency (%GE) and degree of monomers conversion (%conversion) were calculated following Eq. 3.1 and 3.2, respectively (Hinchiranan et al. 2013):

$$\% \text{Conversion} = \frac{\text{Weight of total polymer formed}}{\text{Weight of monomers charged}} \times 100 \quad (3.1)$$

$$\% \text{GE} = \frac{\text{Weight of polymer grafted}}{\text{Weight of total polymer formed}} \times 100 \quad (3.2)$$

The chemical structure of GNR obtained after soxhlet extraction was analyzed by using attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR, Perkin Elmer (USA)). To confirm the ATR-FTIR results, the samples swollen in CDCl₃ were characterized by proton (¹H-NMR) and fluorine-19 (¹⁹F-NMR) nuclear magnetic resonance spectroscopy (Bruker:Avance III HD 500 MHz, USA). The results from ¹H-NMR spectroscopy were used to calculate the molar compositions of TFEMA and MMA in the graft product following Eq. 3.3 and 3.4, which was adapted from the previous literature (Hinchiranan et al. 2013):

$$\%C_F = \frac{(S_1/2)}{S_0 + (S_1/2) + (S_2/3)} \times 100 \quad (3.3)$$

$$\%C_M = \frac{(S_2/3)}{S_0 + (S_1/2) + (S_2/3)} \times 100 \quad (3.4)$$

where S₀, S₁ and S₂ are integral peak areas of the olefinic proton in the NR structure (5.1 ppm), methylene proton in the TFEMA (4.3 ppm) and methoxy proton in the MMA

(3.6 ppm), respectively. C_F and C_M are mol% TFEMA and mol% MMA in the graft product, respectively.

3.5 Morphology of the NR and GNR latex

The morphology of NR particle before and after graft copolymerization with poly(TFEMA-co-MMA) was comparatively characterized by using transmission electron microscopy (TEM, JEOL JEM-2100, JAPAN) at 120 kV. The osmium tetroxide solution and sodium phosphotungstic acid (PTA) were used to stain the rubber and GNR particles, respectively. (Peng et al. 2005).

3.6 Evaluation of gel content in GNR film

The gel content in the dry GNR films was evaluated using the gel test apparatus designed following ASTM 3616-95. The sample (0.4 g) was cut as small pieces ($5 \times 5 \times 0.6 \text{ mm}^3$) and distributed over the screen racks of the gel test apparatus. Then, toluene was poured into the bottle, capped and stored in the dark for 20 h at room temperature. Thereafter, the screen rack was removed and 25 mL of solution inside the gel test apparatus was pipetted and put in each of three aluminum pans and dried in a fume hood. The gel content was then calculated following Eq. 3.5 and 3.6.

$$A \times 4 = B \quad (3.5)$$

$$\text{Gel (\%)} = \left(\frac{C - B}{C} \right) \times 100 \quad (3.6)$$

where A is the average weight of rubber in the aluminum weighing pan after drying; B is the weight of total dry samples and C is the initial weight of sample before dissolving in toluene.

3.7 Preparation of modified PTFEMA films

The modified PTFEMA films were prepared by mixing GNR latex (%GE = 23.6%) and PTFEMA latex obtained from the Section 3.3 at the PTFEMA/GNR ratios of 100/0, 90/10, 70/30 and 50/50 (w/w). The latex mixtures were mixed by using a magnetic stirrer for 30 min and then dried in an oven at 40 °C to evaporate water. Afterward the dry film was dissolved in tetrahydrofuran (THF) to receive 10% (w/v) concentration. The obtained solution was casted into a glass mold (300 × 150 × 4 mm³) and dried in ambient temperature until the weight of film was constant. The modified PTFEMA film with 0.18 ± 0.02 mm thickness was obtained.

3.8 Compatibility and topological study of the modified PTFEMA films

The compatibility of the polymeric components in the modified PTFEMA films was evaluated by Molau test. The modified PTFEMA films (25 mg) was dissolved in 5 mL acetone in a transparent test tube (Ø = 10 mm; L = 90 mm). The mixture was vigorously shaken and left to stand for at least 24 h before observing the turbidity of the solution (Yang et al. 2012).

The topology of the modified PTFEMA films (10 × 10 × 0.18 mm³) were also investigated by using atomic force microscopy (AFM) (Asylum research, UK) in tapping mode at ambient condition.

3.9 Thermal properties of modified PTFEMA films

The glass transition temperature (T_g) of the modified PTFEMA films was investigated by using differential scanning calorimetry (DSC, NETZSCH: 204 F1 Phoenix, Germany). The 10 mg sample was placed in an aluminum pan and cooled down to -100 °C using liquid nitrogen and heated up to 150 °C at a heating rate of 10 °C/min. The obtained results were also compared to NR, GNR and PTFEMA films.

3.10 Contact angle and surface free energy of modified PTFEMA films

The static contact angle of water and hexadecane of the modified PTFEMA film at various PTFEMA/GNR ratios was measured using a contact angle meter (Ramé-hart instrument, USA) by the sessile drop method with microsyringe at room temperature. The injection volume of liquid was controlled as 5 μL and the average of five reading of contact angles were reported. The surface free energy (γ_s) could be calculated according to Eq. 3.7 and 3.8.

$$\gamma_l(1 + \cos \theta) = 2[(\gamma_l^d \gamma_s^d)^{1/2} + (\gamma_l^p \gamma_s^p)^{1/2}] \quad (3.7)$$

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad (3.8)$$

where θ is the 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_l^d are the polar and dispersive parameters of the liquid surface tension, respectively; γ_s^p and γ_s^d are the polar and dispersive parameters of the solid surface tension, respectively. γ_s^d and γ_s^p were calculated from the contact angles, surface tension, dispersion and polar parameters of water ($\gamma_l = 72.8 \text{ mN/m}$, $\gamma_l^d = 21.8 \text{ mN/m}$ and $\gamma_l^p = 51.0 \text{ mN/m}$) and hexadecane ($\gamma_l = 27.6 \text{ mN/m}$, $\gamma_l^d = 27.6 \text{ mN/m}$ and $\gamma_l^p = 0 \text{ mN/m}$) (Wei et al. 2011).

3.11 Mechanical properties of the modified PTFEMA films

The tensile strength and the elongation at break of modified PTFEMA films was measured according to ASTM D882-02 (2002). The samples were cut as a rectangular shape ($10 \times 200 \times 0.18 \text{ mm}^3$) and placed in a universal testing machine (UTM). The crosshead speed was kept constant at 20 mm/min. The tensile strength was determined from the maximum force recorded prior to breakage divided by the cross section of the rectangular specimens. Elongation at break value was obtained from the change of the initial length of the specimens.

The dynamic mechanical properties of the modified PTFEMA films on rectangular shape pieces ($8 \times 6 \times 0.18 \text{ mm}^3$) were evaluated by dynamic mechanical analysis (DMA, NETZSCH, Germany) under tension mode with a constant frequency at 1Hz. The testing temperature was in the range of $-80 \text{ }^\circ\text{C}$ to $100 \text{ }^\circ\text{C}$ with a heating rate of $5 \text{ }^\circ\text{C}/\text{min}$ under nitrogen atmosphere.



CHAPTER IV

RESULTS AND DISCUSSION

4.1 Structural characterization and proposed reaction mechanism

The chemical structures of NR, GNR obtained after soxhlet extraction (GE = 23.6 wt%) and poly(TFEMA-co-MMA) (TFEMA contents = 41.4 mol% and MMA content = 58.7 mol%) were comparatively analyzed by using ATR-FTIR spectroscopy as shown in Figure 4.1. The spectra showed that the GNR (Figure 4.1c) had a peak at $1,730\text{ cm}^{-1}$ derived from C=O in both MMA and TFEMA monomers. Moreover, the C=C stretching peak at $1,658\text{ cm}^{-1}$ (Saelao and Phinyocheep 2005), the characteristic signal of NR

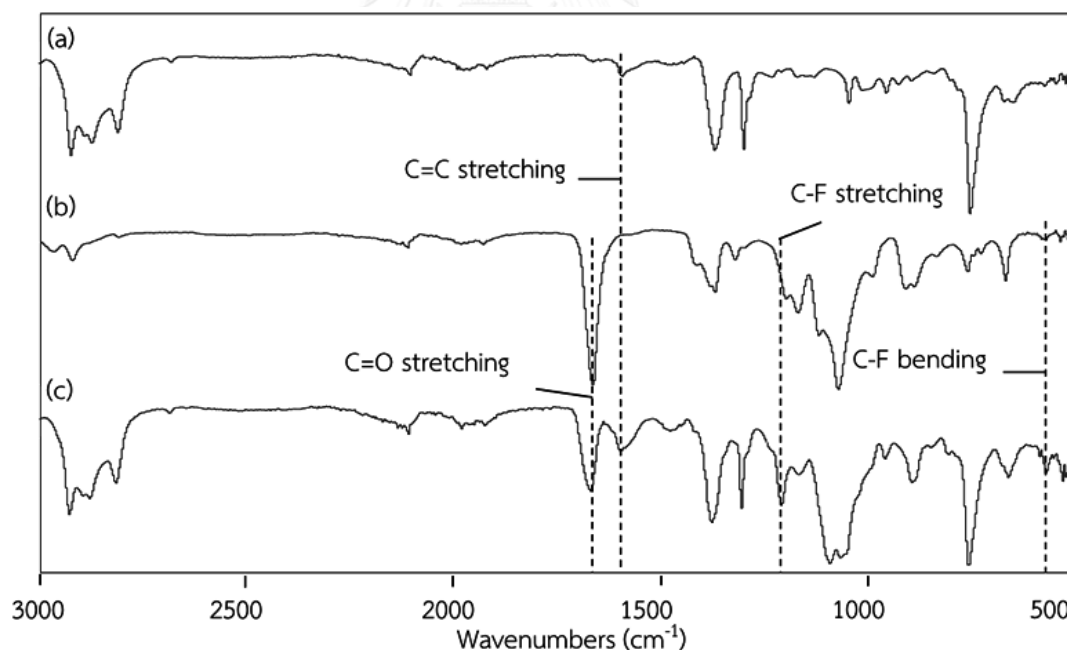


Figure 4.1 ATR-FTIR spectra of (a) NR, (b) poly (TFEMA -co- MMA) (MMA content = 58.7 mol% and TFEMA content = 41.4 mol%) and (c) GNR after soxhlet extraction (GE = 23.6%).

structure, was appeared in the GNR. The two important peaks at 1,280 and 660 cm^{-1} for stretching and bending vibration of C-F bond in CF_3 , respectively were also observed in the GNR structure (Wei et al. 2011; Xu et al. 2016).

The ^1H NMR and ^{19}F NMR spectroscopy were used to confirm the chemical structure as shown in Figure 4.2 and 4.3, respectively. From Figure 4.2, it revealed that the graft product (Figure 4.2c) had the important signals at 5.1, 4.3 and 3.6 ppm attributed to the olefinic proton (5.1 ppm) in NR, methylene proton of TFEMA (4.3 ppm) and methoxy proton of the acrylic group of MMA (3.6 ppm), respectively (Angnanon, Prasassarakich, and Hinchiranan 2011; Che Man, Hashim, and Akil 2007; Xu et al. 2016). The other signals such as the chemical shift (δ) of 1.6 and 1.8–2.0 ppm were the characteristic protons of $-\text{CH}_3$ and $-\text{CH}_2-$, respectively (Angnanon, Prasassarakich, and Hinchiranan 2011; Li, Xu, et al. 2014). The ^{19}F NMR spectra (Figure 4.3) also showed that the graft product had a chemical shift at -74.40 ppm that was similar to poly(TFEMA-co-MMA) (-74.38 ppm). This indicated the success of grafting of poly(TFEMA-co-MMA) onto the NR backbone.

From the structural characterization as explained above, the reaction mechanism of graft copolymerization of poly(TFEMA-co-MMA) onto NR via free radical method could be proposed as shown in Eq. 4.1 - 4.4. When the KPS initiator was thermally decomposed at 60 $^\circ\text{C}$, two free radicals (R_1^\bullet) were produced as shown in Eq. 4.1. Then, the R_1^\bullet reacted with NR structure to generate NR radicals (Eq. 4.2). It was possible to generate via the addition of radicals through the double bonds in the rubber or abstraction of an allylic hydrogen atom of NR to initiate the grafting sites. However, the grafting by hydrogen abstraction was more readily because allylic hydrogen bond had low bond energy (Che Man, Hashim, and Akil 2007). The R_1^\bullet was also reacted with monomers to produce polymeric radicals, which could combine with other monomers to form homopolymers or copolymers radicals as exhibited in Eq.

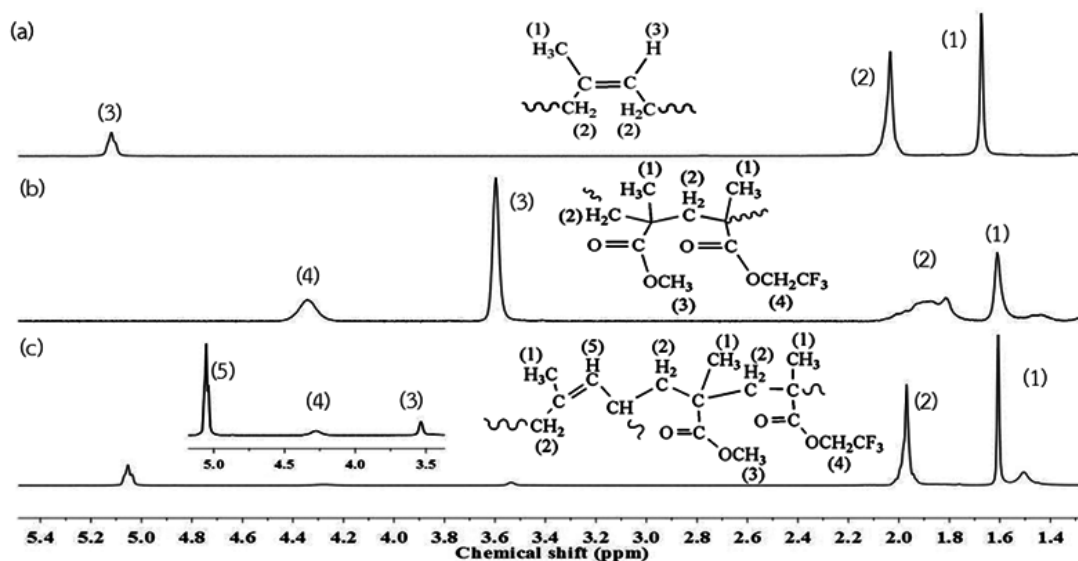


Figure 4.2 ^1H NMR spectra of (a) NR, (b) poly(TFEMA-co-MMA) (MMA content = 58.7 mol% and TFEMA content = 41.4 mol%) and (c) GNR after soxhlet extraction (GE = 23.6%).

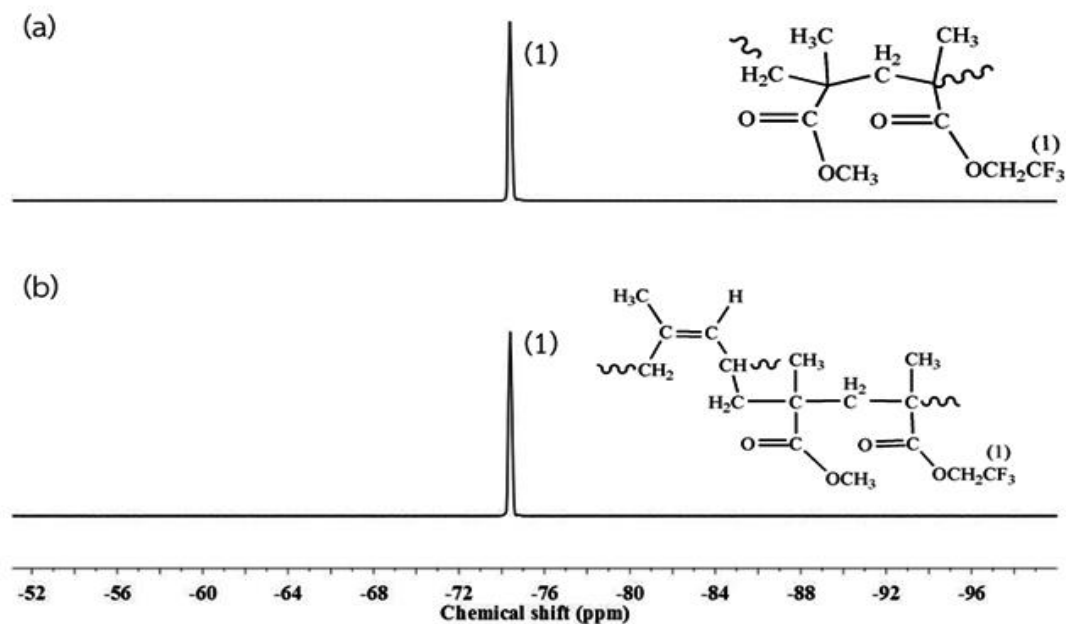
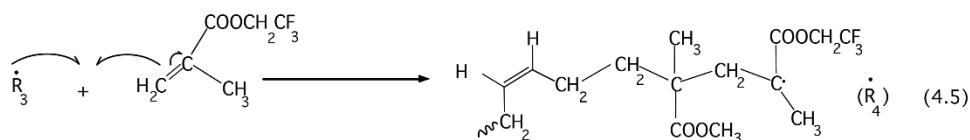
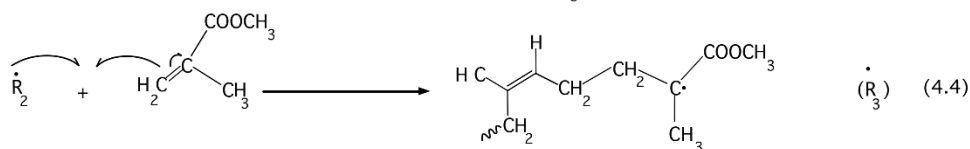
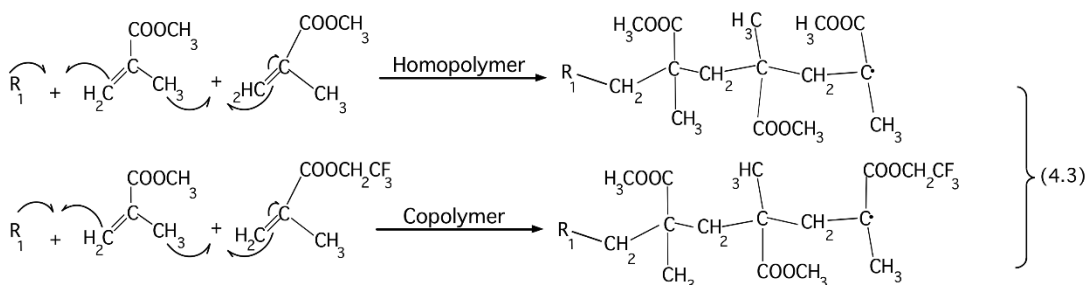
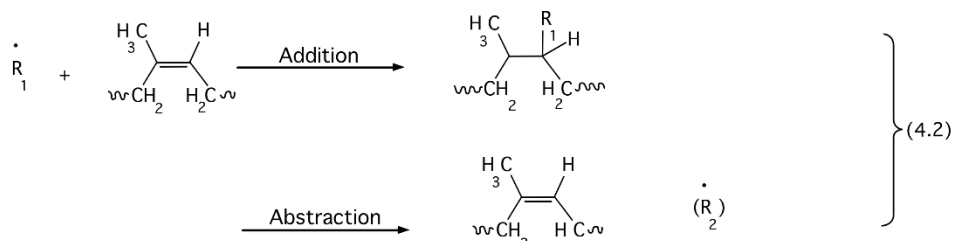
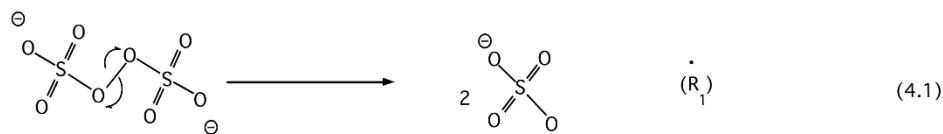


Figure 4.3 ^{19}F NMR spectra of (a) poly(TFEMA-co-MMA) MMA content = 58.7 mol% and TFEMA content = 41.4 mol% and (b) GNR after soxhlet extraction (GE = 23.6%).



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4.3. For the graft copolymerization of TFEMA and MMA onto NR, the MMA monomer was possibly first reacted with NR backbone (Eq. 4.4) to form NR-g-PMMA macroradicals (R_3^\cdot) since MMA was more reactive than TFEMA due to the electronic charge (e-value) of TFEMA (0.98) (Patil and Ameduri 2013) higher than value of MMA (0.4) (O'dian 2004). Generally, the monomer with relatively high e-value will produce radicals that are relatively less reactive toward propagation (Okieimen and Urhohide 2002) therefore TFEMA radicals will react relatively less readily than radicals derived from MMA in graft polymer formation. Afterward, the R_3^\cdot reacted with TFEMA (Eq. 4.5) to generate graft copolymer.

4.2 Effect of reaction parameters on graft copolymerization of poly(TFEMA-co-MMA) onto NR particles

The univariate experiments of the central composite design (initiator = 0.75 phr, MMA/TFEMA = 50/50 (w/w), reaction temperature = 60 °C and reaction time = 6 h) of studied parameters were carried out to individually investigate the influence of these factors on the degree of monomer conversion, grafting efficiency (GE), grafted MMA and TFEMA content, grafting properties and gel fraction in the graft product as shown in Figure 4.4 – 4.7 and Table 4.1 – 4.4.

4.2.1 Initiator concentration

For the effect of potassium persulphate (KPS) initiator concentration on the properties of graft product, it was varied in the range of 0.5 to 2.0 phr. The monomer concentration, temperature, MMA/TFEMA wt ratio and time were kept constant at 100 phr, 60 °C, 50/50 (w/w) and 6 h, respectively. Figure 4.4a shows that the degree of monomer conversion and GE drastically increased from 5.5 to 80.5% and 0 to 18%, respectively when the initiator concentration increased from 0.5 to 1.0 phr. This range of initiator content also induced the amount of TFEMA and MMA in the obtained graft NR 6.3 and 3.9 mol%, respectively (Table 4.1). This could be explained that the increase in the initiator concentration to the appropriate content provided the sufficient amount of macroradicals for grafting (Angnanon, Prasassarakich, and Hinchiranan 2011; Arayaprane and Rempel 2008; Kochthongrasamee, Prasassarakich, and Kiatkamjornwong 2006). However, the increasing initiator concentration above 1.0 phr did not significantly increase the level of monomer conversion. The maximum conversion reached to 88% for using 2 phr initiator concentration. Moreover, the excessive initiator content decreased the GE to 7.4% with the reduction of the TFEMA

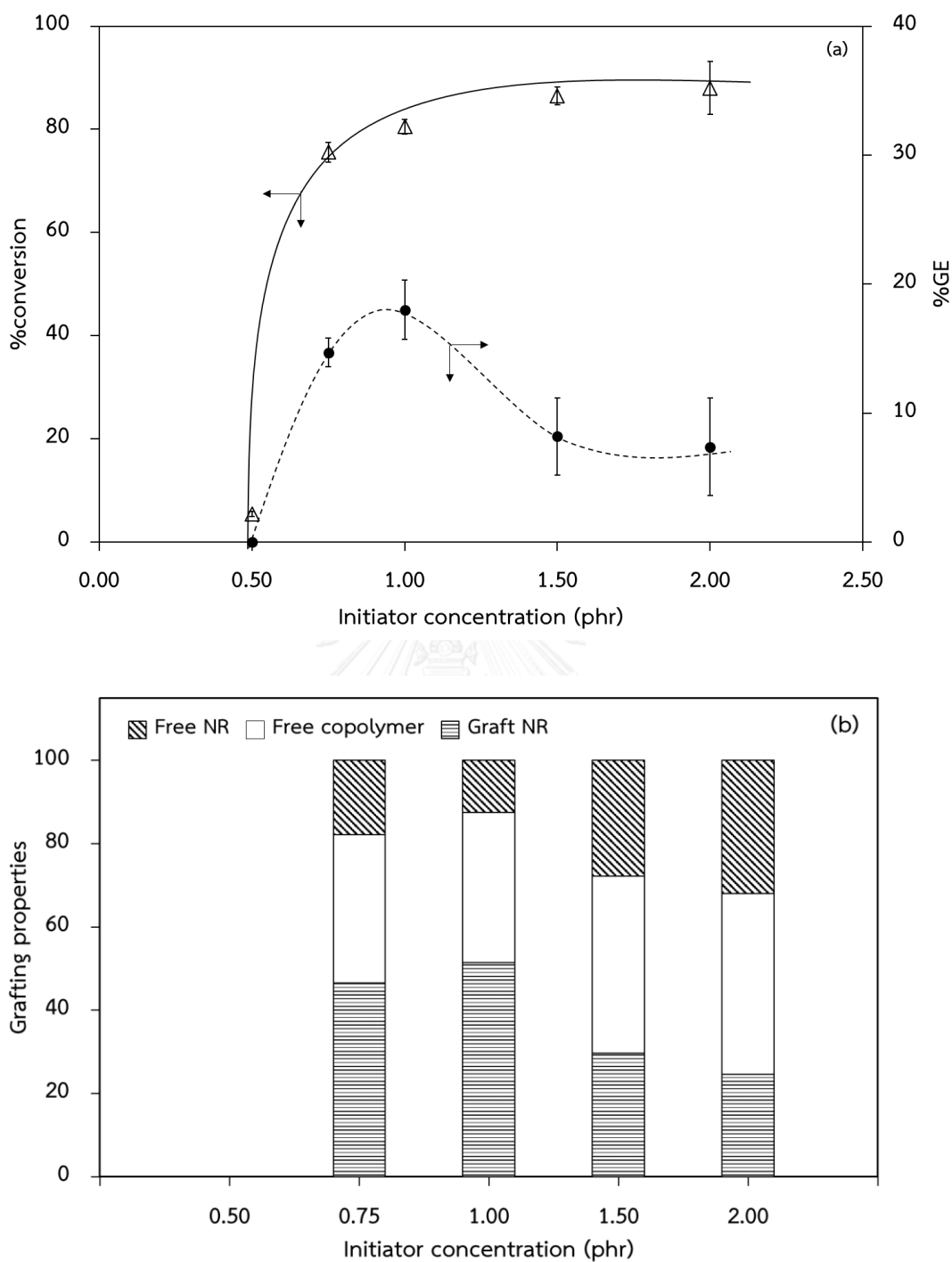


Figure 4.4 Effect of initiator concentration on (a) % conversion and %GE and (b) grafting properties of the graft product (Condition: monomers content = 100 phr, MMA/TFEMA = 50/50 (w/w), T = 60 °C, t = 6 h).

Table 4.1 Effect of initiator concentration on TFEMA and MMA components evaluated by $^1\text{H-NMR}$ spectroscopy in the graft NR fraction and gel content in the graft product.

Initiator concentration (phr)	Components in graft copolymer		Gel content (wt%)
	(mol%)		
	TFEMA	MMA	
0.50	N/A	N/A	15.0±2.4
0.75	4.8±2.1	3.4±0.8	6.7±5.6
1.00	6.3±1.8	3.9±0.1	2.6±1.6
1.50	3.7±0.0	3.0±0.2	1.6±0.9
2.00	2.8±1.3	2.7±0.7	0.3±0.1

and MMA content in the graft NR to 2.8 and 2.7 mol%, respectively when the initiator concentration increased to 2.0 phr. It was possible that the overdose initiator concentration could promote the recombination of the generated free radicals resulting in the termination of grafting reaction. In addition, the excessive copolymer radicals had higher possibility to react with each others to increase the amount of free copolymer resulting in the lower content of graft NR (Figure 4.4b) and gel content in the graft product as shown in Table 4.1. This phenomenon was also observed in graft copolymerization of MMA onto NR (Arayapranee and Rempel 2008; Kochthongrasamee, Prasassarakich, and Kiatkamjornwong 2006; Thiraphattaraphun et al. 2001).

4.2.2 MMA/TFEMA ratio

The effect of MMA content in the MMA/TFEMA monomer mixture in the range of 0/100 to 100/0 (w/w) on %conversion, %GE and grafting properties of graft product was exhibited in Figure 4.5. The reaction was operated at 0.75 phr initiator concentration

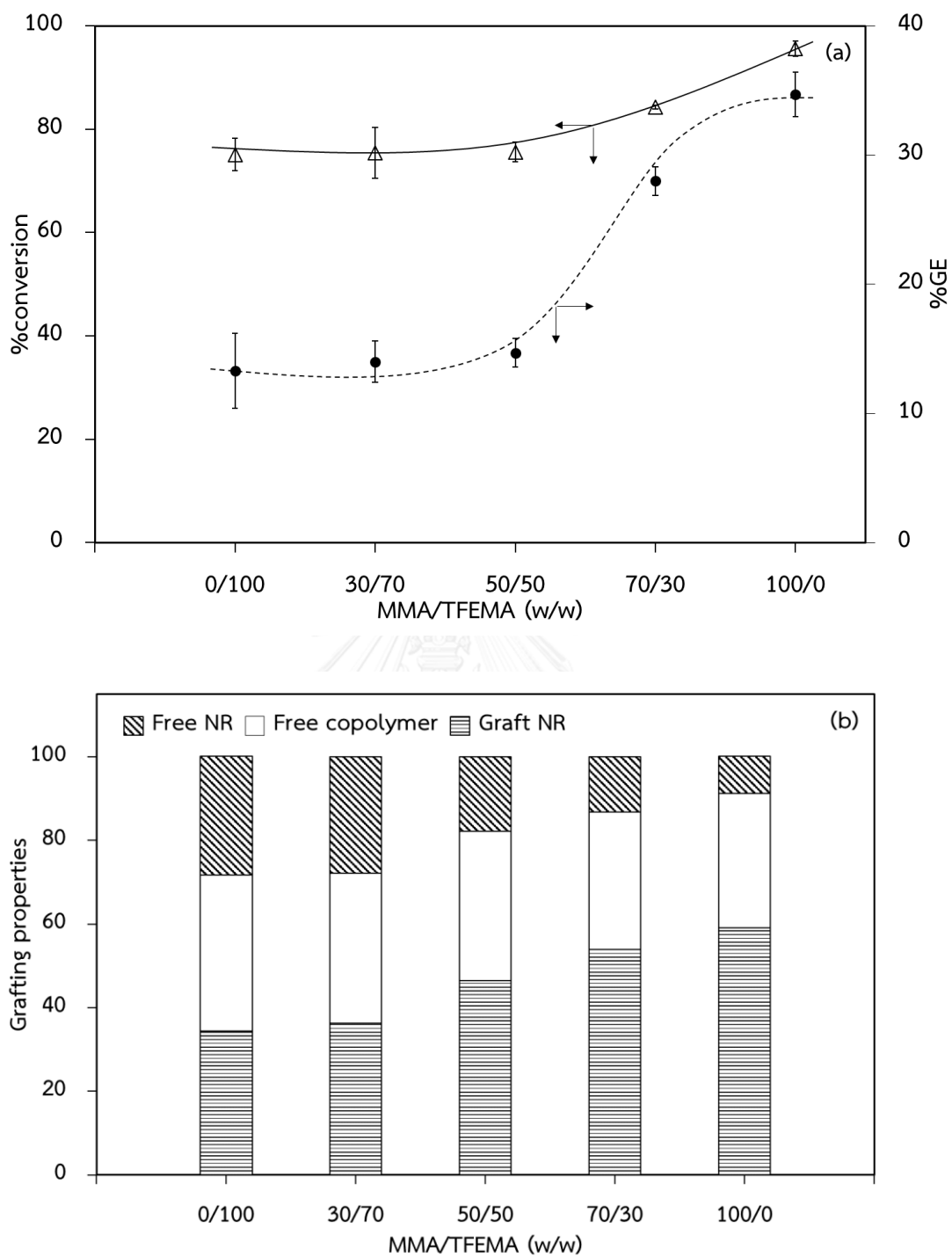


Figure 4.5 Effect of MMA/TFEMA ratio on (a) % conversion and %GE and (b) grafting properties of the graft product (Condition: monomers content = 100 phr, Initiator = 0.75 phr, T = 60 °C, t = 6 h).

and 60 °C for 6 h. Without the addition of MMA, Figure 4.5a showed that the %conversion and %GE of this system were ca. 75% and 13%, respectively with high level of free NR (28.4 wt%) and low graft NR content (34.4 wt%) (Figure 4.5b). When the MMA was added into the MMA/TFEMA monomer mixture to 50/50 (w/w), the amount of graft NR increased to 46.5 wt% with drastic reduction of ungraft NR content to 17.8 wt% and the level of conversion and GE were not different.

To consider the composition of graft NR as seen in Table 4.2, the 50/50 (w/w) MMA/TFEMA also provided the higher contents of both TFEMA and MMA in the graft NR from 3.8 to 4.8 and 0 to 3.4%, respectively. To compare the affinity to react with NR between TFEMA and MMA, Figure 4.5a indicated that the use of only MMA provided the higher level of conversion and GE as 95.6% and 34.7%, respectively. These results indicated that MMA was more reactive to be grafted onto NR structure than TFEMA. Thus, it was possibly that MMA was firstly grafted onto the NR backbone and acted as the active sites for copolymerizing with TFEMA. This result was similar to the grafting of maleic anhydride onto deproteinized NR that styrene (ST) assisted increase the grafting efficiency (Wongthong et al. 2014) For the gel formation in graft product, Table 4.2 showed that the gel content was significantly decreased from 41.7 to 0.6% when the amount of MMA in the MMA/TFEMA mixture increased. This was due to the higher portion of MMA in the grafted section that could be easily dissolved in toluene.

4.2.3 Reaction temperature

To study the effect of reaction temperature on the graft copolymerization, the reaction temperature was varied in the range of 50 to 80 °C. The monomer concentration, reaction time, MMA/TFEMA ratio and initiator concentration were kept constant at 100 phr, 6 h, 50/50 (w/w) and 0.75 phr. From Figure 4.6, it was found that

Table 4.2. Effect of MMA/TFEMA ratio on TFEMA and MMA components evaluated by $^1\text{H-NMR}$ spectroscopy in the graft NR fraction and gel content in the graft product

MMA/TFEMA (w/w)	Components in graft copolymer		Gel content (wt%)
	(mol%)		
	TFEMA	MMA	
0/100	3.8±0.7	0.0±0.0	41.7±1.5
30/70	4.0±0.3	2.3±0.2	26.6±2.6
50/50	4.8±2.1	3.4±0.8	6.7±5.6
70/30	0.9±0.0	7.2±0.2	3.6±3.1
100/0	0.0±0.0	8.4±0.3	0.6±0.2

no degree of GE in the graft product was observed when the reaction temperature was 50 °C. However, the highest gel content (14 wt%) might be produced from the NR structure in the presence of initiator (Table 4.3). This indicated that this reaction temperature provided insufficient energy to activate the grafting reaction (Hinchiranan et al. 2013), but this temperature could promote the crosslinking since KPS was dissociated at 50 °C (Van Herk and Monteiro 2002). When the reaction temperature increased to 70 °C, the levels of monomer conversion, GE and the amounts of grafted TFEMA and grafted MMA in the graft NR portion increased to 75.1%, 14.1%, 8.6 mol% and 5.3 mol%, respectively. This could be explained that the higher reaction temperature increased the decomposition rate of initiator resulting in the higher amount of free radicals, which could be reacted with the rubber chain to produce the higher grafting sites (Wongthong et al. 2013). However, the degree of GE and the grafted TFEMA and MMA contents tended to be decreased when the reaction temperature increased to 80 °C possibly due to the excessive free radicals generated from the initiator decomposition at high reaction temperature. These free radicals could be

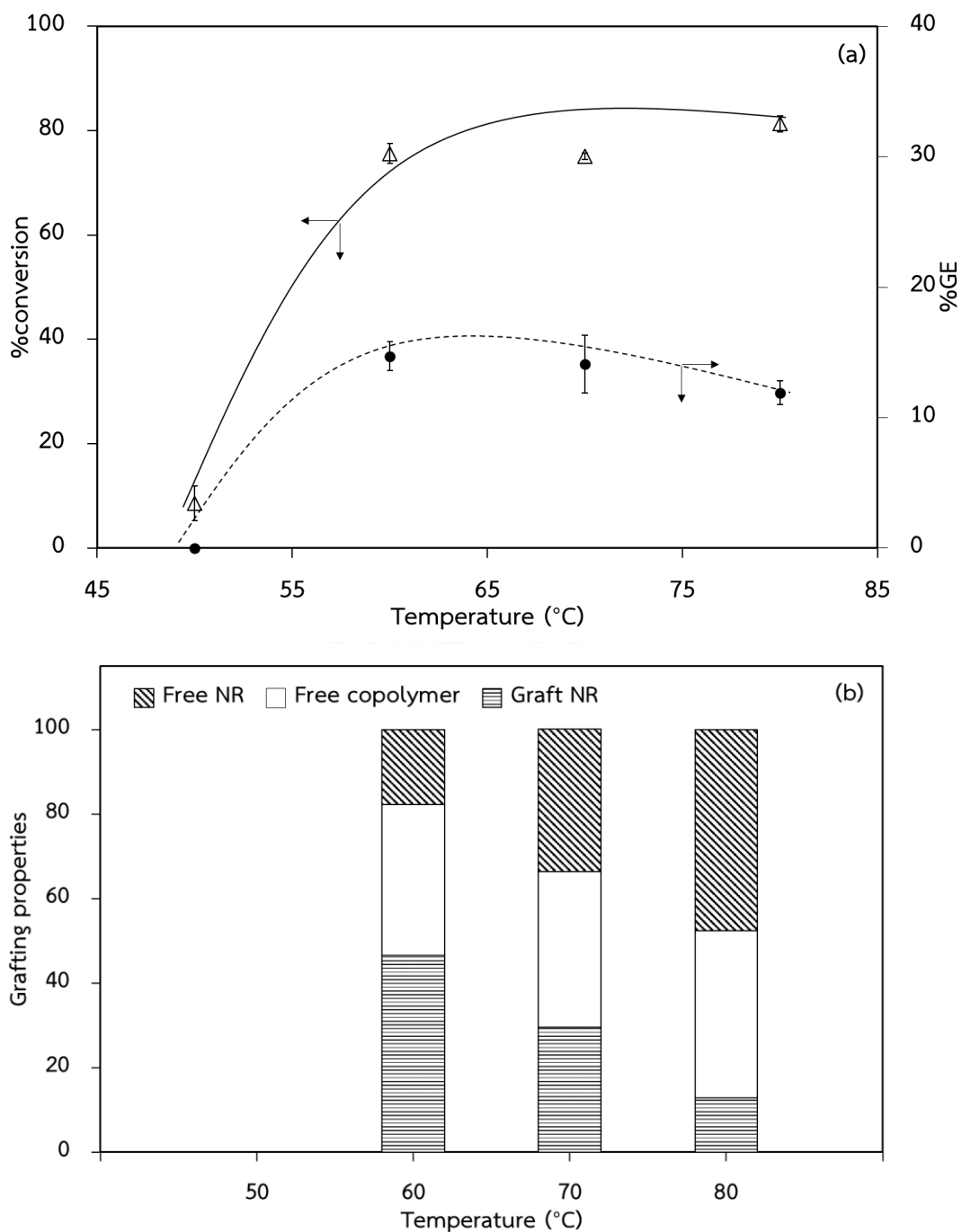


Figure 4.6 Effect of reaction temperature on (a) % conversion and %GE and (b) grafting properties of the graft product (Condition: monomers content = 100 phr, Initiator = 0.75 phr, MMA/TFEMA = 50/50 (w/w), $t = 6$ h)

Table 4.3. Effect of reaction temperature on TFEMA and MMA components evaluated by $^1\text{H-NMR}$ spectroscopy in the graft NR fraction and gel content in the graft product

Temperature ($^{\circ}\text{C}$)	Components in graft copolymer (mol%)		Gel content (wt%)
	TFEMA	MMA	
50	N/A	N/A	14.0 \pm 0.7
60	4.8 \pm 2.1	3.4 \pm 0.8	6.7 \pm 5.6
70	8.6 \pm 1.0	5.3 \pm 0.9	7.8 \pm 2.4
80	2.1 \pm 1.9	1.9 \pm 0.6	11.0 \pm 0.6

recombined resulted in the higher amount of free copolymer (Figure 4.5b) with lower GE value (Angnanon, Prasassarakich, and Hinchiranan 2011; Thiraphattaraphun et al. 2001).

To consider the gel formation, Table 4.3 exhibited that the increase in the reaction temperature to 80 $^{\circ}\text{C}$ increased the gel content to 11.0 % since the higher temperature promoted the higher cross-linking reaction to form gel in the polymer matrix (Wongthong et al. 2014).

4.2.4 Reaction time

The effect of reaction time (2–8 h) on the graft copolymerization of poly(TFEMA-co-MMA) was investigated under 100 phr monomer concentration with 50/50 (w/w) MMA/TFEMA ratio initiated by 0.75 phr KPS concentration at 60 $^{\circ}\text{C}$. The results in Figure 4.6a show that the level of monomer conversion increased from 67.6 to 78.6% when the reaction was allowed from 2 to 8 h. However, it was observed that the maximum %GE at 23.6% was achieved when the reaction time was 4 h. This indicated that the longer reaction time could not generate new active sites and the previous grafted

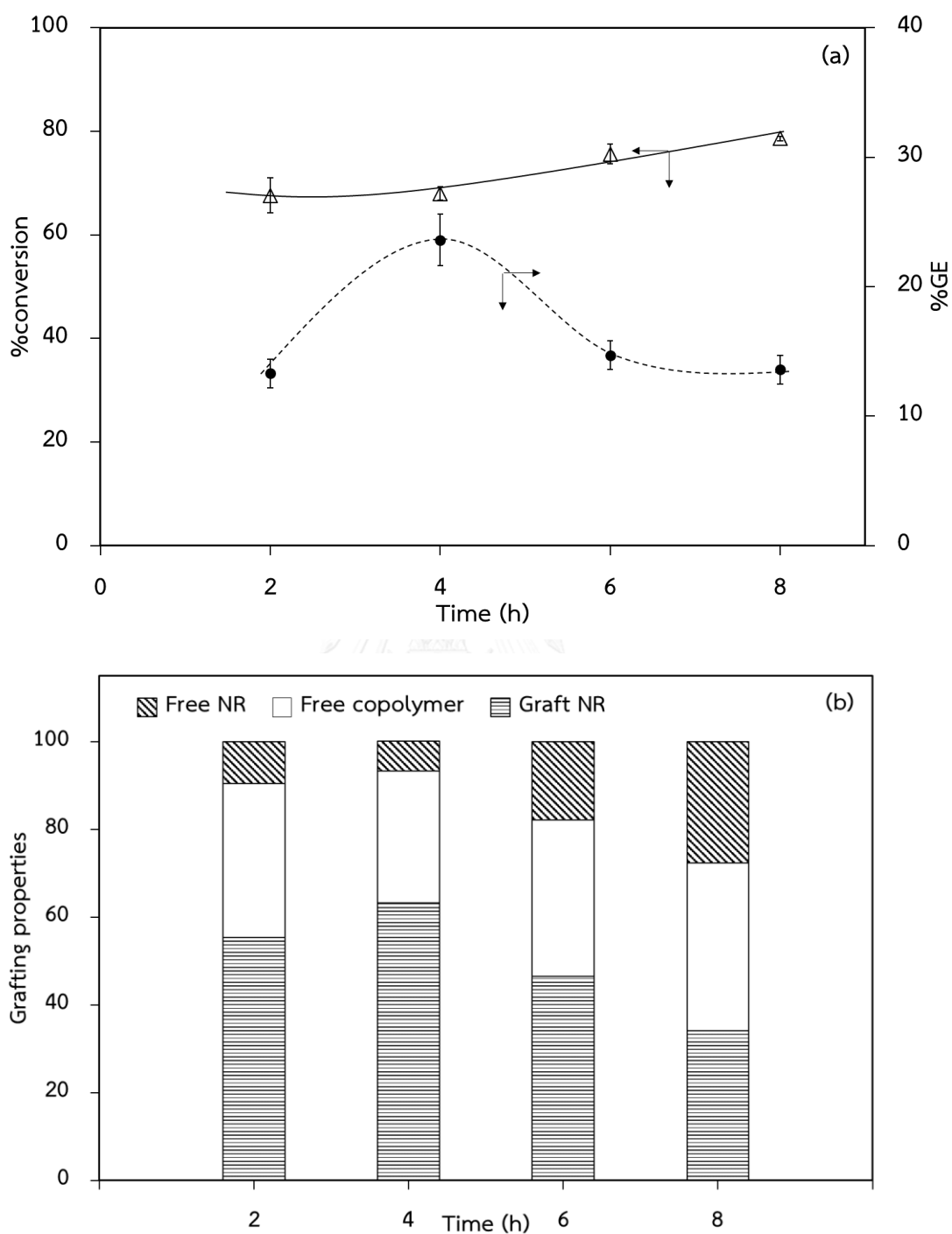


Figure 4.7 Effect of reaction time on (a) % conversion and %GE and (b) grafting properties of the graft product (Condition: Initiator = monomers content = 100 phr 0.75 phr, MMA/TFEMA = 50/50 (w/w), T = 60 °C)

Table 4.4 Effect of reaction time on TFEMA and MMA components evaluated by ^1H -NMR spectroscopy in the graft NR fraction and gel content in the graft product

Time (°h)	Components in graft copolymer (mol%)		Gel content (wt%)
	TFEMA	MMA	
2	2.1±1.0	2.5±1.3	3.6±2.1
4	7.3±1.4	3.4±1.0	3.8±1.1
6	4.8±2.1	3.4±0.8	6.7±5.6
8	4.3±2.7	3.9±1.8	10.3±0.3

chains would obstruct the new coming monomers to be grafted on the NR backbone. Moreover, the longer reaction time provided the opportunity for self-polymerization to form copolymer or crosslink reaction to produce higher gel content as shown in Table 4.4 (Nakason, Kaesaman, and Yimwan 2003; Thiraphattaraphun et al. 2001; Wongthong et al. 2014). This reason was also confirmed by the greater amount of free copolymer (Figure 4.6b) or lower %GE (Figure 4.6a) with higher amount of gel.

Thus, the appropriate condition for preparation of graft product used in further experiments was 0.75 phr KPS concentration with 50/50 (w/w) MMA/TFEMA ratio at 60 °C for 4 h.

4.3 Morphology of graft product

The morphology of NR particles before and after graft copolymerization with poly(TFEMA-co-MMA) was characterized by transmission electron microscopy (TEM) as shown in Figure 4.8. The TEM micrograph of NR latex particles (Figure 4.8a) stained by osmium tetroxide exhibited dark spheres with smooth surface. On the other hand, the graft product latex obtained from 30/70 (w/w) MMA/TFEMA mixture stained by sodium

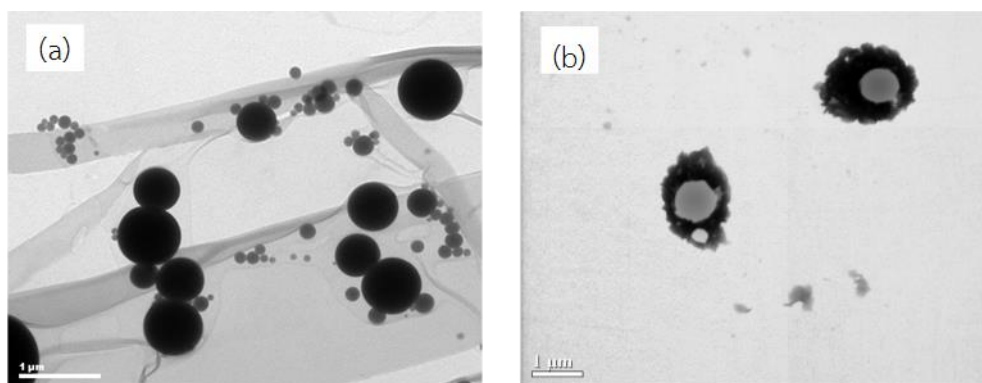


Figure 4.8 TEM micrograph of NR latex (a) before and (b) after grafting with poly(TFEMA-co-MMA) (14.0 %GE)

phosphotungstic acid (PTA) showed the grey spherical particles covered by shell with rough surface (Figure 4.8b). This indicated that the graft product showed the core-shell morphology type. The darker color was the copolymer and the light color covered by dark color was the NR particle. The core-shell type was obtained due to the effect of separation between polymer and NR during period of polymerization. Moreover, KPS used as the initiator is water-soluble which induced the grafting reaction mainly occurred on the surface of NR particles. Moreover, the generated free radicals could not diffuse inside the rubber particles due to the high viscosity of NR (Thiraphattaraphun et al. 2001).

4.4 Appearance and compatibility study of PTFEMA/GNR films

Figure 4.9 shows the appearance of PTFEMA and PTFEMA/GNR films with various composition ratios. The results were also compared to PTFEMA/NR films at the same film composition. From the Figure 4.9a, the PTFEMA film was translucent. However, the addition of NR into the PTFEMA with the PTFEMA/NR ratio of 90/10 to 50/50 (w/w) showed the phase separation as presented in Figure 4.9b - 4.9d. To compare with the PTFEMA/GNR at the similar film compositions, the higher homogeneity of the opaque films was observed for 90/10 and 70/30 PTFEMA/GNR films as shown in Figure 4.9e and

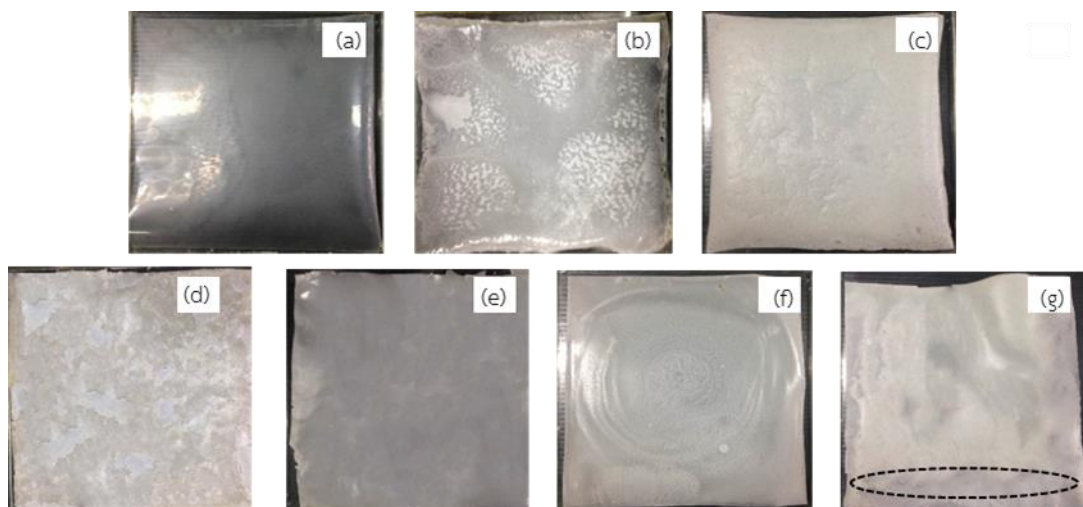


Figure 4.9 Appearance of the films: (a) PTFEMA, (b) 90/10 (w/w) PTFEMA/NR, (c) 70/30 (w/w) PTFEMA/NR, (d) 50/50 (w/w) PTFEMA/NR, (e) 90/10 (w/w) PTFEMA/GNR, (f) 70/30 (w/w) PTFEMA/GNR and (g) 50/50 (w/w) PTFEMA/GNR (%GE of GNR = 23.6%).

4.9f, respectively. This result indicated that the use of graft product could improve the phase compatibility of the polymeric constituents in the films. However, the addition of GNR up to 50 wt% into the film showed the phase separation (Figure 4.9g) as seen in the black circle. This could be explained that the imbalance of polarity in the blends lead a phase separation (Angnanon, Prasassarakich, and Hinchiranan 2011)

The Molau test (Figure 4.10) is also the method to assess the compatibility of blends (Carone Jra et al. 2000; Yang et al. 2012). In the present work, the solubility of films with various compositions was observed in the presence of acetone, which is a good solvent for PTFEMA, but it is a poor solvent for NR. The turbidity of the obtained solution was used as the indicator of high compatibility (Vallim et al. 2009) As shown in Figure 4.10a NR could not be dissolved in acetone due to the difference of polarity. On the other hand, the PTFEMA was completely dissolved in acetone and showed the transparent solution (Figure 4.10b). To consider the blend films, the PTFEMA/NR films could not be dissolved in acetone for any film compositions (Figure 4.10c - 4.10e). This

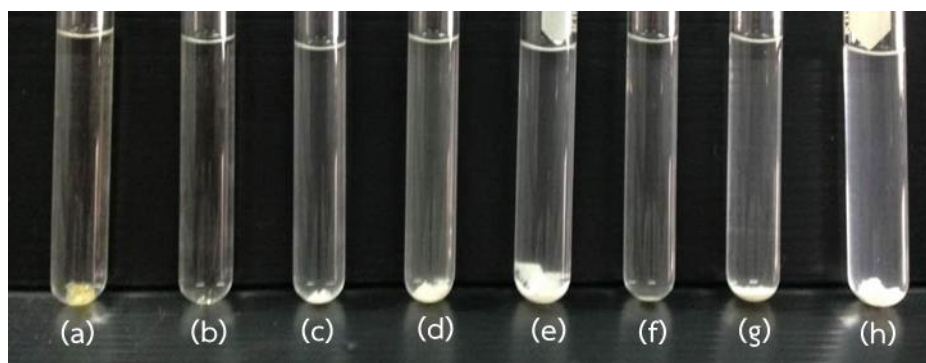


Figure 4.10 Molau test of (a) NR, (b) PTFEMA, (c) 90/10 (w/w) PTFEMA/NR, (d) 70/30 (w/w) PTFEMA/NR, (e) 50/50 (w/w) PTFEMA/NR, (f) 90/10 (w/w) PTFEMA/GNR, (g) 70/30 (w/w) PTFEMA/GNR and (h) 50/50 (w/w) PTFEMA/GNR (GNR had 23.6% GE).

indicated the incompatibility between polymeric constituents in the films. However, the solution of PTFEMA/GNR films exhibited the more turbidity reflecting the higher compatibility between phases (Figure 4.10f - 4.10h) (Vallim et al. 2009). It was also observed that the increase in the GNR content in the PTFEMA/GNR blend up to 50/50 (w/w) induced the higher amount of solid residue in the solution (Figure 4.10h) due to the over saturation of interface that could not improve the compatibility polymeric constitute (Hinchiranan et al. 2007). This could be concluded that the 90/10 (w/w) PTFEMA/GNR (Figure 4.10f) was the appropriated ratio to provide the highest phase compatibility.

AFM are used to study the film surface morphologies. Figure 4.11 showed the 2D and 3D AFM images presenting the average roughness (R_a) of the modified PTEMA films with various NR or GNR contents. The PTFEMA/NR at blend ratios of 90/10 (w/w) (Figure 4.11a) and 70/30 (w/w) (Figure 4.11b) films had R_a as 323.7 nm and 192.8 nm, respectively. The dark zone and white zone represented the hole and hill, respectively (Zheng et al. 2015). The large holes and numerous hills may from the accumulation of hard phase due to the mismatch of polymeric components in the

blend film (Zheng et al. 2015). However, the PTFEMA/NR film at the blend ratio of 50/50 (w/w) showed the smoother surface with R_a as 81.9 nm due to the less content of PTFEMA and the large NR area that could not be well dispersed in the blend film. To compare with the films containing GNR at the same blend ratio, the white zone was homogeneously dispersed throughout the film surface and the R_a value was decreased from 323.7 nm (Figure. 4.11a) to 83.9 nm (Figure. 4.11d) and 192.8 (Figure. 4.11b) nm to 78.1 nm (Figure. 4.11e) for blend ratio 90/10 and 70/30 (w/w), respectively. These results indicated that the accumulation of hard phase was decreased due to the high interfacial adhesion between PTFEMA and GNR phases (Zheng et al. 2015). However, the excessive content of GNR in the blend film promoted the incompatibility of the polymeric constituents in the films resulted in agglomeration of white zone resulting in the larger R_a again as seen in Figure 4.11f.

4.5 Surface properties of NR, poly(TFEMA), GNR, PTFEMA/NR and PTFEMA/GNR films.

Table 4.5 presents the contact angles and surface free energy of NR, PTFEMA, and blend films. It was found that the water and hexadecane contact angles of PTFEMA film were 106° and 63° , respectively with low surface energy as 16.0 mN/m. This result indicated that PTFEMA had higher hydrophobic and oleophobicity than NR, which had water and hexadecane contact angles as 86° and 28° , respectively with surface energy as 29.4 mN/m. This was due to the effect of $-CF_3$ in the PTFEMA structure, which had the lower critical surface tension (15 dyn/cm) than $-CH_3$ in the polyisoprene unit in NR (30 dyn/cm) (Xu et al. 2016). When the NR was grafted with poly(TFEMA-co-MMA) (%GE = 23%), the water and hexadecane contact angles including the surface free energy of obtained GNR were between those of PTFEMA and NR. Moreover, the existence of MMA in the GNR provided the high surface energy (PMMA surface free energy = 40.2

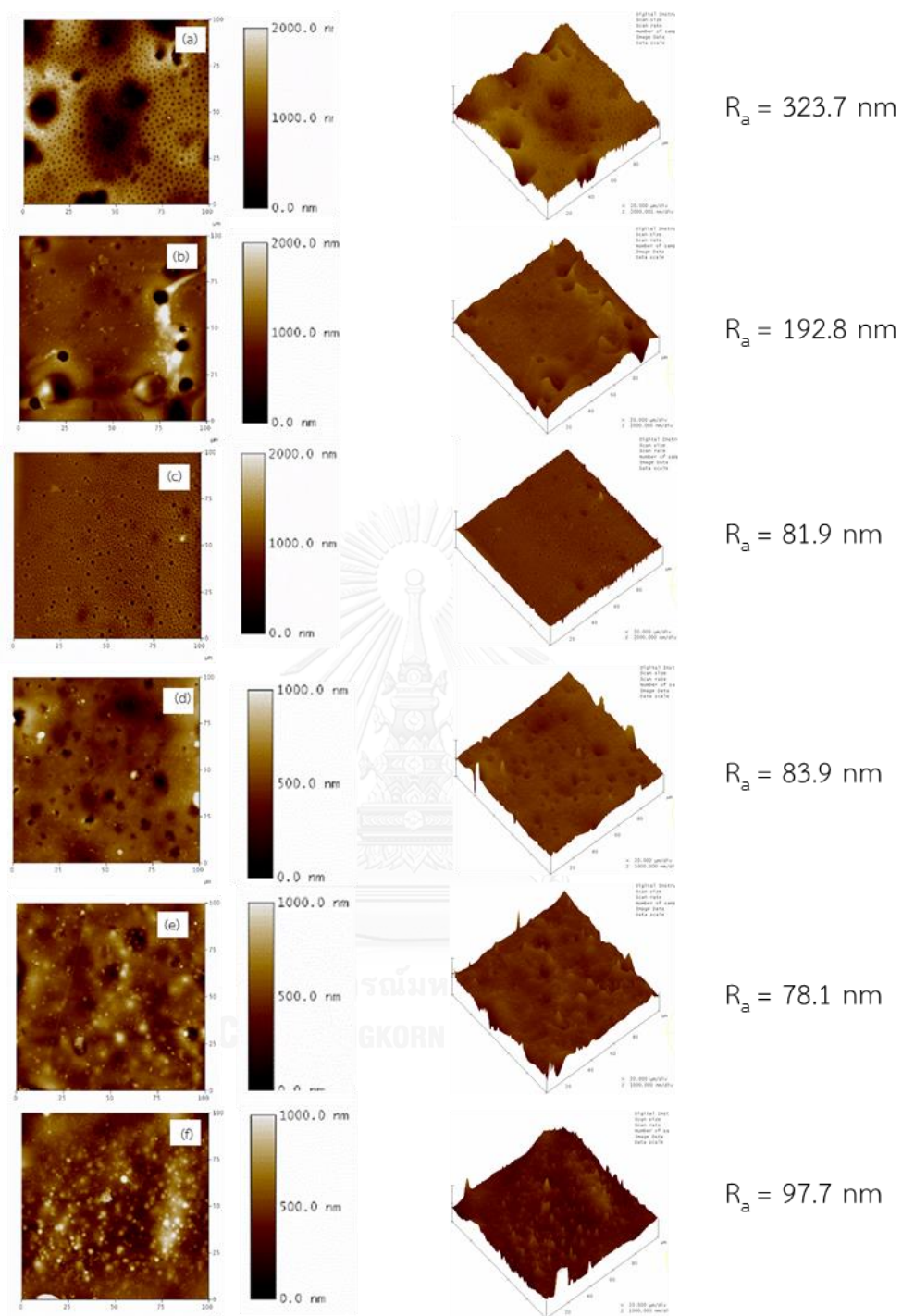










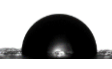











Figure 4.11 Topographic mode generated from AFM observation of blended films: (a) 90/10 (w/w) PTFEMA/NR, (b) 70/30 (w/w) PTFEMA/NR, (c) 50/50 (w/w) PTFEMA/NR, (d) 90/10 (w/w) PTFEMA/GNR, (e) 70/30 (w/w) PTFEMA/GNR and (f) 50/50 (w/w) PTFEMA/GNR (%GE in GNR = 23%).

mN/m) (Ho and Khew 2000), which could induce GNR having higher surface free energy than PTFEMA.

For the blend films, it was observed that the addition of NR into the PTFEMA decreased the hydrophobicity and oleophobicity with increasing the surface free energy. Moreover, the standard deviations of PTFEMA/NR films for all compositions were high reflecting the heterogeneity of the polymeric constituents in the films. On the other hand, the incorporation of GNR into the PTFEMA at 90/10 (w/w) PTFEMA/GNR showed the similar water and hexadecane contact angles including the surface free energy to the PTFEMA film. This indicated that this blend composition showed the improved compatibility between polymeric phases in the blends. However, the GNR content in the blend film over 10 wt% caused the incompatibility and induced the lower value of water and oil contact angles with higher surface free energy.

Table 4.5 Contact angle and surface energy of NR, PTFEMA, GNR and blend films

Film	Blend ratio (w/w)	Water contact angle (°)		Oil contact angle (°)		Surface free energy (mN/m)
PTFEMA	-	106 ± 5.3		63 ± 4.5		16.0
NR	-	86 ± 3.7		28 ± 3.3		29.4
GNR ^(a)	-	95 ± 2.2		33 ± 5.9		25.6
PTFEMA/NR	90/10	95 ± 3.3		43 ± 8.3		23.5
	70/30	89 ± 3.4		30 ± 0.4		28.0
	50/50	84 ± 14.1		33 ± 15.5		29.5
PTFEMA/GNR	90/10	106 ± 1.8		61 ± 7.4		16.5
	70/30	92 ± 2.7		31 ± 7.4		26.8
	50/50	80 ± 0.6		31 ± 2.8		31.6

^(a)GNR film prepared from GNR latex having 23% GE.

4.6 Mechanical properties of modified PTFEMA films

The effect of the rubber content (NR or GNR having 23 %GE) on the mechanical properties of the modified PTFEMA films was investigated. Figure 4.12 shows that the tensile strength and elongation at break of PTFEMA films were 25.2 MPa and 1.87%, respectively. When NR was added into the PTFEMA to form PTFEMA/NR films, the tensile strength of PTFEMA/NR films decreased with increasing the NR content. At 50/50 (w/w), the PTFEMA/NR film had tensile strength only 0.55 MPa with high elongation at break (13.7%) reflecting the low crosslink density (Hinchiranan et al. 2013) resulted from the poor interaction between PTFEMA and NR with polarity differences (George, Britto, and Sebastian 2003)

To consider the PTFEMA/GNR films, the results in Figure 4.12a shows that the tensile strength of PTFEMA/GNR film was higher than that of the PTFEMA/NR film for all blend compositions This was due to the presence of the poly(TFEMA-co-MMA) portion in the GNR providing the higher compatibility with PTFEMA (Pisuttisap et al. 2013). The maximum tensile strength of PTFEMA/GNR film at 26.4 MPa with 1.99% elongation at break was obtained when the amount of GNR in the film was only 10 wt%. Above this point, the tensile strength of films decreased due to the interfacial saturation of GNR in the PTFEMA (Hinchiranan et al. 2007).

4.6 Thermal properties

The thermal properties are the important parameters for determining the application scope of polymers. T_g and compatibility of modified PTFEMA films was investigated by differential scanning calorimetry (DSC) Figure 4.13 and Table 4.6 show only one T_g of NR and PTFEM at -61.1 and 73.8 °C, respectively (Kongparakul, Prasassarakich, and Rempel 2008; Xu et al. 2016). The GNR exhibited two T_g s at -62.0

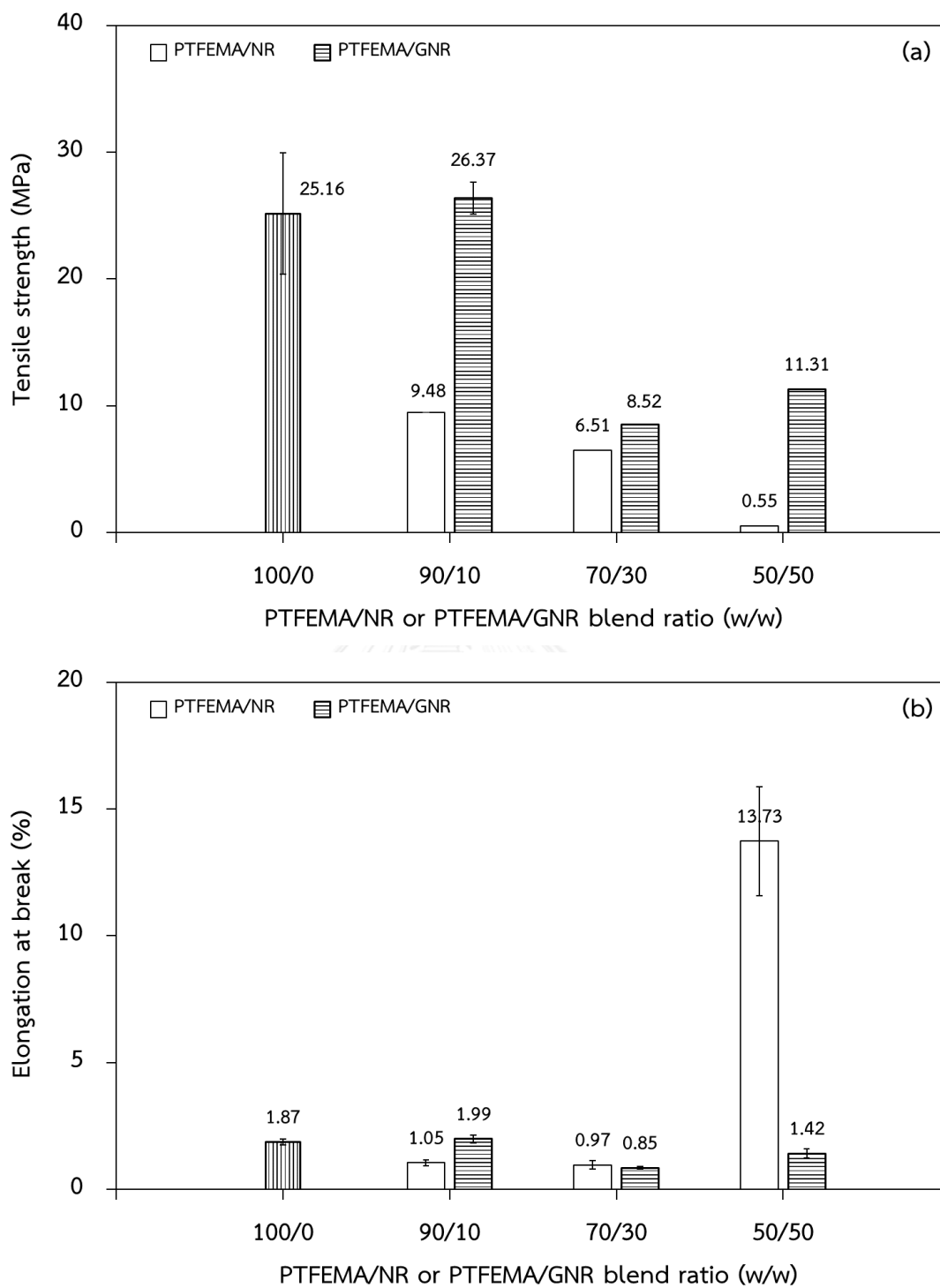


Figure 4.12 Tensile properties of the PTFEMA and the modified PTFEMA films: (a) tensile strength and (b) elongation at break (%GE in GNR = 23%).

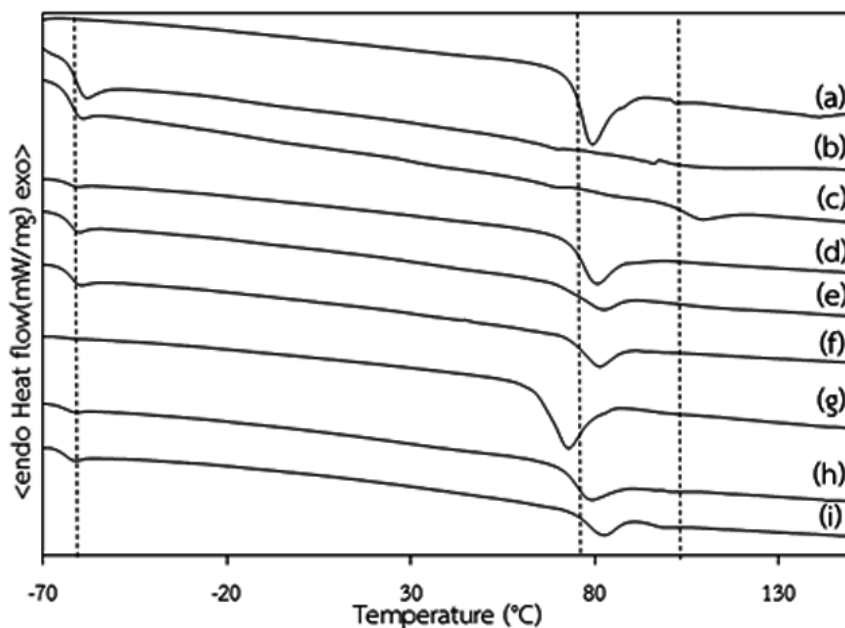


Figure 4.13 DSC curves of (a) PTFEMA (b) NR, (c) GNR (23.6% GE), (d) 90/10 (w/w) PTFEMA/NR, (e) 70/30 (w/w) PTFEMA/NR, (f) 50/50 (w/w) PTFEMA/NR, (g) 90/10 (w/w) PTFEMA/GNR, (h) 70/30 (w/w) PTFEMA/GNR and (i) 50/50 (w/w) PTFEMA/GNR (%GE in GNR = 23%).

and 104.2 °C. The lower T_g belongs to the NR phase and the higher T_g is related to the copolymer phase, which PMMA homopolymers was found to be 118 °C (Park, Soo-Bok, and Kyun Choi 1997). The appearance of two T_g s attributed to the existence of immiscibility between core and shell components (Chang et al. 2014; Junyan, Ling, and Yuansuo 2009) corresponding to the TEM micrograph (Figure 4.8b). The PTFEMA/NR and PTFEMA/GNR films with various blend ratios (90/10, 70/30 and 50/50 (w/w)) also exhibited two T_g s, the lower T_g belongs to the NR phase of pure NR and GNR and the higher T_g is related to the PTFEMA and copolymer phases in blends. It was observed that both T_g s of PTFEMA/NR films did not significantly change from original polymers, indicating the immiscibility of two polymer constituents in the blend (Hinchiranan et al. 2013). For the PTFEMA/GNR films, the T_g of the copolymer phased decreased to 64

Table 4.6 Glass transition temperature (T_g) of the NR, PTFEMA, GNR, PTFEMA/NR and PTFEMA/GNR films measured by the DSC technique.

Sample	T_g (°C)		
	NR phase	PTFEMA phase	copolymer phase
NR	-61.0	-	-
PTFEMA	-	73.8	-
GNR ^(a)	-62.0	-	104.2
PTFEMA/NR (90/10 (w/w))	-62.5	73.6	-
PTFEMA/NR (70/30 (w/w))	-62.3	73.2	-
PTFEMA/NR (50/50 (w/w))	-62.5	73.3	-
PTFEMA/GNR (90/10 (w/w))	-62.0	-	64.0
PTFEMA/GNR (70/30 (w/w))	-64.0	-	73.2
PTFEMA/GNR (50/50 (w/w))	-64.1	-	76.2

^(a)%GE in GNR in GNR = 23%

– 76 °C depended on the GNR contents. This result implied that the grafting enhanced interfacial adhesion between PTFEMA and NR. (Peng et al. 2005). However, the T_g of the GNR phase in the PTFEMA/GNR films at 70/30 and 50/50 (w/w) were higher (73 – 76 °C) than that at 90/10 (w/w). This attributed to the immiscibility of polymeric constitutes (Tan et al. 2015). This result was also consistent to the Molau test. Thus, it could be concluded that the 90/10 (w/w) PTFEMA/GNR was the appropriated ratio to provide the highest phase compatibility.

Dynamic mechanical analysis (DMA) was used to evaluate the compatibility and stiffness of modified PTFEMA films under dynamic force from damping factor ($\tan \delta$) and storage modulus (E') as a function of temperature. Figure 4.14a show plots of temperature dependence of $\tan \delta$ for PTFEMA, PTFEMA/NR and PTFEMA/GNR films. The results of T_g and the storage modulus (E') of PTFEMA and modified films were summarized in Table 4.7. For the PTFEMA film, it exhibited a single $\tan \delta$ indicating a T_g at 88.2 °C. For the series of PTFEMA/NR films exhibited $\tan \delta$ peaks at nearly the original PTFEMA resulted from the immisibility of these blends (Yang et al. 2012). To

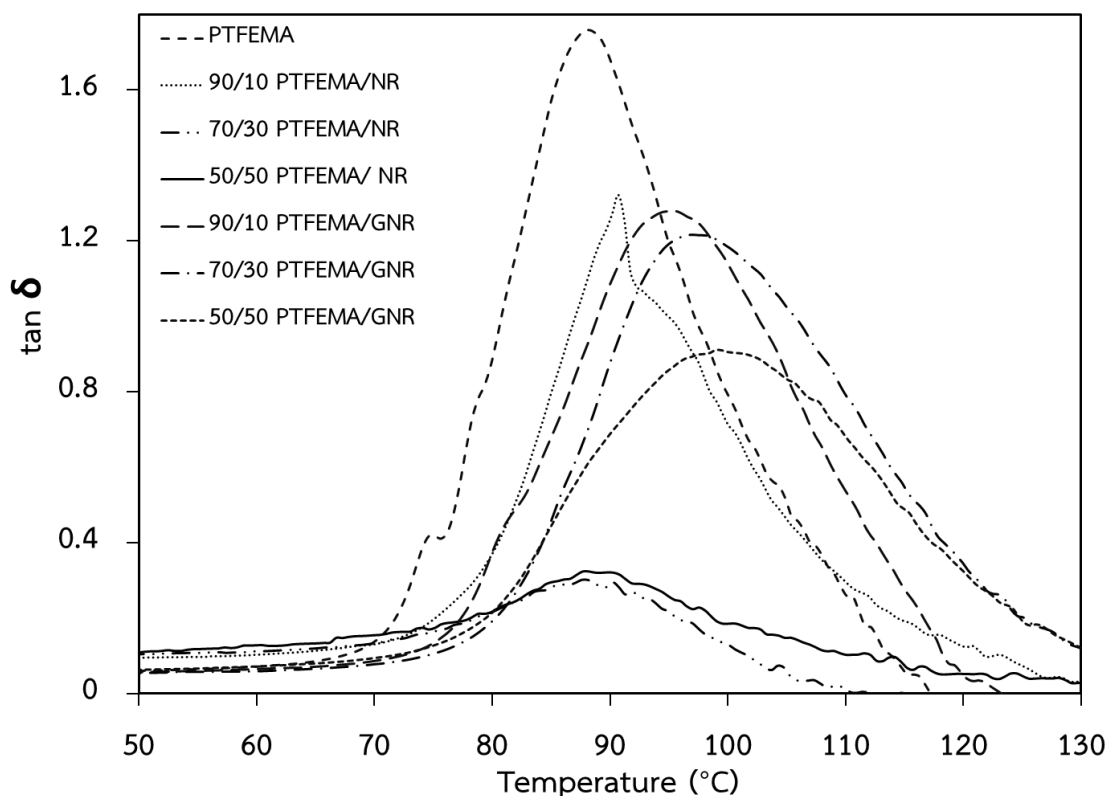


Figure 4.14 Variation of the $\tan \delta$ as a function of temperature of PTFEMA, 90/10 (w/w) PTFEMA/NR, 70/30 (w/w) PTFEMA/NR, 50/50 (w/w) PTFEMA/NR PTFEMA, 90/10 (w/w) PTFEMA/GNR, 70/30 (w/w) PTFEMA/GNR and 50/50 (w/w) PTFEMA/GNR (%GE in GNR = 23%).

Table 4.7 T_g and $\text{Log } E'$ at T_g evaluated from $\tan \delta$ peak measured by DMA of PTFEMA, PTFEMA/NR and PTFEMA/GNR films (%GE in GNR = 23%).

Sample	T_g (°C)	$\text{Log } E'$ (MPa)
PTFEMA	88.2	1.14
PTFEMA/NR (90/10 (w/w))	90.7	1.00
PTFEMA/NR (70/30 (w/w))	86.6	0.72
PTFEMA/NR (50/50 (w/w))	89.2	0.62
PTFEMA/GNR (90/10 (w/w))	95.6	1.16
PTFEMA/GNR (70/30 (w/w))	97.6	1.12
PTFEMA/GNR (50/50 (w/w))	100.0	1.11

consider the PTFEMA/GNR films, they exhibited that the $\tan \delta$ peaks were shifted toward the higher temperature from 94.5 to 98.9 °C when GNR content in the films was increased from 10 to 50 wt%. This was related to the influence of PMMA in GNR, which had high T_g (118 °C) (Park et al., 1997) than that of PTFEMA (88.2 °C) (Alyamac and Soucek 2011) and a restriction in chain mobility caused by chemical interaction of the shifting of $\tan \delta$ attributed chemical interaction of the GNR in the modified films. (Nakason et al. 2006). Figure 4.15 shows plots of $\log E'$ as a function of temperature of PTFEMA and modified PTFEMA films. The values of $\log E'$ is also shown in Table 4.7.

According to ISO 6721-1, the storage modulus represents the stiffness of viscoelastic materials. Therefore, the increase in the storage modulus (E') reflects the increasing stiffness of materials. The results in Figure 4.15 and Table 4.7 show that E' of PTFEMA/GNR film was higher than that of PTFEMA/NR films. In addition, the increasing content of NR or GNR also decreased E' . These phenomena were resulted from poor compatibility of polymeric phase in films. However, the 90/10 PTFEMA/GNR films exhibited the highest E' value as 1.16 MPa. The stiffness behavior of films were corresponded to results of tensile strength as explained in the previous section. This could be concluded that the 10 wt% of GNR was the appropriated content to improved the dynamic mechanical properties of the modified PTFEMA films.

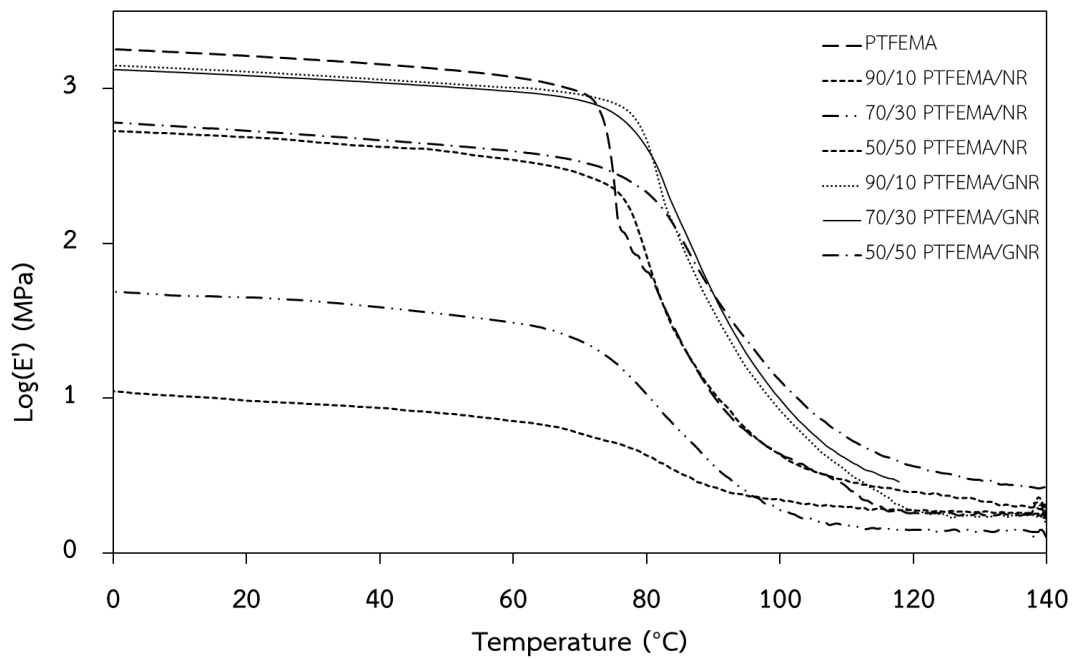


Figure 4.15 Variation of the storage modulus as a function of temperature for PTFEMA, 90/10 (w/w) PTFEMA/NR, 70/30 (w/w) PTFEMA/NR and 50/50 (w/w) PTFEMA/NR, 90/10 (w/w) PTFEMA/GNR, 70/30 (w/w) PTFEMA/GNR and 50/50 (w/w) PTFEMA/GNR (%GE in GNR = 23%)

CHAPTER V

CONCLUSION

5.1 Conclusion

The graft copolymer of methyl methacrylate (MMA) and 2,2,2-trifluoroethyl methacrylate (TFEMA) onto natural rubber (NR) was successfully prepared via emulsion copolymerization by using potassium persulphate (KPS) as an initiator. The study of this research was divided into two parts: synthesis of gross graft NR (GNR) and properties analysis of modified poly(2,2,2-trifluoroethyl methacrylate) (PTFEMA) films.

Influence of initiator concentration, MMA/TFEMA wt ratio, temperature and time on the degree of monomer conversion, grafting efficiency (GE), grafted MMA and TFEMA content, grafting properties and gel fraction in the graft product were investigated. The central condition applied for the univariate experiments was 0.75 phr KPS and 50/50 (w/w) MMA/TFEMA at 60 °C for 6 h. The monomer concentration was kept constant at 100 phr. The degree of monomer conversion, GE and the amount of TFEMA and MMA in the obtained graft NR increased when the initiator concentration increased. However, the increasing initiator concentration above 1.0 phr did not significantly increase the level of monomer conversion, but the GE and TFEMA contents were decreased. The increase in MMA/TFEMA wt ratio promoted amount of graft NR, conversion and GE. In addition, the results indicated that MMA was more reactive to be grafted onto NR backbone than TFEMA when the reaction temperature increased, the levels of monomer conversion, GE and the amounts of grafted TFEMA and grafted MMA in the graft NR portion increased. However, the degree of GE and the grafted TFEMA and MMA contents tended to be decreased when the reaction temperature was 80 °C. The level of monomer conversion and GE also increased when

the reaction time was increased. It was observed that the reaction time at 4 h promoted the maximum GE value at 23.6% with 7.3 mol% TFEMA and 3.8% gel.

The morphology of the GNR obtained by using transmission electron microscopy (TEM) showed the core-shell morphology type affecting the glass transition temperature (T_g) showing as two T_g s (-62.0 and 104.2 °C) near the original polymers. The GNR was applied as the modifier for a PTFEMA film. The modified PTFEMA films contained GNR (23.6% GE) at various PTFEMA/GNR blending ratios via the solution-casting technique using tetrahydrofuran (THF) as the casting solution. It was found that the graft copolymerization of poly(TFEMA-co-MMA) onto NR improved the compatibility between NR and PTFEMA phase. However, the overdose of GNR content (30 and 50 wt%) promoted the incompatibility of the film surface.

PTFEMA/GNR film also exhibited better film properties than PTFEMA/NR film in terms of surface energy and mechanical properties. It was found that the appropriate content of GNR as 10 wt% provided the good film properties of the modified PTFEMA film. The T_g values of this modified film showed at -62 °C for NR phase and 64 °C for the polymer phase, which was lower than that of PTFEMA (73.8 °C). The water and hexadecane contact angles and surface free energy were 106°, 61° and 16.5 mN/m, respectively. However, the incorporation of GNR did not significantly improve the mechanical properties of PTFEMA film. The tensile strength, elongation at break and storage modulus were increased from 25.2 to 26.4 MPa, 1.87 to 1.99% and 1.14 to 1.16 MPa, respectively.

5.2 Recommendations

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

5.2.1 The graft copolymerization of various fluorine containing monomers onto NR should be explored to obtain the graft copolymer with the superhydrophobic surface with the better mechanical properties.

5.2.2 The modified PTFEMA film should be directly prepared by using the latex form.



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APPENDIX

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APPENDIX A

Properties of natural rubber and monomers used in this research

Table A-1 Properties of natural rubber latex

Properties	Content (%)
Total solid content by weight	61.50
Dry rubber content by weight	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 A-2 Properties of 2,2,2-trifluoroethyl methacrylate (TFEMA)

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 A-3 Properties of methyl methacrylate (MMA)

Properties	Reported values
Molecular weight (g/mol)	100.12
Boiling point (°C)	100
Density at 25 °C (g/ml)	0.936
Flash point in closed cup (°C)	9



APPENDIX B

Calculations used in this research

B.1 Calculation of grafted TFEMA and MMA contents

The molar compositions of TFEMA and MMA in the GNR could be determined by using the $^1\text{H-NMR}$ spectroscopy of GNR as shown in Figure B-1. The molar compositions of TFEMA and MMA in the GNR was calculated by the following equations, which was adapted from the previous literature (Hinchiranan et al., 2013):

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

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

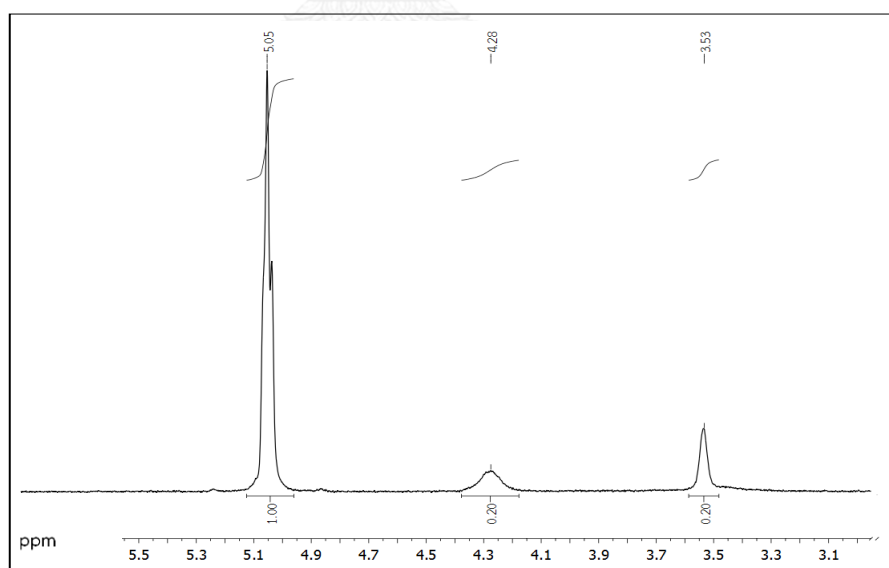


Figure B-1 $^1\text{H-NMR}$ spectra of GNR (condition: monomers content = 100 phr, MMA/TFEMA = 60/40 (w/w), Initiator = 0.75 phr, T = 60 °C, t = 6 h).

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 MMA = S_2 .

For example: $S_0 = 1.00$, $S_1 = 0.20$ and $S_2 = 0.20$

$$\begin{aligned} \text{\%mol of graft TFEMA in GNR } (C_F) &= \frac{(0.2/2)}{1.00 + (0.20/2) + (0.20/3)} \times 100 \\ &= 8.57\% \end{aligned}$$

$$\begin{aligned} \text{\%mol of graft MMA in GNR } (C_M) &= \frac{(0.20/3)}{1.00 + (0.20/2) + (0.20/3)} \times 100 \\ &= 5.71\% \end{aligned}$$

B.2 Calculation of grafting properties and %GE

For example: all obtained data from GNR

(condition: monomers content = 100 phr, MMA/TFEMA = 50/50 (w/w), Initiator = 0.75 phr, T = 60 °C, t = 4 h).

Weight of NR (A)	=	4.29
Weight of monomer charged (B)	=	4.31
Weight of obtained product (C)	=	7.25
Weight of sample (D)	=	1.06
Weight of sample after extraction with PE (E)	=	0.98
Weight of sample after extraction with acetone (F)	=	0.65

1. %Conversion

$$\begin{aligned}\% \text{Conversion} &= (C-A)/B \times 100 \\ &= (7.25 - 4.29)/4.31 \times 100 \\ &= 68.68\end{aligned}$$

2. Graft natural rubber, GNR

$$\begin{aligned}\% \text{GNR} &= F/D \times 100 \\ &= 0.65/1.06 \times 100 \\ &= 61.32\end{aligned}$$

3. %Free NR

$$\begin{aligned}\% \text{Free NR} &= (D-E)/D \times 100 \\ &= (1.06 - 0.98)/1.06 \times 100 \\ &= 7.55\end{aligned}$$

4. %Free copolymer

$$\begin{aligned}\% \text{Free copolymer} &= (E-F)/D \times 100 \\ &= (0.98 - 0.65)/1.06 \times 100 \\ &= 31.13\end{aligned}$$

5. %Grafting efficiency (%GE)

$$\begin{aligned}\text{Weight total polymer formed} &= C - A \\ &= 7.25 - 4.29 \\ &= 2.96 \text{ g}\end{aligned}$$

$$\begin{aligned}\text{Weight of free copolymer} &= (\% \text{free copolymer} \times C)/100 \\ &= (31.13 \times 7.25)/100 \\ &= 2.26 \text{ g}\end{aligned}$$

Weight of copolymer grafted

= weight total polymer formed - weight of free copolymer

$$= 2.96 - 2.26$$

$$= 0.7 \text{ g}$$

$$\%GE = (0.7/2.96) \times 100$$

$$= 23.75$$

B.3 Calculation of %gel

For example: all obtained data from GNR

(condition: monomers content = 100 phr, MMA/TFEMA = 50/50 (w/w), Initiator = 0.75 phr, T = 60 °C, t = 4 h).

Average weight of rubber in the aluminum weighing pan after drying (A) = 0.1088

Weight of total dried solution (B) = 0.4352

Initial weight of sample before dissolving in toluene (C) = 0.4491

$$B = 4 \times A$$

$$= 4 \times 0.1088$$

$$= 0.4352$$

$$\text{Gel (\%)} = (C-B)/C \times 100$$

$$= (0.4491 - 0.4352)/0.4491 \times 100$$

$$= 3.10$$

B.4 Calculation of surface energy

For example: all obtained data from PTFEMA film

Contact angle of hexadecane on the PTFEMA film surface (θ_H)	= 63.0 °
Surface tensions of hexadecane (γ_H)	= 27.6 mN/m
Dispersive parameters of hexadecane surface tension (γ_H^d)	= 27.6 mN/m
Polar parameters of hexadecane surface tension (γ_H^p)	= 0.0 mN/m
Contact angle of water on the PTFEMA film surface (θ_W)	= 106.0 °
Surface tensions of water (γ_W)	= 72.8 mN/m
Dispersive parameters of water surface tension (γ_W^d)	= 21.8 mN/m
Polar parameters of water surface tension (γ_W^p)	= 51.0 mN/m

1. Dispersive parameters of PTFEMA film surface tension (γ_F^d)

$$\gamma_H(1 + \cos \theta) = 2[(\gamma_H^d \gamma_F^d)^{1/2} + (\gamma_H^p \gamma_F^p)^{1/2}]$$

$$27.6(1 + \cos 63) = 2[(27.6 \gamma_F^d)^{1/2} + (0.0 \gamma_F^p)^{1/2}]$$

$$((27.6 \gamma_F^d)^{1/2})^2 = (27.6(1 + \cos 63)/2)^2$$

$$\gamma_F^d = 402.6/27.6$$

$$\gamma_F^d = 14.59 \text{ mN/m}$$

2. Polar parameters of PTFEMA film surface tension (γ_F^p)

$$\gamma_w(1 + \cos \theta) = 2[(\gamma_w^d \gamma_F^d)^{1/2} + (\gamma_w^p \gamma_F^p)^{1/2}]$$

$$72.8(1 + \cos 106) = 2[(21.8 \times 14.59)^{1/2} + (51.0\gamma_F^p)^{1/2}]$$

$$((51.0\gamma_F^p)^{1/2})^2 = ((72.8(1 + \cos 106)/2) - (21.8 \times 14.59)^{1/2})^2$$

$$51.0\gamma_F^p = 72.80$$

$$\gamma_F^p = 1.43 \text{ mN/m}$$

3. Surface tensions of PTFEMA film (γ_F)

$$\gamma_F = \gamma_F^d + \gamma_F^p$$

$$= 14.59 + 1.43$$

$$= 16.02 \text{ mN/m}$$



Table C-1 Raw data of %conversion, %GE and components in graft copolymer of graft NR

Exp.	KPS (phr)	MMA/TFEMA (w/w)	Temperature (°C)	Time (h)	Conversion (%)	GE (%)	Components in graft copolymer (mol%)	
							TFEMA	MMA
GNR 1	0.50	50/50	60	6	5.80	N/A	N/A	N/A
	0.50	50/50	60	6	5.10	N/A	N/A	N/A
GNR 2	0.75	50/50	60	6	75.9	16.8	3.29	2.82
	0.75	50/50	60	6	73.6	18.6	6.29	3.89
GNR 3	1.00	50/50	60	6	81.5	21.6	5.01	3.95
	1.00	50/50	60	6	81.2	21.6	7.53	3.84
GNR 4	1.50	50/50	60	6	85.3	8.53	3.74	2.80
	1.50	50/50	60	6	84.9	11.1	3.73	3.11
GNR 5	2.00	50/50	60	6	83.5	11.5	3.76	2.19
	2.00	50/50	60	6	86.1	6.75	1.90	3.16

Table C-1 Cont.

Exp.	KPS (phr)	MMA/TFEMA (w/w)	Temperature (°C)	Time (h)	Conversion (%)	GE (%)	Components in graft copolymer (mol%)	
							TFEMA	MMA
GNR 6	0.75	0/100	60	6	97.2	33.2	0.00	8.26
	0.75	0/100	60	6	94.2	34.2	0.00	8.61
GNR 7	0.75	30/70	60	6	84.4	27.4	0.92	7.06
	0.75	30/70	60	6	83.8	27.3	0.92	7.34
GNR 8	0.75	70/30	60	6	80.1	16.4	4.20	2.49
	0.75	70/30	60	6	75.9	15.7	3.76	2.19
GNR 9	0.75	100/0	60	6	71.5	13.5	4.31	0.00
	0.75	100/0	60	6	76.7	16.0	3.38	0.00
GNR 10	0.75	50/50	50	6	10.9	N/A	N/A	N/A
	0.75	50/50	50	6	6.26	N/A	N/A	N/A

Table C-1 Cont.

Exp.	KPS (phr)	MMA/TFEMA (w/w)	Temperature (°C)	Time (h)	Conversion (%)	GE (%)	Components in graft copolymer (mol%)	
							TFEMA	MMA
GNR 11	0.75	50/50	70	6	74.7	14.7	7.87	4.66
GNR 12	0.75	50/50	70	6	75.8	16.0	9.32	5.93
GNR 13	0.75	50/50	80	6	80.9	12.9	1.45	1.93
GNR 14	0.75	50/50	60	2	71.5	14.4	1.45	1.62
GNR 15	0.75	50/50	60	4	68.0	25.6	6.36	2.73
	0.75	50/50	60	8	78.9	14.4	7.40	5.52

Table C-2 Raw data of grafting properties and gel content of graft NR

Exp.	KPS (phr)	MMA/TFEMA (w/w)	Temperature (°C)	Time (h)	Grafting properties (wt%)			Gel content (wt%)
					Free NR	Free Copolymer	Graft NR	
GNR 1	0.50	50/50	60	6	N/A	N/A	N/A	13.4
	0.50	50/50	60	6	N/A	N/A	N/A	16.7
GNR 2	0.75	50/50	60	6	17.5	35.9	46.6	10.6
	0.75	50/50	60	6	17.8	34.6	47.7	2.72
GNR 3	1.00	50/50	60	6	12.9	35.3	51.7	1.49
	1.00	50/50	60	6	12.0	35.2	52.8	3.81
GNR 4	1.50	50/50	60	6	24.3	42.1	33.6	2.25
	1.50	50/50	60	6	27.6	41.0	31.4	0.93
GNR 5	2.00	50/50	60	6	35.6	40.4	24.0	0.24
	2.00	50/50	60	6	27.0	43.2	29.7	0.33

Table C-2 Cont.

Exp.	KPS (phr)	MMA/TFEMA (w/w)	Temperature (°C)	Time (h)	Grafting properties (wt%)			
					Free NR	Free Copolymer	Graft NR	Gel content (wt%)
GNR 6	0.75	0/100	60	6	7.77	33.0	59.2	42.8
	0.75	0/100	60	6	8.49	32.1	59.5	40.7
GNR 7	0.75	30/70	60	6	13.8	33.2	53.1	28.5
	0.75	30/70	60	6	13.7	33.1	53.2	24.8
GNR 8	0.75	70/30	60	6	29.4	37.3	33.3	1.42
	0.75	70/30	60	6	28.0	36.5	35.5	5.84
GNR 9	0.75	100/0	60	6	28.6	36.2	35.2	0.68
	0.75	100/0	60	6	29.9	36.5	33.6	0.42
GNR 10	0.75	50/50	50	6	N/A	N/A	N/A	13.6
	0.75	50/50	50	6	N/A	N/A	N/A	14.5

Table C-2 Cont.

Exp.	KPS (phr)	MMA/TFEMA (w/w)	Temperature (°C)	Time (h)	Grafting properties (wt%)			
					Free NR	Free Copolymer	Graft NR	
GNR 11	0.75	50/50	70	6	30.4	36.5	33.0	9.6
	0.75	50/50	70	6	36.3	36.3	27.5	5.16
GNR 12	0.75	50/50	80	6	45.2	39.4	15.4	10.6
	0.75	50/50	80	6	49.5	39.1	11.4	11.5
GNR 13	0.75	50/50	60	2	9.65	34.9	55.5	5.15
	0.75	50/50	60	2	10.2	35.8	54.0	2.10
GNR 14	0.75	50/50	60	4	9.01	28.8	62.2	4.59
	0.75	50/50	60	4	3.77	30.2	66.0	3.10
GNR 15	0.75	50/50	60	8	26.3	38.6	35.1	10.1
	0.75	50/50	60	8	29.1	37.9	33.0	10.5

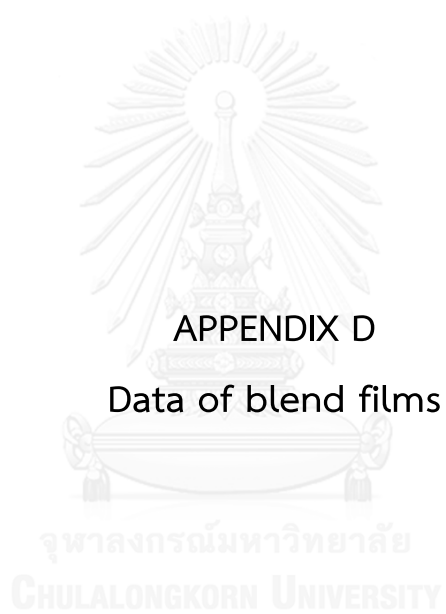


Table D-1 Raw data of contact angle and mechanical properties of blend film

Exp.	PTFEMA (g)	NR (g)	GNR (g)	Contact angle (°)		Mechanical properties	
				Water	Hexadecane	Tensile strength (MPa)	Elongation at break (%)
90/10 NR	7.13	0.83	-	96.2	33.9	8.76	1.07
				94.5	44.0	9.02	0.93
				99.3	50.4	10.7	1.14
70/30 NR	5.67	2.51	-	92.5	29.3	7.05	0.82
				85.7	30.0	4.35	0.95
				89.3	29.8	8.14	1.15
50/50 NR	4.26	4.47	-	90.8	30.6	0.55	11.9
				67.6	21.3	0.52	16.1
				93.0	55.2	0.59	13.2

Table D-1 Cont.

Exp.	PTFEMA (g)	NR (g)	GNR (g)	Contact angle (°)		Mechanical properties	
				Water	Hexadecane	Tensile strength (MPa)	Elongation at break (%)
90/10 GNR	7.36	-	0.82	106.5	70.1	26.0	2.15
				106.5	56.4	27.5	1.94
				106.7	62.1	25.6	1.87
70/30 GNR	5.70	-	2.54	93.9	39.4	8.41	0.87
				93.7	24.8	8.64	0.81
50/50 GNR	4.26	-	4.11	89.0	29.9	8.50	0.86
				79.9	28.5	12.1	1.57
				79.7	30.4	12.0	1.47
				80.9	34.0	9.84	1.22

VITA

Kritiya Homchoo was born on October 2, 1990 in Bangkok, Thailand. She was graduated with a Bachelor's degree of Science (Industrial Chemistry) from Department of Chemistry, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang in 2012. She has continued her study in Master's degree in Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University since 2013 and finished her study in 2016.

