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GRAFT COPOLYMERIZATION OF NATURAL RUBBER WITH FLUORINE
CONTAINING MONOMER

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ภมรบดี วรรณโก : กราฟต์โคพอลิเมอร์ไรเซชันของของยางธรรมชาติด้วยมอนอเมอร์ที่มีฟลูออรีน. (GRAFT COPOLYMERIZATION OF NATURAL RUBBER WITH FLUORINE CONTAINING MONOMER) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ.ดร.นพิตา ใหญ่ชี่ระนันท์, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม: ผศ.ดร.บุญโชติ เผ่าสวัสดิ์ยรรยง, 86 หน้า.

การผสมยางสองชนิดที่มีทั้งสภาพขี้และระบบการคงรูปที่แตกต่างกันเช่นยางธรรมชาติและยางฟลูออโรคาร์บอนเข้าด้วยกันส่งผลให้เกิดความไม่เข้ากันและการแยกวัฏภาคในยางผสม ทำให้สมบัติเชิงกลของผลิตภัณฑ์มีค่าด้อยลง การตัดแปรทางเคมีผ่านปฏิกิริยากราฟต์โคพอลิเมอร์ไรเซชันจึงเป็นวิธีที่ใช้กันอย่างแพร่หลายเพื่อเพิ่มความเข้ากันได้ในการผสมยางที่มีสมบัติต่างกันเข้าด้วยกัน มอนอเมอร์ที่มีฟลูออรีนที่ใช้ในการศึกษา คือ 2,2,2-ไตรฟลูออโรเอทิลเมทาคริเลตถูกกราฟต์ลงบนโครงสร้างของยางธรรมชาติผ่านปฏิกิริยากราฟต์โคพอลิเมอร์ไรเซชันแบบอนุมูลอิสระทั้งในระบบหลอมผสมและระบบสารละลายโดยใช้เบนโซอิลเปอร์ออกไซด์เป็นตัวริเริ่มปฏิกิริยาศึกษาผลของกระบวนการกราฟต์ ความเข้มข้นของสารริเริ่มปฏิกิริยาและมอนอเมอร์ อุณหภูมิ และระยะเวลาในการทำปฏิกิริยา พบว่าภายใต้ภาวะที่เหมาะสมทำให้ได้ยางธรรมชาติกราฟต์ภายหลังการสกัดร้อน มีประสิทธิภาพการกราฟต์สูงสุดร้อยละ 1.34 โดยมีปริมาณพอลิ (2,2,2-ไตรฟลูออโรเอทิลเมทาคริเลต) กราฟต์ 0.26 ส่วนในยางธรรมชาติ 100 ส่วน วิเคราะห์โครงสร้างของยางธรรมชาติกราฟต์ด้วยเทคนิคเอกซเรย์เอกซเรย์ฟลักซ์อินฟราเรดสเปกโตรสโคปี และนิวเคลียร์แมกเนติกเรโซแนนซ์สเปกโตรสโคปี และวิเคราะห์อุณหภูมิคล้ายแก้วด้วยดีฟเฟอเรนเชียลสแกนนิ่งแคลอริเมตรี ยางธรรมชาติกราฟต์ถูกนำไปประยุกต์ใช้เป็นสารเพิ่มความเข้ากันได้ในการผสมระหว่างยางธรรมชาติและยางฟลูออโรคาร์บอน พบว่าการเติมยางธรรมชาติกราฟต์ 15 ส่วนในยางผสม 100 ส่วน ทำให้ได้ยางผสมที่มีสมบัติเชิงกลดีที่สุดโดยมีความต้านต่อแรงดึง 9.93 เมกะปาสคาล สูงกว่ายางผสมที่ไม่เติมยางกราฟต์ 5.31 เท่า (1.87 เมกะปาสคาล) เนื่องจากมีความเข้ากันได้ของวัฏภาคอย่างมากขึ้น

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PAMONBORDEE WANNAKO: GRAFT COPOLYMERIZATION OF
NATURAL RUBBER WITH FLUORINE CONTAINING MONOMER.
ADVISOR: ASST. PROF. NAPIDA HINCHIRANAN, Ph.D.,
CO-ADVISOR: ASST. PROF. BOONCHOAT PAOSAWATYANYONG,
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The blending of two elastomers with different polarities and vulcanization systems such as natural rubber (NR) and fluoroelastomers (FKM) leads to the incompatibility and phase separation resulting in poor mechanical properties of finishing rubber products. The chemical modification via graft copolymerization is the technique to promote the compatibility of the blends with dissimilar properties. In this study, the fluorine containing monomer used for grafting onto NR backbone was 2,2,2-trifluoroethyl methacrylate (TFEM) via free radical graft copolymerization carried out by both of melt-mixing and solution-grafting processes initiated by benzoyl peroxide (BPO). The grafting properties were investigated as functions of grafting process, initiator and monomer concentration, reaction temperature and time. Under the optimum conditions, it was found that the obtained graft natural rubber (GNR) contained the maximum level of grafting efficiency as 1.34 % with grafted poly (2,2,2-trifluoroethyl methacrylate) (PTFEM) content as 0.26 phr. The structure of GNR was analyzed by using attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) and nuclear magnetic resonance spectroscopy (NMR). The glass transition temperature of samples was characterized by differential scanning calorimetry (DSC). The GNR was then applied as the compatibilizer for NR/FKM vulcanizates. The amount of GNR at 15 phr yielded the maximum tensile strength of the vulcanizate as 9.93 MPa, which was 5.31 times higher than that of incompatibilized one (1.87 MPa) due to the higher homogeneity of constituent phases.

Field of Study: Petrochemistry and Polymer Science Student's Signature

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LIST OF ABBREVIATIONS

AIBN	:	2-2'-Azobisisobutyronitrile
ATR	:	Attenuated Total Reflectance
Ave.	:	Average
BPO	:	Benzoyl peroxide
CV	:	Conventional vulcanization
Ca(OH) ₂	:	Calcium hydroxide
DCP	:	Dicumyl peroxide
DSC	:	Differential scanning calorimetry
EV	:	Efficient vulcanization
Exp.	:	Experiment
FKM	:	Fluoroelastomer
FTIR	:	Fourier Transform Infrared spectroscopy
GE	:	Grafting efficiency
GNR	:	Graft natural rubber
MDR	:	Moving die rheometer
MgO	:	Magnesium oxide
MH	:	Maximum torque
ML	:	Minimum torque
NMR	:	Nuclear Magnetic Resonance spectroscopy
NR	:	Natural rubber
PFS	:	2,3,4,5,6-Pentafluorostyrene
phr	:	Parts per hundred of rubber by weight
PTFEM	:	Poly(2,2,2-Trifluoroethyl methacrylate)
S.D.	:	Standard deviation
TAIC	:	Triallyl isocyanurate
T _{c90}	:	Optimum cure time
Temp.	:	Temperature
T _g	:	Glass transition temperature
THF	:	Tetrahydrofuran

TFEM	:	2,2,2-Trifluoroethyl methacrylate
T _{s2}	:	Scorch time
UTM	:	Universal testing machine
ZnO	:	Zinc oxide

CHAPTER I

INTRODUCTION

1.1 The statement of problem

Fluoroelastomers (FKM) are the fluorocarbon based-synthetic rubbers having high polarity and stability due to their higher strength of carbon-fluorine bonds than that of carbon-carbon bonds of other general elastomers. Moreover, they also have strong intermolecular interaction between hydrogen and fluorine in their molecules (Ameduri and Boutevin, 2001). Therefore, they provide variously superior performance such as chemical and oxidation resistance, heat stability and good weatherability to be extensively used in the high performance applications such as automotive and chemical industries including other activities requiring severe conditions for operation. However, FKMs have some disadvantages such as difficulty for processing due to the high Mooney viscosity, poor solubility in common organic solvents and high production cost (Kader, Lyu and Nah, 2006).

To consider the natural rubber (NR), it is one of outstanding bio-based elastomers with excellent mechanical and dynamic properties for applying as engineering parts used in many industries. It is also claimed as the low cost-sustainable material with availability in tropical countries. Nevertheless, the use of NR in some applications is limited because NR is quite sensitive to thermal and oxidative degradation when it is exposed to severe operating conditions due to its unsaturated carbon-carbon double bonds. In addition, it cannot be used in the presence of oil and hydrocarbon solvents (Derouet et al., 2009).

To improve the resistance to heat, oxidation and solvent of NR and reduce the production cost for using only FKM in any applications, the blending of NR with FKM is expected to give the resulting product containing both desirable properties with reasonable price. However, NR cannot be directly blended with FKM because of their different polarity and vulcanization system resulting to phase separation with undesired properties (Akiba and Hashim, 1997).

To enhance the compatibility of rubberic constituents containing different properties, the chemical modification via graft copolymerization is supposed to produce the graft copolymers containing segments with identical structure or ones providing the specific reactive interaction among the immiscible rubber components in the blends to decrease the rubber phase separation and enhance mechanical properties (Cho, 1997). Several studies have extensively revealed that the grafting of fluorine monomers onto polymers such as polypropylene (Cheng, Wen and Wu, 2009) and polybutadiene (Paz-pazos and Pugh, 2005) including fibers (Louati et al., 1999) promoted the desired properties in terms of low surface energy, high water and oil repellency and high chemical and thermal stabilities. These were resulted from the strongest single carbon-fluorine bonds in the fluorine containing monomer due to the small size of fluorine atom with high electronegativity and polarity (Torrens, 2005). The graft copolymerization of fluorine containing monomer onto polymeric backbone can be prepared by solution polymerization and melt mixing techniques (Vidéki, Klébert and Pukánsky, 2005).

Thus, the aim of this research was to study the functionalization of NR via graft copolymerization of fluorine-containing monomer: 2,2,2-trifluoroethyl methacrylate (TFEM). The grafting properties were investigated as functions of reaction systems, initiator concentration, monomer concentration, reaction time and reaction temperature. After soxhlet extraction for removing of the ungrafted parts, the structure of the obtained graft NR (GNR) was analyzed by using attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) and nuclear magnetic resonance spectroscopy (NMR). The glass transition temperature (T_g) of samples was characterized by using differential scanning calorimetry (DSC) and the effect of the addition of GNR acting as the compatibilizer on the mechanical property and the morphology of NR/FKM vulcanizates were also evaluated and reported.

1.2 Objectives of the research work

The objectives of this research are stated as followed:

1. To prepare the graft copolymer of TFEM onto NR by melt mixing process and solution polymerization.
2. To investigate the effects of initiator concentration, monomer concentration, reaction temperature and reaction time on the grafting properties.
3. To characterize the chemical structure of resulting graft copolymer by using ATR-FTIR, $^1\text{H-NMR}$ and $^{19}\text{F-NMR}$ spectroscopy. The glass transition temperature (T_g) of the graft product was also examined by using DSC.
4. To study the effect of the addition of GNR on mechanical properties and morphology of NR/FKM vulcanizates.

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. Design and construct the stainless steel reactor equipped with a thermocouple, a pressure gauge, inlet and outlet ports for nitrogen gas (N_2), a heater and a temperature controller for solution graft copolymerization.
3. Prepare the graft copolymer of fluorine containing monomers onto NR via both of melt mixing and solution grafting processes initiated by benzoyl peroxide (BPO).
4. Characterize the structure of graft copolymer after soxhlet extraction by using FTIR, $^1\text{H-NMR}$ and $^{19}\text{F-NMR}$ spectroscopy.
5. Determine the gel content, the amount of grafted poly (2,2,2-trifluoroethyl methacrylate) (PTFEM) and thermal properties of graft copolymer.
6. Prepare the NR/FKM vulcanizates containing various contents of GNR used as a compatibilizer.
7. Determine the cure characteristics and mechanical properties of the vulcanizates in terms of tensile properties and hardness. The morphology of the

fractural surface of vulcanizates was also investigated by using scanning electron microscope (SEM).

8. Summarize and conclude results.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Graft copolymerization

Graft copolymers are polymers containing long sequences of two different monomers in the copolymer chain. The side or grafting chains are structurally distinct from the main chain as shown in Figure 2.1 where A and B are two different monomers. Graft copolymers exhibit the properties of both (or more) polymeric backbone and the oligomeric or polymeric grafts rather than averaging the properties of both homopolymers (Sauguet, Boyer, Ameduri and Boutevin, 2006).

Graft copolymerization allows the synthesis providing an almost unlimited number of the different products by the variations in the properties and compositions of monomer units. There are three methods existing for producing the graft copolymers as shown in Eq. 2.1-2.3. “Grafting onto” (Eq. 2.1) involves the reaction between functional groups on two different polymers. It is the least useful method since reactions between polymers are slow and there are the relatively limited numbers of polymers with functional groups capable of reaction with each other. “Grafting from” (Eq. 2.2) relates to a polymer with functional groups that can initiate polymerization of monomer. This method is useful since many polymers can be used together with a range of reaction conditions (radical and ionic). “Grafting through” (Eq. 2.3) means the polymerization (or copolymerization) of macro-monomers; usually vinyl macro-monomer. It is also convenient, but it requires the prior synthesis of a macro-monomer (Odian, 2004).

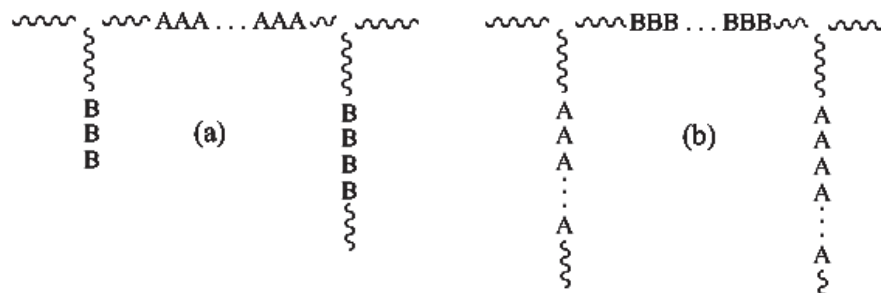
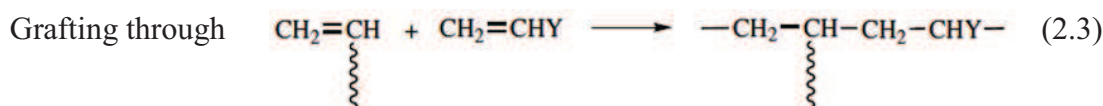
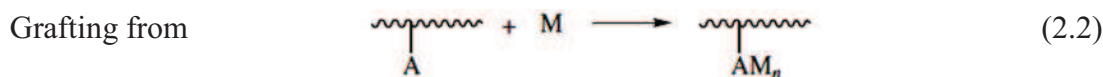
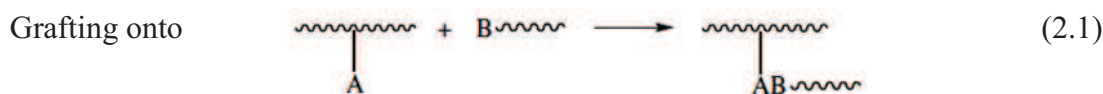


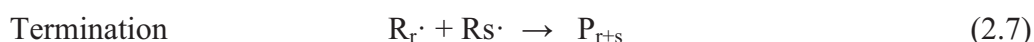
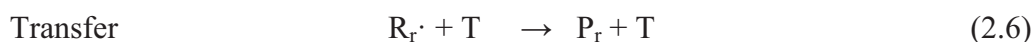
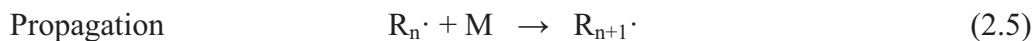
Figure 2.1 Scheme of the graft copolymer.



The graft copolymerization of natural rubber (NR) and vinyl polymers is prepared by polymerization of monomer initiated by free radicals for the attachment of polymers onto the rubber backbone. Normally, there are two methods to synthesize graft copolymers. The side chain polymer can be directly linked by a suitable chemical reaction to the polymer backbone initiated by free radicals or ions to give active sites (Chansook, 2001).

The mechanism of graft copolymerization onto NR chains consists of 3 steps: initiation, propagation and termination. The mechanism is shown in Eq. 2.4-2.7. Initiation takes place by thermal decomposition of an initiator (I), followed by the addition of the monomer unit (M) (Eq. 2.4). Then, the propagation quickly takes place with the addition of many monomer units (Eq. 2.5). Moreover, the transfer of reactive atoms such as hydrogen or halogen (usually from the transferring agent to cap the radical end) and transfer of the radical activity to the transferring agent residue could be occurred in this step (Eq. 2.6). The new radicals are usually added to monomer to continue the propagation of the growing chain. If the transferring radicals have low reactivity toward propagation, they might act as a retarder or inhibitor to decrease the polymerization rate. The termination by combination of radicals is assumed to be valid for most polymerization systems (Eq. 2.7) (Moore, 2006).

The graft copolymerization via free radical polymerization can be carried out with the three different copolymerization processes: solution process (Pazpazos and Pugh, 2005), emulsion process (Oliveira et al., 2005) and melt mixing process (Guo et al., 2010).



2.1.1 Solution graft copolymerization process (Odian, 2004)

A solution grafting process can be referred as a homogeneous process to synthesize polymers and copolymers in the solution. In the earlier study, many researchers studied the graft copolymerization of vinyl monomers onto elastomers backbone via solution process. For example, maleic anhydride was grafted onto NR (Nakason, Kaesaman and Supasanthitikul, 2004). 2, 3, 4, 5, 6-Pentafluorostyrene was grafted onto polybutadiene (Paz-pazos and Pugh, 2005). Acrylonitrile and styrene were also grafted onto NR via this system (Angnanon, Prasassarakich and Hinchiranan, 2011). Graft copolymerization with this process has some advantage in terms of the ease to control the released heat and viscosity during the reaction (Ebewele, 2000). However, it is usually not considered as economically process for scaling up because of the remaining solvent inside the obtained product and the difficulty in removing of the solvent at the end of this process. Moreover, the solvent may serve as a chain transferring agent, to decrease the molecular weight below the target point. The inert solvents are normally used in the solution grafting process to prevent the undesirable reactions or other effects that can be occurred from auto-acceleration promoted by accumulated heat produced from reactions (Long, Mcgrath and Turner, 2001).

2.1.2 Emulsion graft copolymerization process (Odian, 2004)

To expand the application of NR, the grafting of a secondary polymer within NR latex particles via emulsion copolymerization process was also studied. The emulsion copolymerization was firstly developed during World war II for

synthesizing the copolymers of 1,3-butadiene and styrene. Recently, the emulsion copolymerization has been an interesting process for preparation of graft copolymers and many vinyl monomers were applied for this process such as styrene (Chuayjuljit, Moolsin and Potiyaraj, 2005), methyl methacrylate and dimethylaminoethylmethacrylate (Oliveira et al., 2005) et al. The emulsion graft copolymerization is a radical copolymerization to give several advantages such as the ease to control heat and viscosity of the system. The product of this process is also in the latex forms that can be directly used without further separation for many applications such as paints, coating, finishes and floor polishes. Moreover, the emulsion graft copolymerization can produce copolymers with high molecular weights in high rate of reaction. This process requires four main components: monomers, dispersing medium, emulsifier (surfactant) and water-soluble initiator. NR latex has been generally modified by graft copolymerization via emulsion process. The resulting latexes are commonly known as “core-shell” latex as show in Figure 2.2 (Pukkate, et al., 2009). NR particle is a core and the monomers absorbed on the NR-core were then polymerized to form a shell (George, Maiti and Varma, 2006). The grafted NR latex having soft core and hard shell is usually applied as impact modifiers. On the other hand, NR particle with hard core and soft shell are generally used in the coating and adhesive applications (Arayaprenee, Presassarakich and Rempel, 2002).



Figure 2.2 The formation of core shell structure (Khan, Ray and Dolui, 2008).

2.1.3 Melt mixing process (Moad, 1999)

The graft copolymerization of NR with vinyl monomers initiated by the free radical initiators can also be performed in the molten state by using an extruder or an internal mixer. Among these bulk modification methods, the melt-grafting based on free radical polymerization is particularly attractive due to its low cost with simplicity, no requirement of solvent, less vulnerable by impurity and the ease of product separation after termination or reaction (Long, Mcgrath and Turner, 2001). The graft copolymerization via this process can be achieved by heat and shear forces during mixing. Unfortunately, the graft copolymerization in the molten state has normally performed at high processing temperature. This can induce the polymer degradation and severe crosslinking during the reaction (Yang et al., 2012).

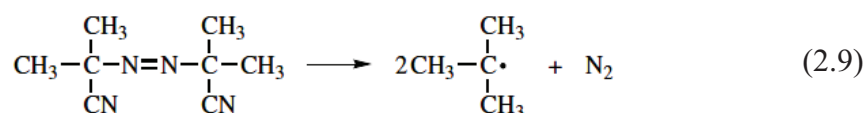
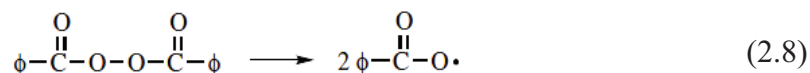
2.2 Initiator systems (Odian, 2004)

A variety of initiator systems can be extensively used for preparation of graft copolymerization for vinyl monomers onto polymeric backbone in recent years as followed:

2.2.1 Thermal decomposition

This type of initiators should have bond dissociation energies in the range of 100-170 kJ/mol to break O-O, S-S, or N-O bonds presented in their structures. The initiators with higher or lower dissociation energies will be dissociated at very slow or rapid rates. The peroxides are extensively used as the sources of free radicals such as acyl peroxides (such as acetyl and benzoyl peroxides), alkyl peroxides (eg. cumyl and tert-butyl peroxides), hydroperoxides (eg. tert-butyl and cumyl hydroperoxides) and peresters (eg. tert-butyl perbenzoate). The reaction temperature of graft copolymerization is depended on the decomposition rate of initiators. For azobisisobutyronitrile (AIBN), it is commonly active at 50-70°C. Whereas, acetyl peroxide, benzoyl peroxide (BPO) and dicumyl or di-t-butyl peroxide are reactive at 70-90 °C, 80-95 °C and 120-140 °C, respectively.

The scheme of the thermal decomposition of BPO and AIBN is shown in Eq. 2.8 and 2.9, respectively (Odian, 2004).



2.2.2 Redox initiation

The initiators related to the oxidation-reduction reactions producing free radicals to initiate polymerization have been well known as redox initiators. The advantage of this initiator is the reasonable rate of free radicals production over a wide range of temperatures. This is depended on the particular redox system, including initiation at moderate temperatures (0-50°C) and below. This allows a greater freedom of choice for the polymerization temperature. The redox initiators selected for graft copolymerization are peroxides with the combination of a reducing agent.

2.2.3 Photochemical initiation

The photochemical initiation produces free radicals by using ultraviolet and visible light irradiation. Some compounds in this system are excited by energy absorption and subsequent decomposition as radicals. The photo-initiation can control the amount of free radicals for polymerization by directly adjustment of the power of light to limit the light intensity and temperature. In the industry, the photochemical polymerization is typically claimed as solvent-free system, which offer advantages for both economic and/or environmental considerations. The significant factor to control the photochemical polymerization is the thickness of materials. They should be very thin to provide the high penetration of light energy. Thus, photochemical polymerization is well suited for surface and other thin-layer applications.

2.3 The graft copolymerization of fluorine containing monomers

The graft copolymerization of fluorine containing monomers onto polymer backbones lead the development of products in many industrial applications such as aerospace, engineering, optics, textile finishing and microelectronics in spite of their high price and are undergoing an increasing market (Ameduri and Boutevin, 2000). Because fluorinated graft copolymers have drawn great interest, the number of articles dealing with the synthesis, properties and applications of fluorinated graft polymers has been increasing (Sauguet, Boyer, Ameduri and Boutevin, 2006). The interesting properties of fluorinated graft copolymer are in terms of higher thermal stability, chemical inertness (to acids, bases, oil and hydrocarbon solvents), low water absorptivity, excellent weatherability, good resistance to oxidation, low flammabilities and very interesting surface properties (Ameduri and Boutevin, 2000).

To reduce the cost of using only fluoroelastomers (FKM) and to improve the properties of NR which is a low cost natural elastomer, graft copolymerization of NR with fluorine containing monomers is possible to prepare new materials which are able to be used as compatibilizer to promote the compatibility of the blends between NR and FKM. The incorporation of fluorine containing monomers grafted onto polymer chains has been widely studied to obtain the materials with desired properties such as low surface energy (Tan et al., 1999), low surface tension (Cheng, Wen and Wu, 2009), the higher thermal and chemical stabilities (Paz-pazos and Pugh, 2005). The obtained graft product can be also applied as the compatibilizer for using in the blends between fluoroelastomer and silicone rubber (Guo et al, 2010).

The several types of fluorine containing monomers were used in the graft copolymerization in the earlier research works such as 2,3,4,5,6-pentafluorostyrene (PFS) grafted onto polybutadiene (PB) via solution polymerization (Paz-pazos and Pugh, 2005). Perfluoroalkylethyl methacrylate grafted onto poly (methyl methacrylate) (PFMA-g-PMMA) (Park, Lee and Choi, 1996) and 2,2,2-trifluoroethyl methacrylate (TFEM) grafted onto silicone rubber (MVQ) (Guo et al., 2010). Both of latter systems were prepared by the melt mixing process.

There are some previous literatures that studied on the preparation of graft copolymerization of fluorinated monomers on the polymer backbones via solution or melt mixing process.

Park, Lee and Choi (1996) studied the synthesis of Perfluoroalkylethyl methacrylate grafted onto poly (methyl methacrylate) (PFMA-*g*-PMMA) by using the macromonomer technique. A macromonomer was an oligomer having an end group to copolymerize with co-monomers to form comb-type graft copolymers. The PMMA macromonomers having an acryloxy functional group at one end were synthesized by acylation of hydroxyl-group terminated PMMA, prepared by radical oligomerization of methyl methacrylate with a chain-transfer agent. The PMMA macromonomer was then copolymerized by emulsion polymerization with a co-monomer of perfluoroalkylethyl methacrylate (FMA).

Tan et al. (1998) studied the graft copolymerization of polypropylene (PP) with 1-heptadecafluorooctylethyl acrylate (FA) via melt mixing process in an internal mixer at 180 °C. The addition of styrene as the third component increase the amount of grafted FA and prevented chain degradation. However, the higher FA concentration was occurred at the lower initiator concentration because the increasing in initiator concentration generated the higher content of free radicals that caused a competition between the chain degradation and the graft copolymerization.

Louati et al. (1999) studied the preparation of fluorinated polyester fibers by graft copolymerization of perfluorooctyl-2 ethanol acrylic monomer (AC8) onto poly (ethylene terephthalate) (PET) fiber initiated by BPO via solution grafting process. The optimum grafting yield was obtained from a monomer concentration of 1.125 M and initiator concentration of 1.8×10^{-2} M. The overdose of monomer concentration caused the competition between graft copolymerization and the homopolymerization or disproportionation of AC8. Moreover, a higher initiator concentration induced the more recombination of free radicals. The higher reaction temperature increased the %grafting due to the increase in the initiation and propagation rates.

Paz-pazos and Pugh (2005) studied the graft copolymerization of polybutadiene (PB) with 2,3,4,5,6-pentafluorostyrene (PFS) via solution polymerization initiated by BPO in the presence of tetrahydrofuran (THF). The graft

copolymerizations were performed under nitrogen atmosphere and investigated as a function of reaction temperature (50-80°C) by using PFS (0.70 mol), PB (0.36 mol) and BPO (18 mmol). The results showed that the increase in the reaction temperature, increased grafting yield. The optimum condition was PB 5 mmol, BPO 0.25 mmol, PFS 10 mmol at 80°C for 48 h yielded the highest %conversion as 58.7 and the ratio (w/w) between PFS in graft copolymer and PB as 0.297.

Cheng et al. (2008) studied the graft copolymerization of polypropylene (PP) with 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-hexadecafluoro-nonyl ester (HFNAE) via melt mixing process by internal mixer at 165-190°C with 70 rpm of screw speed. The structural analysis showed the characteristic peaks of HFNAE in FTIR spectra of grafted product to confirm that the fluorinated PP was successfully prepared. The presence of carbon-fluorine bond in the structure of fluorinated PP increased thermal stability and impact strength due to the higher intermolecular interaction. However, the tensile strength of samples was decreased due to the lower crystallinity of fluorinated PP.

Zhai et al. (2008) reported the grafting of perfluorinated vinyl ether monomer (2-bromotetrafluoroethyl trifluorovinyl ether (BrTFF)) onto poly(ethylene-co-tetrafluoroethylene) (ETFE) films by γ -rays irradiation at room temperature. The obtained grafted films was easily applied for further applications such as brine electrolysis membranes and polymer electrolyte membranes for fuel cells. The irradiation with absorbed doses higher than 400 kGy gave the poly(BrTFF) grafted ETFE membranes with grafting yields more than 20% due to low polymerization reactivity of fluorinated monomers. FTIR spectra and SEM-EDS results confirmed the successfully graft copolymerization of BrTFF onto ETFE films. The thermal analysis of the grafted films indicated no phase separation between poly(BrTFF) grafts and ETFE films, probably owing to high compatibility of the fluorinated grafts and based polymers.

2.4 Rubber blending

The blending of various polymer types to achieve an economics and properties advantages has been investigated for many years. Rubber blending is frequently used in the rubber industries to obtain the desirable properties including physical properties, processibilities and production cost because the use of a single elastomer cannot provide the properties required for specific applications. Blending of two or many elastomers is a useful, easy and efficient technique to develop many new high performance materials by the combination of the desired properties of individual components to a single material. The commercial production of rubber blends is normally processed by the melt-processing machinery (Ismail and Hairunezam, 2000). There are a lot of factors affecting the miscibility and properties of the blends (Tinker, 1998). For examples,

- Blends ratio: The properties of the blends were affected by the the relative amounts of each elastomers and the relative viscosity. If the minor phase (dispersed phase) has lower viscosity than the major phase, the minor phase will be finely dispersed.
- Phase morphology: the phase size is affected by the condition of blends preparation. In general, the higher shear force of mixing generates the smaller phase size. However, some elastomers may degrade due to the chain scission during mixing process.
- Interfacial adhesion: the lower interfacial tension of blend constituents induces the smaller phase size. For two elastomers with largely different solubility parameters, the large phase size was generated due to the high interfacial tension. Moreover, the interfacial tension also controls the interfacial adhesion and crosslink formation between the two elastomers. The higher interfacial tension means the lower efficiency of mixing of the compositions at the interface. This can reduce the opportunity to obtain crosslinking between the phases of constituents resulting to the poor physical properties due to the weakness at the interface.

- Crosslink distributions: the even distribution of crosslinking between the constituent phases has a potential to yield the good physical properties of the vulcanizates.
- Additive distributions: the good interaction of the elastomer and the surface of the carbon black or additives lead the even distribution between the constituent phases.

Although, the blending of elastomers shows the superior properties than the pure one, the simple blending of elastomers with different properties may decrease the mechanical properties of finished products due to the thermodynamically immiscible with each other (Cartier and Hu, 2001).

2.5 Compatibilization

The mechanical properties of the rubber blends containing dissimilarity can be improved by the addition of a suitable components acting as compatibilizers to lead the more compatibility. These components can improve the interfacial adhesion between phases of blend constituents and stabilize the blend morphology resulting to the higher homogeneity with better mechanical properties of the rubber blends (Datta, 2005).

The third component normally applied as the compatibilizer may be graft copolymer, diblock copolymer, random copolymer, triblock copolymer and even a homopolymer (Guzman et al., 2011). The effect of the addition of graft copolymer used as the compatibilizer in the polymer blends is shown in Figure 2.3.

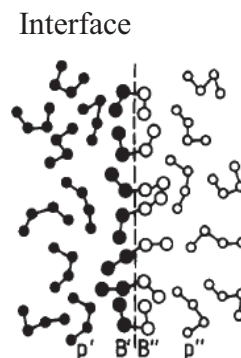


Figure 2.3 Scheme of the compatibilization of the polymer blends by using the compatibilizer (Braun, Fischer and Hellmann, 1996).

2.6 Natural rubber (NR) and its vulcanization

NR is one of natural polymers, which has been commercially available for over a hundred years. NR has high molecular weight with the chemical structure of *cis*-1,4-polyisoprene (Figure 2.4) originally derived from *Hevea Brasiliensis*. The raw rubber contains the hydrocarbon content about 94% with the small numbers of non-hydrocarbon groups distributed along the chain such as small quantities of proteins, fats, fatty acids, carbohydrates and mineral matter. The long linear polymer chain of NR is composed with molecules having the different sizes. The average molecular weight (M_w) of NR is in the range of 30,000 to about 10 million. The high linearity of NR chain results the strain-induced crystallization to induce the rapid crystallization upon stretching to promote the high tensile strength and tear resistance. Moreover, NR is also claimed as the low cost-sustainable material with availability in tropical countries (Derouet et al., 2009).

Nevertheless, the use of NR in some applications is limited because NR is quite sensitive to thermal and oxidative degradation when it is exposed to severe operating conditions due to the presence of carbon-carbon double bond in its structure. In addition, it cannot be used in the presence of non-polar organic solvents, oil and fuels due to the non-polarity of NR structure. For these reasons, many efforts have been applied to improve the properties of NR to be used in wider applications.

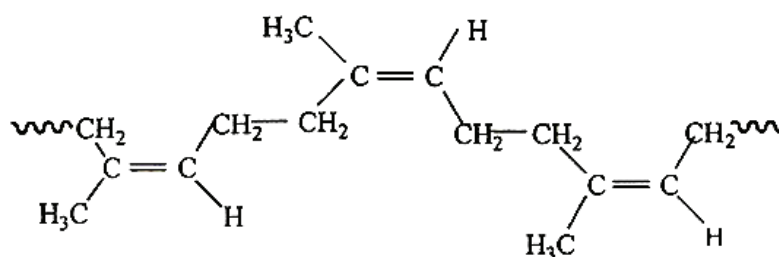


Figure 2.4 Chemical structure of *cis*-1,4-polyisoprene.

The vulcanization is the most important factor for properties of finishing rubber products. This is generally achieved by reaction with sulfur and accelerators at an elevated temperature. Vulcanization transforms the linear polymer into a three-dimensional macromolecules by locking the chains to each other and decrease the amount of chain slippages. The NR can be mainly vulcanized by two main systems: peroxide and sulfur vulcanization (Robert, 1988).

- Sulfur vulcanization: the first step is the formation of an active sulfurating agent from sulfur, accelerators and activators. After abstracting a hydrogen atom from the rubber, the single or more sulfur atoms can connect the carbon atom of one chain to others as shown in Figure 2.5. This systems require a high ratio of accelerator to sulfur giving predominantly monosulphidic crosslinks are called as the efficient vulcanization (EV) systems. For the low ratio value, it is called as the conventional vulcanization systems (CV) but the. A compromise between two systems is a semi-EV system. The vulcanizates obtained from the CV system have better fatigue life in a cyclic deformation environment but the poorer compression set and thermal resistance than a semi EV or EV system. Moreover, the disadvantage point is that sulfur to sulfur bonds are weaker (less thermally stable) than a sulfur to carbon link. (Ciesielski, 1999).

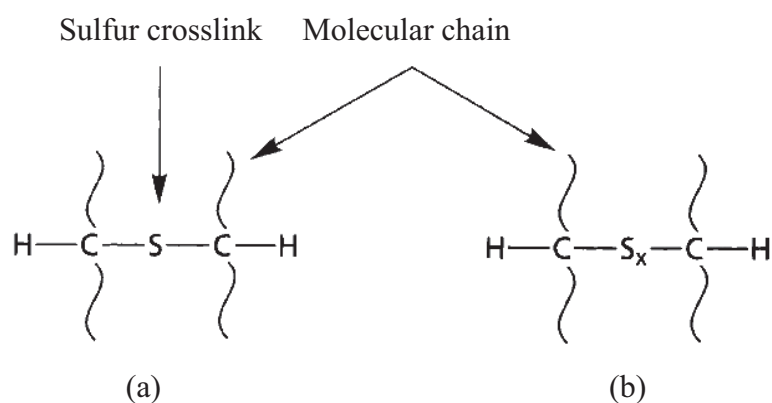


Figure 2.5 Scheme of sulfur vulcanizations: (a) single sulfur atom and (b) multiple sulfur atoms linked between two polymer chains (Ciesielski, 1999).

- Peroxide vulcanization: this system does not need the reactivity of a double bond to cure. Thus, it can cure the saturation rubbers. When the peroxides are decomposed, they typically react with the elastomer chains by removing hydrogen atoms from the carbon backbone of the polymers. The free radicals are formed and reacted with polymers to produce the highly active sites providing carbon to carbon crosslinks, which are quite thermally stable than a sulfur to carbon crosslinks (Figure 2.6). Therefore, these vulcanizates exhibit the better thermal aging characteristics which are superior to those of even EV systems and also lower compression set at elevated temperature. However, the resistance and resistance to low temperature crystallization and fatigue are low. In addition, the major disadvantage of this system is its lack of processing safety (Ciesielski, 1999).

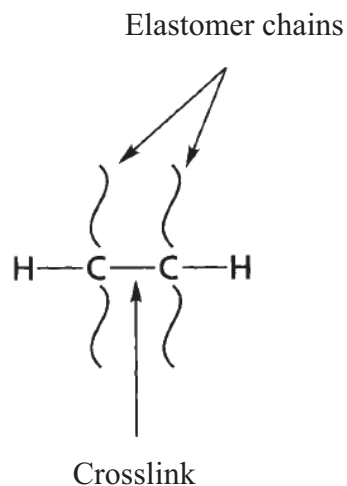


Figure 2.6 Scheme of peroxide vulcanization: two elastomer chains directly linked through carbon atoms (Ciesielski, 1999).

2.7 Fluoroelastomer (FKM) and its vulcanization

FKM is the fluorocarbon based-synthetic rubbers with high polarity and stability resulting from the higher strength of carbon-fluorine bonds compared to carbon-carbon bond of other general elastomers. The carbon-fluorine bond is the most stable single bond with high bond dissociation energy (Table 2.1) resulting to the high thermal, oxidative and chemical stability (Wang and Legare, 2003). Moreover, they also have strong intermolecular interaction between hydrogen and fluorine in their molecules (Ameduri and Boutevin, 2000). It can be used in high performance applications such as aerospace, engineering, automotive and chemical industries including other activities requiring severe conditions for operation (Kader et al., 2006). Figure 2.7 shows the FKM components used in automotive industries that are the largest market for FKM consumption. Moreover, FKM is also used as seals and barrier layers subjected to severe environments. FKM components have long service life at temperatures above 150°C and have resistance to various kinds of fluid. Moreover, they also have and low permeability. However, FKM has some disadvantages such as difficulty for processing due to its high mooney viscosity, poor solubility in common organic solvents and high production cost (Kader et al., 2006).

Table 2.1 Typical bond dissociation energies (Wang and Legare, 2003)

Chemical bonding	Bond dissociation energies (kJ/mol)
C-C	234-368
C-H	381-410
C-Cl	326
C-F	452
C-O	350-389
C-N	293-343

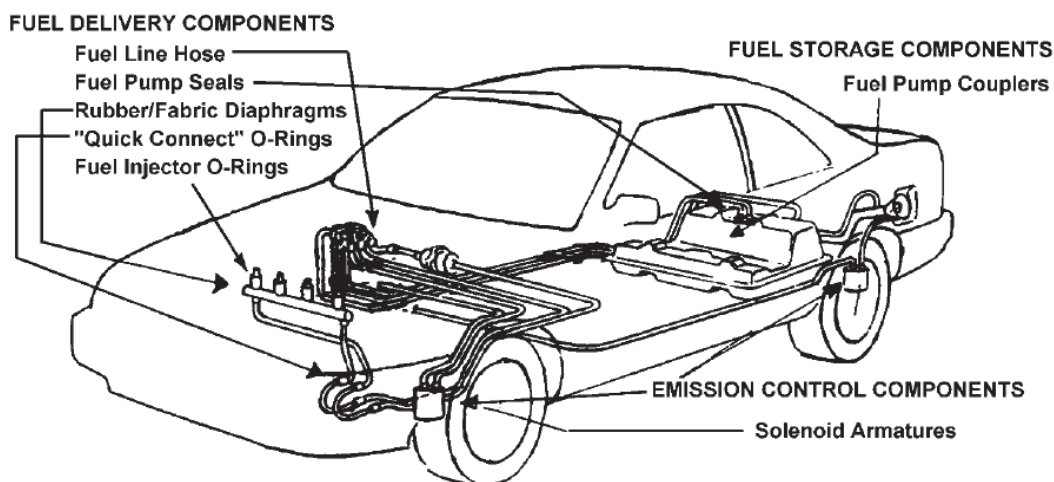


Figure 2.7 FKM components in automobile (Moore, 2006).

2.7.1 Classification of FKM (Moore, 2006)

The properties of FKM such as fluid resistance, stability at high temperatures, chemical inertness, flexibility at low temperatures and difficulty of processing and curing are depended on the composition of FKM. The most widely available FKM elastomers are generally produced from copolymerization of two or more monomers such as such as vinylidene fluoride (VF₂), hexafluoropropylene (HFP), perfluoromethyl vinyl ether (PMVE) and tetrafluoroethylene (TFE) as shown in Figure 2.8 (Wang and Legare, 2003). One or more monomers give straight chain segments, which can crystallize if the resulting polymer chain is long enough.

The four commercial FKMs are summarized in Table 2.2. The first widely available FKM is a copolymer of VF₂ and HFP. This copolymer normally contains 66% of fluorine content is called as Type A. It is possible to produce a terpolymer FKM called as type B by incorporation of TFE along with VF₂ and HFP by adding TFE in place of VF₂. The fluorine level can be increased to the range of 68–70%. The enhancement of fluorine level improves chemical resistance by lowering the total hydrogen content in the polymer. FKM type GF, a third type of commercial FKM is a tetrapolymer containing a TFE–VF₂–HFP backbone with a small level of cure site monomer (CSM) incorporated to impart peroxide curability. Examples of CSMs for such commercial FKM include bromine and iodine-containing

vinyl monomers such as 4-bromo-3,3,4,4-tetrafluorobutene-1 (BTFB), bromotrifluoroethylene (BTFE), 4-iodo-3,3,4,4-tetrafluorobutene-1 (ITFB) (Moore, 2006). These peroxide curable FKM exhibit improved resistance to water, acid and steam. A fourth type of commercial FKM named as Type GFLT is a low temperature tetrapolymer where PMVE replaces HFP in the backbone to improve low temperature sealing capability as indicated by a lower glass transition temperature (Wang and Legare, 2003).

Nowadays, there are four major global manufacturers of FKM elastomer: DuPont Dow Elastomers, Dyneon, Ausimont and Daikin.

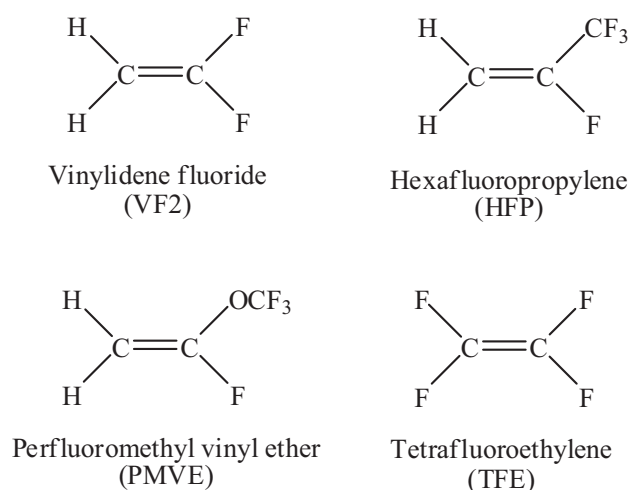


Figure 2.8 Chemical structure of fluorine containing monomers.

Table 2.2 The commercial fluoroelastomers (Wang and Legare, 2003)

Fluoroelastomers	Monomer sequence	Fluorine level (% w/w)
Fluoroelastomer-A	VF2-HFP	66
Fluoroelastomer-B	VF2-HFP-TFE	68
Fluoroelastomer-GF	VF2-HFP-TFE-CSM	70
Fluoroelastomer-GFLT	VF2-PMVE-TFE-CSM	67

2.7.2 Vulcanization system of FKM (Moore, 2006)

FKM also requires curing in order to get the better similar to other elastomers. The best vulcanizate properties are obtained by a two-step process. The first step is carried out in a compression molding with heat (150-180°C). The second step or post-cure process is also utilized to achieve the optimum physical properties. This step is performed in air under atmospheric pressure at 200-250°C for a day (Ameduri, Boutevin and Kostov, 2001).

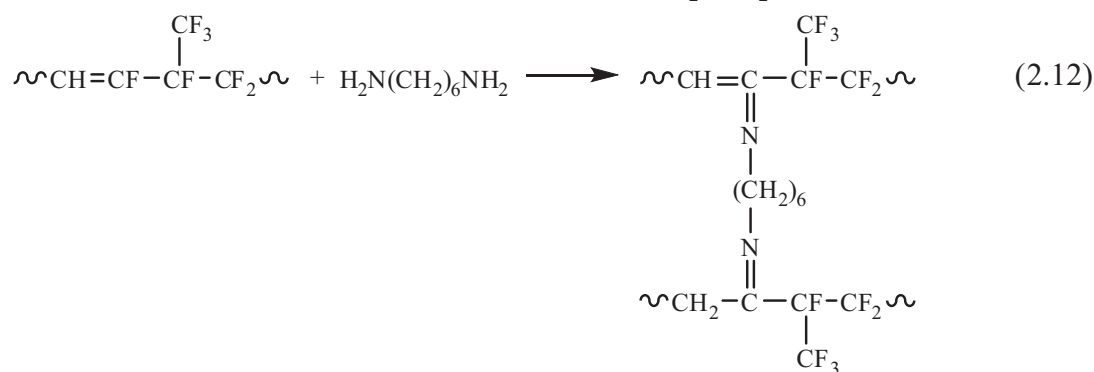
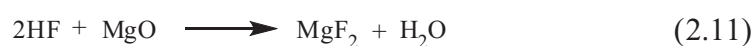
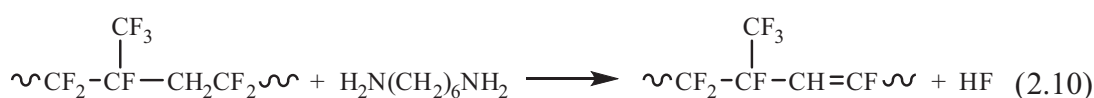
There are three primary curing systems for curing FKM. The diamine and bisphenol are normally used to cure FKM containing fluorine monomers that can be reacted via nucleophilic attack such as VF2 and HFP. The bisphenol curing system gives the best processing compounds. Nowadays, it is the most popular fluoroelastomer curing system. Amines are very seldom used due to the difficulty of processing and short scorch time. Peroxides are used in FKM containing halogenated CSMs. This cure system induces the maximum chemical resistance and there is the only cure system to vulcanize PMVE containing low temperature tetrapolymers. Similar to other elastomers, FKM are normally compounded with fillers, processing aids, curatives etc. Mechanical properties of FKM are not only depended on the polymer, but they are also depended on other ingredients. A wide range of mechanical properties can be achieved by varying polymer structure as well as compounding technology.

2.7.2.1 Diamine vulcanization (Moore, 2006)

The diamine system is composed with dehydrofluorinating, crosslinker and the magnesium oxide (MgO) took up the hydrofluoric acid (HF) formed. Diamine such as hexamethylene diamine is very reactive at low temperature, so it may cause the scorch during cure. Its derivatives are designed to the moderate activity and acceptable safety for processing. The most commonly diamine is the carbamate salt of hexamethylene diamine (sold by Dupont as DIAK no. 1 curative).

The reaction mechanism of diamine vulcanization starts with the elimination of HF to form double bonds as shown in Eq. 2.10. Then, magnesium

oxide (MgO) acted as the acid acceptor catches the resulting hydrofluoric acid (HF) to yield magnesium fluoride (MgF) and water (H₂O) as shown in Eq. 2.11. Finally, the nucleophilic diamine reacts with double bonds to form crosslinks with imine structure as shown in Eq. 2.12. However, the importance of the diamine cure has decreased because of its processing difficulty and the relatively poor retention of physical properties at high temperatures. (Ameduri, Boutevin and Kostov, 2001).

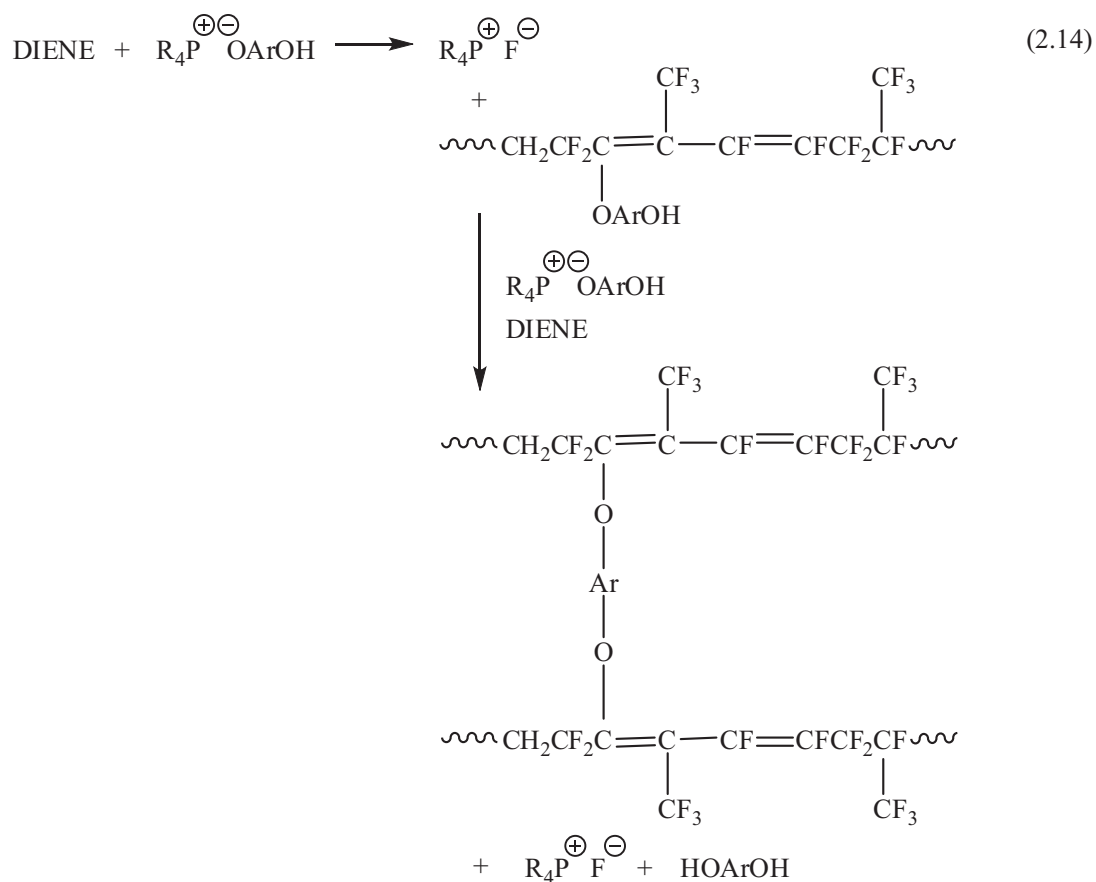
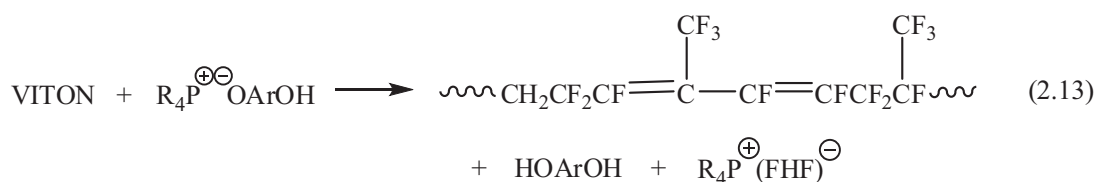


2.7.2.2 Bisphenol vulcanization (Moore, 2006)

The bisphenol curing system was discovered for replacing the diamine vulcanization in the early 1970s. This system has the advantages in terms of excellent safety for processing and fast cure rate with excellent final properties of finished products. The reaction mechanism for the bisphenol crosslinking with polymer chains is proposed as shown in Eq.2.13 – 2.17. The FKM produced from vinylidene fluoride (VF2) is necessary to develop a crosslinking site. The crosslink agents in this system are the simple bisphenol and the preferred crosslinker bisphenol AF. An accelerator (phosphonium, ammonium, etc.) in the combination with a metal compound as an activator such as benzyltriphenylphosphonium chloride (BTPPC) is necessary along with the acid acceptors such as magnesium oxide and calcium hydroxide. The cure rate and states can be varied by the adjustment of bisphenol and accelerator levels.

The bisphenol reacts with the metal oxides to give the phenolate ion to react with the phosphonium ion or tetraalkylammonium ion to produce the intermediate $R_4P^+OArOH^-$ or $R_4N^+OArOH^-$. These intermediates are strong bases which have some compatibility with the polymers and can abstract hydrogen fluoride from the polymer backbone (Ameduri, Boutevin and Kostov, 2001).

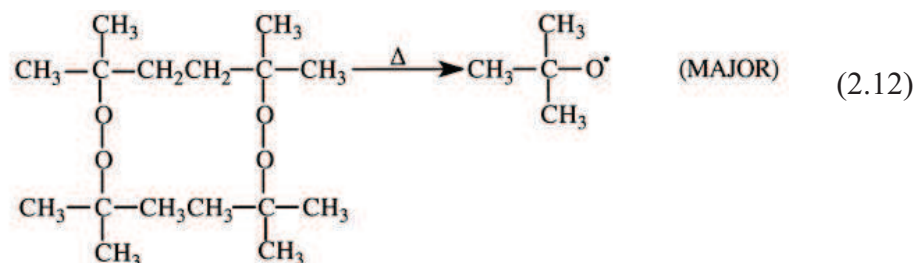
The double bonds rearrange and a second molecule of HF can be abstracted from the polymer to give a diene. A bisphenol-derived phenolate attacks the diene structure in the FKM backbone leading the dienic phenyl ether crosslinks as shown in Eq. 2.13 and 2.14.



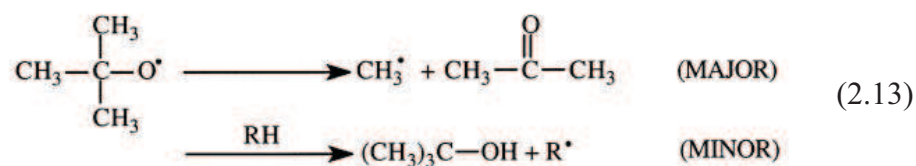
2.7.2.3 Peroxide vulcanization (Moore, 2006)

Peroxide crosslinking is basically a free radical process. It involves the thermal decomposition of peroxide to generate free radicals for abstracting hydrogen from the methylene groups along the polymer chains. The resultant polymeric radicals then directly interact or through the intermediary of radical traps to form crosslinks. FKM cured with peroxides, or free radicals exhibits the improved resistance to steam, hot water and aqueous acids over FKM cured with bisphenols. The crosslinking occurs at specific sites available on the cure-site monomer (CSM). CSM and curing mechanism are originally developed for an improved low-temperature FKM based on vinylidene fluoride (VF2) and perfluoromethyl vinyl ether (PMVE). The crosslinking agents called “radical traps” result products having lower thermal stability than bisphenols. The most effective crosslinker is triallylisocyanurate (TAIC), as judged by cure state and compression set of vulcanizates.

The proposed reaction mechanism resulting from the thermal decomposition of peroxide for generating free radicals, as shown in Eq. 2.12 – 2.16.



Most of the primary *t*-butox radicals undergo β -scission to acetone and methyl radicals (Eq. 2.12).



2.8 Blends of FKM with other polymers and their properties

Due to the higher cost of FKM with the difficulty of processing, there were several previous research to investigate the properties of the blends of FKM with other polymers or rubbers. However, the rubber constituents in these rubber blends were required to be modified or having suitable functional groups. For example,

Kader and Bhowmick (2003) studied the thermal aging and degradation behaviour of acrylate rubber (ACM), FKM and blends of ACM and FKM containing polyfunctional acrylates such as hexanediol diacrylate (HDDA), trimethylol propane triacrylate (TMPTA) and dipentaerythritol hexaacrylate (DPHA) in air and nitrogen atmospheres. The results indicated the higher thermal stability because these acrylates induced the crosslinking of the rubber phase to increase resistance for bond cleavage at the degradation temperature. The tensile strength and elongation at break of the aged ACM/FKM blends (50/50 (w/w)) containing different polyfunctional acrylates decreased with increasing functionality of the acrylates due to the higher crosslinking sites. The higher levels of polyacrylate in the blend resulted an additional step of degradation compared to polyacrylate. The swelling index of the blends decreased with increasing level of polyfunctional acrylates.

Wang et al. (2009) studied the the aging behavior of the blends between FKM (copolymer of vinylidene fluoride and hexafluoropropylene) and polyphenol hydroxy ethylene propylene diene monomer rubber (PHEPDM). Moreover, their thermal and oil resistant properties were also investigated. The results showed that the aging process increased the crosslinking density and the content of double bond. The O/F or O/C ratios increased and then decreased during aging because of the oxidation reaction of molecular chain and the surface migration of fluoro group. The FPM/PHEPDM blends had higher thermal degradation temperature and higher equilibrium-swelling ratio than FPM before aging and lower equilibrium-swelling ratio after aging due to the complete vulcanization of blends. The equilibrium-swelling ratio decreased when the content of PHEPDM increased because the fluoroelastomers molecular chains were connected through flexible chains of PHEPDM in the FPM/PHEPDM reactive blends. The long flexible PHEPDM chains facilitated the movement of fluoroelastomers molecules and induced the solvent to

swell the blended fluoroelastomer. When the content of PHEPDM was low, the crosslinking density was decreased with increasing the equilibrium-swelling ratio.

Moreover, some of FKM blends needed to add the compatibilizers for increasing the compatibility and improving the properties of the finishing products. For example,

Guo et al. (2010) studied the copolymerization of 2,2,2-trifluoroethyl methacrylate (TFEM) onto silicone rubber (MVQ) and the blends between fluoroelastomer and silicone rubber and the compatibilization properties of 2,2,2-trifluoroethyl methacrylate grafted silicone rubber (MVQ-g-TFEM). The results indicated that the scorch time increased with incorporation of the MVQ-g-TFEM as the compatibilizer because the sufficient adhesion between two phases of elastomers due to the increased polar interaction. The increasing of MVQ-g-TFEM improved the mechanical properties.

Nair, Kurian and Joseph (2012) studied the blends of hexafluoropropylene–vinylidene fluoride dipolymer fluoroelastomer (FKM) and ethylene propylene diene monomer rubber (EPDM) with and without compatibilizer (MA-g-EPDM). For the non-compatibilized blends, the maximum torque, scorch safety and the optimum cure time increased with the increasing of FKM contents. For the compatibilized blends, the optimum cure time, tensile strength and thermal stability increased with the increasing of the compatibilizer content. It is also indicated the higher chemical interaction and physical entanglement between two elastomer phases.

2.9 Motivation for the preparation of NR/FKM vulcanizates

Since the rapid decrease in the amount of fossil fuels and the higher pollution problems resulted from the increasing of the energy consumption of the transportation and industries, the alternative energy such as biodiesel and gasohol has become more interesting for the replacement of fossil liquid fuels. To consider gasohol, the addition of ethanol changes the polarity of the oil. Thus, the oil-resistant rubber materials generally used in fuel transmission lines and engine parts are required to be modified to improve the resistivity against a polar component. From

this purpose, the fluoroelastomers (FKM) is an excellent choice among the general other rubbers (Hazeeb et al., 2011). However, the price of FKM is still higher than that of the others. Thus, the blend between FKM and natural rubber (NR) was expected to reduce the cost of using only fluoroelastomers and achieve the desirable properties. Unfortunately, NR cannot be directly blended with FKM because of their different polarity and vulcanization system resulting to phase separation with undesired properties of finished products.

Thus, the aim of this research was to prepare the graft copolymer of fluorinated monomer, 2,2,2-trifluoroethyl methacrylate (TFEM) onto NR. The effect of reaction parameters: initiator concentration, monomer concentration, reaction temperature and reaction time on the amount of grafted fluorinated monomer, grafting efficiency (%GE) and gel content was investigated. The graft product with various amount of grafted fluorinated monomer was then applied as the compatibilizer for NR/FKM vulcanizates. The tensile properties, morphology and gasohol resistance of the obtained vulcanizates were examined and reported.

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

Solid natural rubber (NR, STR-5L) was supplied by Innovation Co.Ltd. (Thailand). 2,2,2-trifluoroethyl methacrylate (TFEM) and 2,3,4,5,6-pentafluorostyrene (PFS) were received from Sigma-Aldrich (USA). Benzoyl peroxide (BPO) was purchased from Panreac (Spain). The chemical structure of TFEM and PFS were shown in Figure 3.1. Petroleum ether, methanol, ethanol and tetrahydrofuran (THF) were all obtained from J.T.Baker (USA). The 99% purity of nitrogen gas (N₂) was manufactured by Thai Industrial Gas Co.Ltd. (Thailand). Hexane and acetone were received from Honeywell Burdick & Jackson (USA) and Qrec (New Zealand), respectively.

Fluoroelastomer used in this research was VITON B70 (Dupont, USA). Triallyl isocyanurate (TAIC), dicumyl peroxide (DCP), magnesium oxide (MgO) and calcium hydroxide (CaOH₂) were purchased from Innovation Co.Ltd. (Thailand).

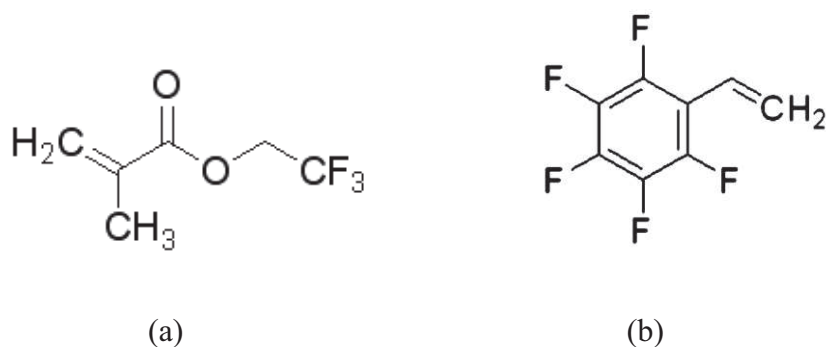


Figure 3.1 Chemical structure of (a) 2,2,2-trifluoroethyl methacrylate (TFEM) and (b) 2,3,4,5,6-pentafluorostyrene (PFS).

3.2 Graft copolymerization of fluorinated monomers onto NR

The graft copolymerization of fluorinated monomers: TFEM and PFS was prepared via both solution and melt mixing process.

3.2.1 Solution grafting process

The procedure for graft copolymerization of fluorinated monomer by the solution grafting process has been studied in previous literature (Paz-pazos and Pugh, 2005). The 0.04 mol of solid NR was dissolved in 170 ml of THF at room temperature. The obtained NR solution was then transferred into the stainless steel reactor equipped with a heater, a thermocouple, a temperature controller, a pressure gauge, N₂-inlet and outlet lines, a magnetic bar and a feeding port as shown in Figure 3.2. This reactor containing NR solution was placed on a magnetic stirrer to stir the reaction mixture during the given period of graft copolymerization. The reaction solution was degassed by purging N₂ gas for 30 min to remove the oxygen inside the solution and the reactor. The fluorinated monomer at desired content and 2 phr of BPO were subsequently added into the reaction solution. The reactor was heated up to the desired reaction temperature. After termination, the crumbed product was isolated in ethanol and then dried under vacuum at 40°C for 24 h to obtain the gross graft NR (GNR).

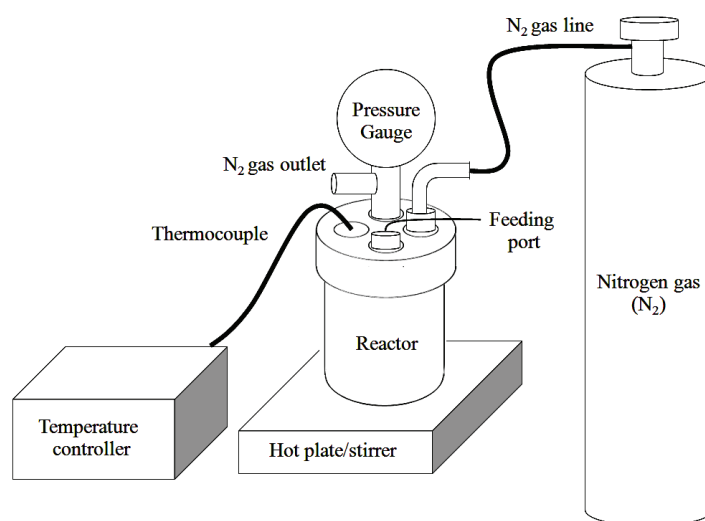


Figure 3.2 The experimental apparatus for solution grafting system.

3.2.2 Melt mixing process (molten state)

The graft copolymerization of fluorinated monomers onto NR prepared via melt mixing process was performed in the internal mixer (Thermo Haake polydrive). The 0.29 mol of NR was charged into the mixing chamber at 30°C with 70 rpm of screw speed. When the torque was steady, The desired amounts of fluorinated monomer and BPO were subsequently added into the system. Then, the mixing temperature was adjusted to the desired point (70 – 110°C). The effect of initiator concentration, monomer concentration, reaction temperature and reaction time on grafting efficiency, fluorine content and the amount of gel of GNR were investigated. The range of these studied parameters was listed as shown in Table 3.1.

Table 3.1 studied parameters for melt mixing process

Parameters		Quantities
Initiator concentration	(phr)*	0.5, 1, 2, 3, 4
Monomer concentration	(phr)	5, 10, 20, 30, 40
Reaction temperature	(°C)	70, 80, 90, 100, 110
Reaction time	(min)	10, 30, 60, 90, 120

*Parts per hundred of rubber by weight

3.3 Purification of GNR

The obtained gross GNR was consisting of three parts: graft copolymer, free NR and homopolymer. The free NR and homopolymer were removed by using soxhlet extraction apparatus (Figure 3.3) with petroleum ether and acetone, respectively. In each step, the sample was leaved in the soxhlet extraction unit for 24 h and then dried in vacuum oven at 40°C for 24 h.

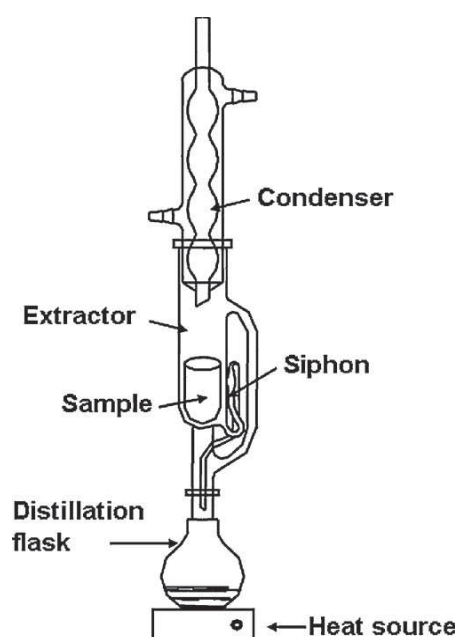


Figure 3.3 Scheme of the soxhlet extraction apparatus (Luque de Castro and Priego-Capote, 2010).

3.4 Structure characterization and determination of grafted fluorinated monomers in GNR

The chemical structure of graft copolymer was analyzed by using FTIR-ATR spectroscopy (Perkin Elmer: spectrum one). To confirm FTIR-ATR results, all swollen samples in CDCl_3 were analyzed by using $^1\text{H-NMR}$ and $^{19}\text{F-NMR}$ spectroscopy (Varian: INNOVA). To avoid the gel formation affecting the calculation of grafting properties of GNR, the results obtained from $^1\text{H-NMR}$ spectroscopy were used to evaluate the actual content of grafted fluorinated monomer on NR backbone. The content of grafted fluorinated monomer in the purified GNR was calculated from the new peak of methylene proton in the obtained polymer grafted on NR backbone (4.3 ppm) and peak of unsaturated methylene proton in NR structure (5.1 ppm) following Eq. 3.1-3.3 (Oliveira et al., 2005). Then, the %grafting efficiency (%GE) was calculated from the grafted fluorinated monomer content and the amount of total polymer formed as shown in Eq. 3.4 and 3.5.

$$C = \left[\frac{\left(\frac{S_1}{2} \right)}{\left(S_0 + \frac{S_1}{2} \right)} \right] \times 100 \quad (3.1)$$

$$C' = \left[\frac{(C \times M_F)}{((C \times M_F) + ((1 - C) \times M_{NR}))} \right] \quad (3.2)$$

$$\text{Grafted PTFEM (g)} = \frac{(C' \times \text{Gross GNR})}{100} \quad (3.3)$$

$$\text{Weight of total polymer formed (g)} = \text{Weight of gross GNR} - \text{Weight of NR} \quad (3.4)$$

$$\%GE = \frac{\text{Weight of grafted fluorinated monomer}}{\text{Weight of total polymer formed}} \times 100 \quad (3.5)$$

where C is the %molar of monomer in the graft copolymer, C' is the %mass composition of fluorinated monomer in the graft copolymer, S_1 is the integrated peak area of methylene proton of fluorinated monomer in the graft copolymer, S_0 is the

integrated peak of unsaturated methylene proton of NR in the graft copolymer, M_F is the molecular weight of monomer and M_{NR} is the molecular weight of NR (68). The example of calculation for evaluation of fluorine content and %grafting efficiency (%GE) in GNR was shown in the Appendix B.

3.5 Determination of gel content

The gel content in GNR after soxhlet extraction was evaluated following ASTM 3616-95. The apparatus for gel content determination shown in Figure 3.4 is consisted of borosilicate weighing bottle containing five stainless steel screen racks (o.d. = 50.0 mm and i.d. = 9.53 mm) which are mounted on 9 mm of stainless steel tube. 0.4 g of sample was cut into small pieces (1 mm x 5 mm) which could not fall through the screen and then distributed over 4 lowest screens by placing the pieces of samples near the center of each screen. Then, the screen rack was put into the borosilicate weighing bottle. 100 ml of THF was delivered into the bottle. The bottle was capped and kept in the dark for 20 h at 25 °C. After the desired time period, the screen racks was removed. 25 ml of remained solution was pipetted to aluminium weighing pan and dried in vacuum oven at 40°C for 24 h. The gel content could be calculated by using Eq. 3.6 and Eq. 3.7:

$$B = 4 \times A \quad (3.6)$$

$$\text{Gel (\%)} = \frac{(C - B)}{C} \times 100 \quad (3.7)$$

where A is the weight of rubber solution (25 ml) after drying, B is the weight of total dried samples and C is the initial weight of sample before dissolving in the solvent.

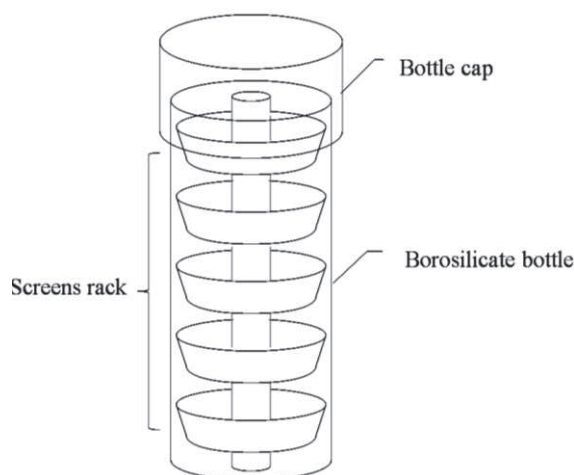


Figure 3.4 The equipment for gel content determination (ASTM 3616-95).

3.6 Preparation of NR/FKM vulcanizates

The formulation for preparation of NR/FKM vulcanizates was applied from the previous literature (Guo et al., 2010). NR/FKM vulcanizates (20/80 w/w) was prepared by using the following typical formulation as summarized in Table 3.2. FKM was firstly pre-mixed with MgO and Ca(OH)₂ used as acid acceptors in an internal mixer at 70 rpm of a screw speed and room temperature for 3 min. NR was masticated before mixing with GNR used as the compatibilizer at various contents by using a two-roll mill at room temperature for 3 min. The FKM compound was then mixed with NR/GNR blend by using the two-roll mill at room temperature for 8 min. DCP and TAIC were further added into the rubber compound and blended for 3 min. The obtained blends were compressed in a hydraulic compression mold at 155 °C for the optimum cure time evaluated by the moving die rheometer (MDR, TECH PRO).

3.6.1 Mechanical properties of NR/FKM vulcanizates

The mechanical properties in terms of tensile properties and hardness of the NR/FKM vulcanizates with and without the compatibilization were evaluated by using universal testing machine (LLOYD model LR5K) with a crosshead speed of 500 mm/min and durometer (type A) according to ASTM D412 and D2240, respectively.

Table 3.2 Typical recipe for preparation of NR/FKM vulcanizates compatibilized by using GNR with various contents

Ingradients	Quantities (phr)
GNR	0, 3, 6, 9, 12, 15, 20
MgO	2.4
Ca(OH) ₂	4.8
TAIC	1.5
DCP	0.6

NR/FKM = 20/80 (w/w)

3.6.2 Morphology of NR/FKM vulcanizates

To study the compatibility of the vulcanizates, the morphology of the tensile fracture surface of the samples obtained from the tensile properties test was investigated using a scanning electron microscopy (SEM, JEOL model JSM-6400) operated at 15 kV. The specimens were mounted on a SEM stub using a double-side tape and the fracture surface of specimens was coated with gold.

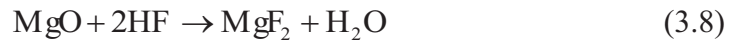
3.6.3 Glass transition temperature of GNR and NR/FKM vulcanizates

The glass transition temperatures (T_g) of GNR after soxhlet extraction compared to that of NR, PTFEM and NR/FKM vulcanizates with and without the addition of GNR were examined by using the differential scanning calorimeter (DSC-Q2000, TA instruments) with a constant heating rate of 10°C/min from -100 to 50°C.

3.6.4 Thermal aging properties of NR/FKM vulcanizates

In the typical rubber industries, elastomers are usually cured only at 90% of their maximum torque. The remains is generally kept to accommodate the introduction of crosslinks in the matrix during services (Radhakrishnan, Alex and Unnikrishnan, 2006). For FKM vulcanization, the amount of water could be produced

during the compression curing in the hydraulic compression molding following Eq. 3.8. This could inhibit the vulcanization and decrease the tensile strength of samples. To eliminate the water-by product, the thermal aging process was recommend to be applied foe FKM vulcanization.



Thus, the effect of thermal aging on the mechanical properties of the vulcanizates were studied. The thermal aging was carried out in an oven at 100°C for 24 h. Then, the specimens were removed from the oven and allowed to cool down in room temperature for 24 h before determination of the mechanical properties.

3.6.5 Oil Resistance of NR/FKM vulcanizates

To apply the NR/FKM vulcanizates for gasohol engine, the oil resistance of the NR/FKM vulcanizates with and without the addition of GNR was investigated by swelling the specimens in gasohol E20 (ethanol = 20% (w/w)) and E85 (ethanol = 85% (w/w)). The NR/FKM vulcanizates (20×20×2 mm) were weighed before immersion in the oil (ca. 60 cm³) and again after immersion at room temperature for 70 h. After removing from the oil, the specimens were quickly dipped in acetone at room temperature and lightly wiped by tissue paper to remove the excess oil from their surface before weighing. The change in mass (%) of the test specimens was calculated following Eq. 3.9:

$$\% \text{Swelling} = \frac{(M_2 - M_1)}{M_1} \times 100 \quad (3.9)$$

where M_1 and M_2 are the weight of the specimens before and after immersion, respectively.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Graft copolymerization of fluorine containing monomers onto natural rubber

4.1.1 Selection of fluorine containing monomer and grafting process

There were some previous literatures reported the possibility to graft fluorine containing monomers onto some elastomers with several processes such as the graft copolymerization of 2,3,4,5,6-pentafluorostyrene (PFS) onto 1,4-polybutadiene via solution process (Paz-pazos and Pugh, 2005) and that of 2,2,2-trifluoroethyl methacrylate (TFEM) onto silicone rubber via melt mixing process (Guo et al., 2010). Thus, this part aimed to select the fluorine containing monomer and grafting process which had potential to graft onto the NR backbone.

Table 4.1 shows the effect of grafting processes and types of fluorine containing monomer (PFS and TFEM) on the %monomer conversion, %grafting efficiency (%GE) and the amount of grafted fluorinated monomer in the GNR after Soxhlet extraction. It was observed that PFS could not be grafted onto NR backbone for either solution or melt mixing process. Although the spectra analyzed by FTIR-ATR (Figure 4.1) revealed the new FTIR signals appeared at 1,501 and 1,270 cm^{-1} attributed to C=C aryl ring and F-aryl, respectively (Colthup, Dary and Wiberley, 1964) and ^{19}F -NMR (Figure 4.2) exhibited the new NMR signals at -143, -154 and -161 ppm which are the characteristic peaks of C-F bonds in poly (2,3,4,5,6-pentafluorostyrene) (PFS) (Riedel et al., 2011), the analysis by using ^1H -NMR (Figure 4.3) could not detect the signal of grafted PPFS on the NR (GNR_PPFS). This implied the very low content of grafted PPFS onto the NR backbone. It was possible that the chemical structure of PFS had more steric hindrance to obstruct the graft copolymerization onto NR.

In the case of TFEM, the results indicated that the NR after grafting with TFEM had new FTIR signals at 1,720-1,600 cm^{-1} , 1,350-1,120 cm^{-1} and 1,350 cm^{-1} attributed to C=O, C-F and C-O bonds as shown in Figure 4.4, respectively (Colthup, Dary and Wiberley, 1964). For ^{19}F -NMR (Figure 4.5), the GNR_PTFEM showed the chemical shift at -73.7 ppm attributed to CF_3 of grafted PTFEM (Zhang et al., 2011). The ^1H NMR spectra of GNR_TFEM (Figure 4.6) also exhibited the new signal at 4.35 ppm for methylene proton ($-\text{CH}_2-$) of grafted PTFEM (Raihane and Ameduri, 2006). Thus, it could be concluded that TFEM had more potential to be grafted onto NR backbone via both solution and melting processes than PFS having more steric hindrance (Ciardelli et al., 1997).

The amount of grafted TFEM calculated from ^1H NMR spectra was 0.007 and 0.004 phr for the preparation from melt mixing and solution processes, respectively. This indicated that the melt mixing process was appropriate for graft copolymerization of TFEM onto NR due to the heat and shear force supplied during mixing resulting to the higher efficiency for grafting than solution grafting process (Long, Mcgrath and Turner, 2001).

Table 4.1 Effect of grafting process and type of fluorine containing monomer on %conversion, %GE and the amount of grafted fluorine containing monomer of purified GNR

Monomer	Grafting process	%Conversion	%GE	Grafted fluorine monomer content (phr)
PFS	Solution ⁽¹⁾	5.10	n/a ⁽³⁾	n/a
	Melt mixing ⁽²⁾	56.3	n/a	n/a
TFEM	Solution	3.15	0.04	0.004
	Melt mixing	20.0	0.17	0.007

(1) Condition: NR = 1.4 g, fluorine containing monomers = 20 phr, BPO = 2 phr and THF = 200 ml at reaction temperature = 80 °C for 24 h.

(2) Condition: NR = 20 g, fluorine containing monomers = 20 phr, BPO = 2 phr at reaction temperature = 130 °C for 20 min.

(3) Could not be analysed.

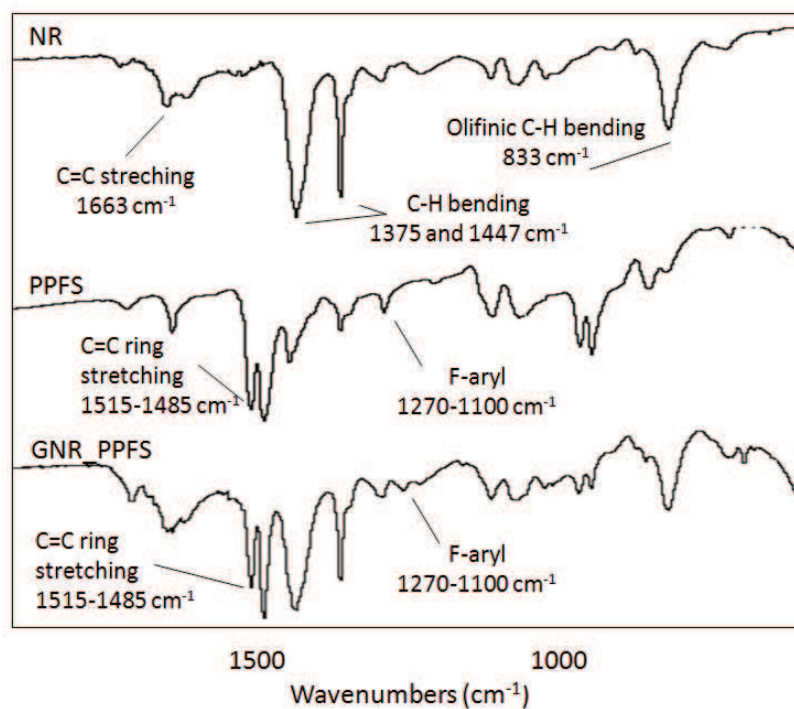


Figure 4.1 FTIR-ATR spectra of NR, PPFS and graft copolymers prepared from PFS (GNR_PFS).

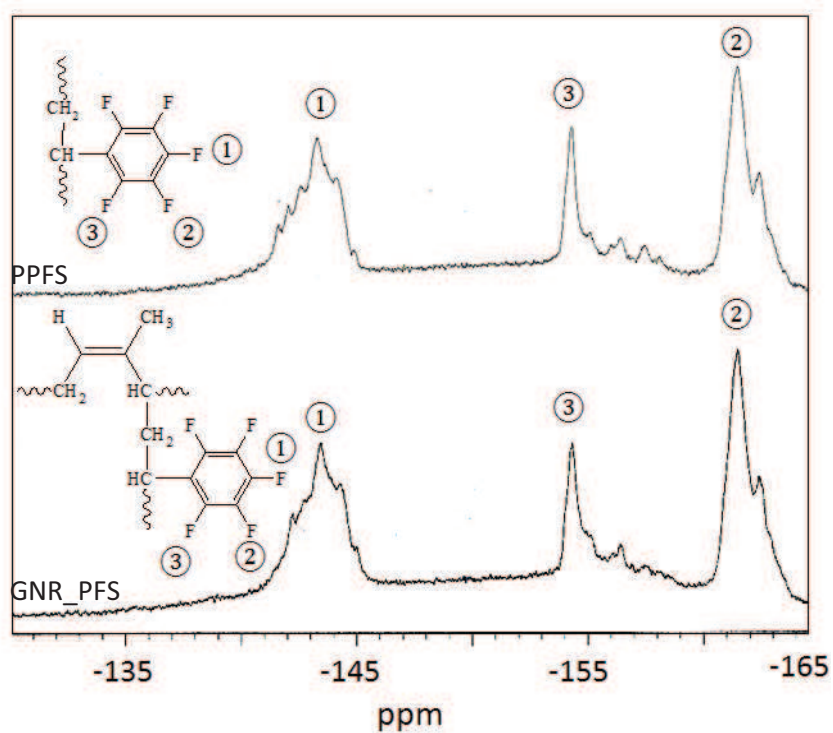


Figure 4.2 ^{19}F -NMR spectra of PPFS and graft copolymers prepared from PFS (GNR_PFS).

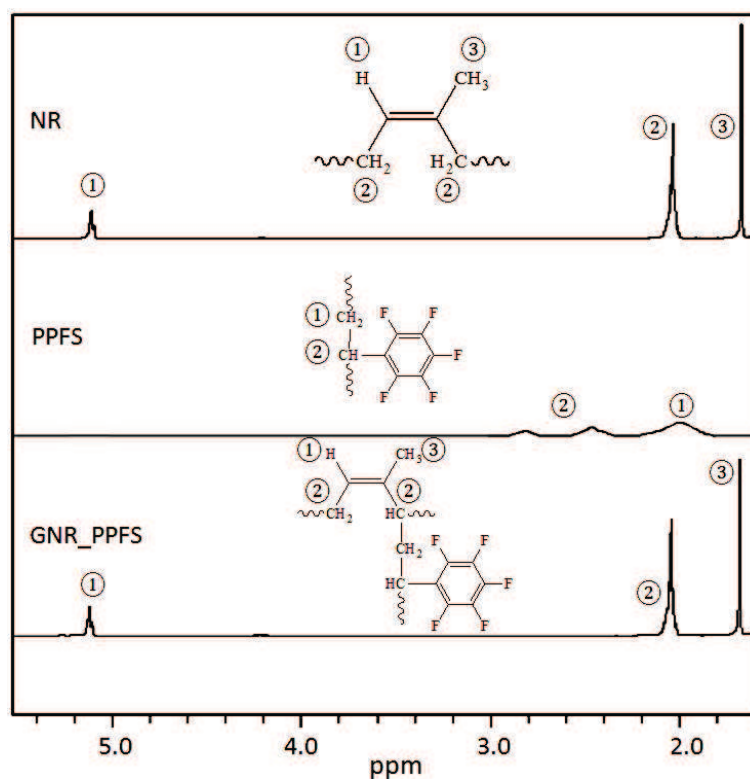


Figure 4.3 ^1H -NMR spectra of NR, PPFS and graft copolymers prepared from PFS (GNR_PFS).

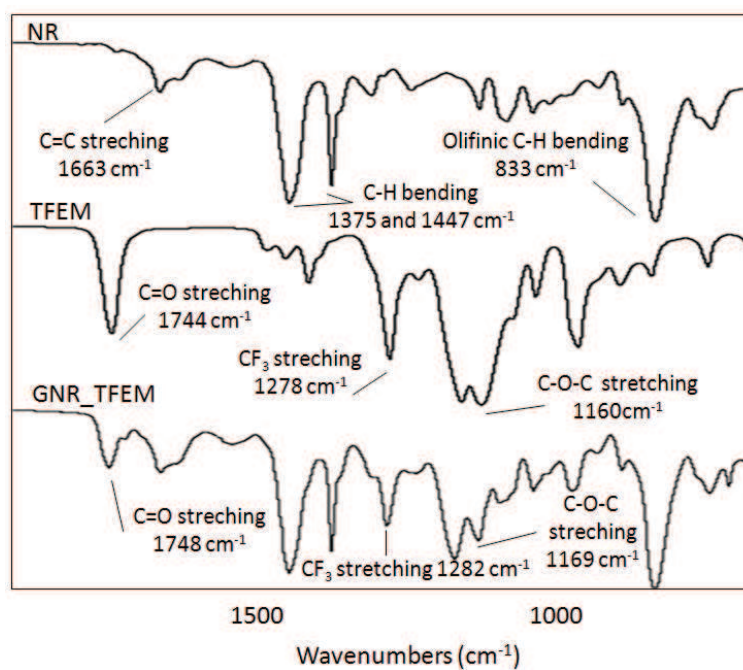


Figure 4.4 FTIR-ATR spectra of NR, PTFEM and graft copolymers prepared from TFEM (GNR_TFEM).

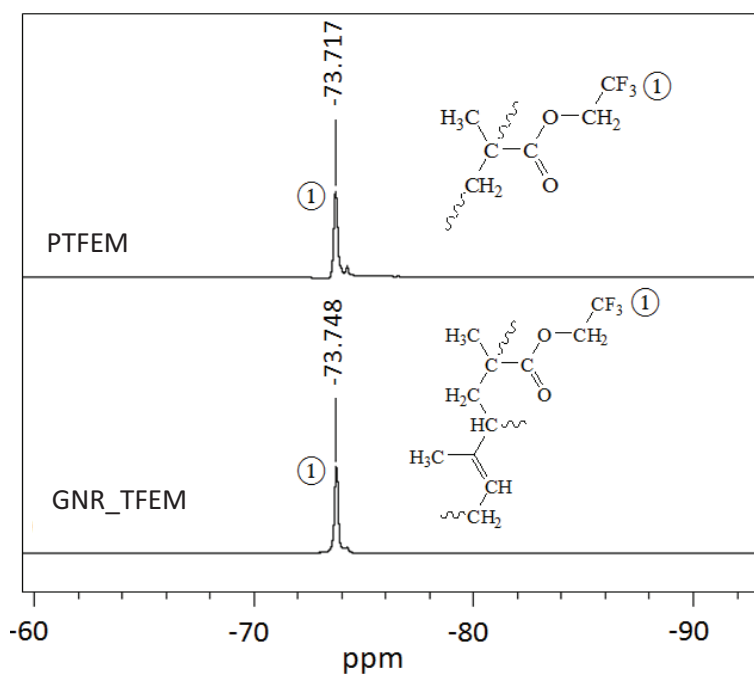


Figure 4.5 ^{19}F -NMR spectra of PTFEM and graft copolymers prepared from TFEM (GNR_TFEM).

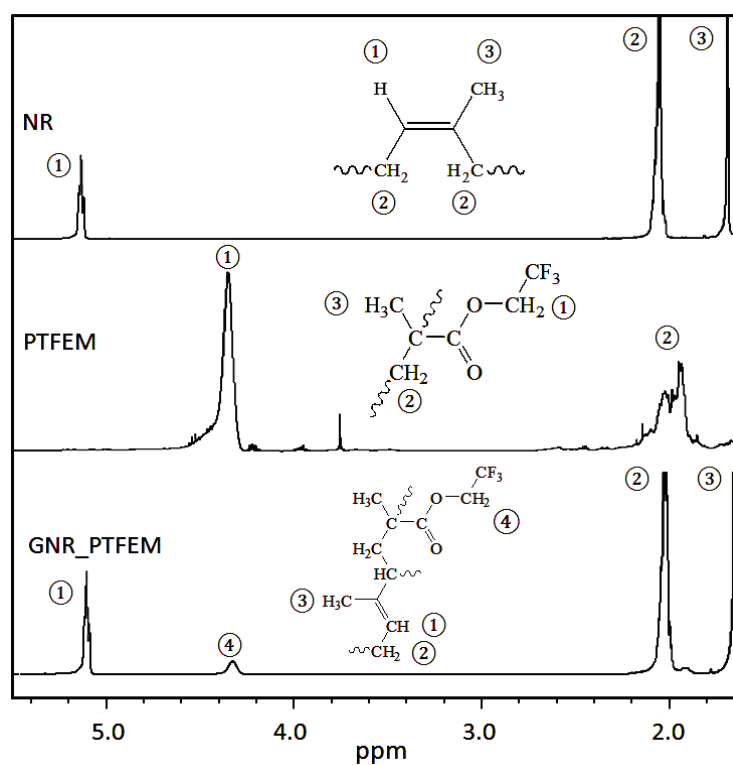


Figure 4.6 ^1H -NMR spectra of NR, PTFEM and graft copolymers prepared from TFEM (GNR_TFEM).

To confirm the results in Table 4.1, the efficiency of grafting process was also exhibited in Table 4.2 with variation of TFEM content in the both reaction systems. All experiments indicated the higher %GE and the amount of grafted PTFEM onto NR backbone. Thus, the melt mixing process was selected to prepare graft copolymer of TFEM onto NR for further experiments.

Table 4.2 The graft copolymerization of TFEM onto NR via solution grafting process and melt mixing process

System	TFEM (phr)	Time (h)	%GE	Grafted PTFEM content (phr)
Solution grafting process ⁽¹⁾	10	24	0	0.00
	20	24	0.20	0.01
	30	24	0.52	0.02
	40	24	0.70	0.02
Melt Mixing process ⁽²⁾	10	0.5	0.19	0.01
	20	0.5	0.48	0.05
	30	0.5	1.02	0.18
	40	0.5	1.34	0.26

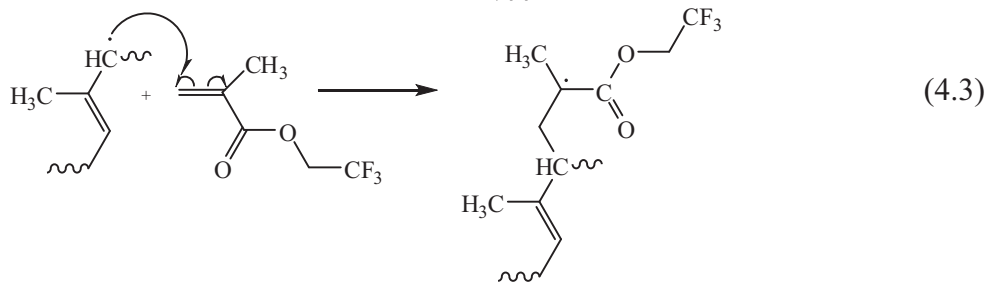
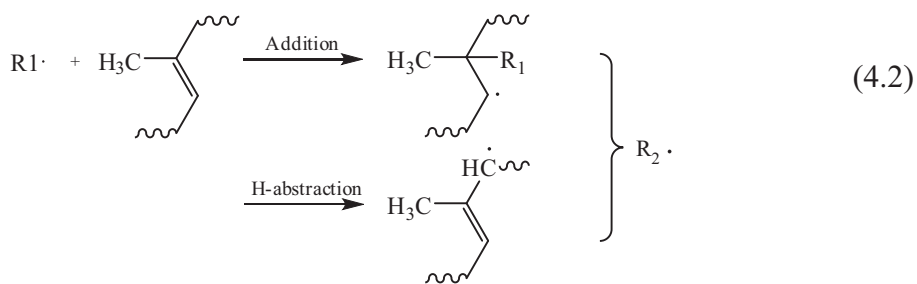
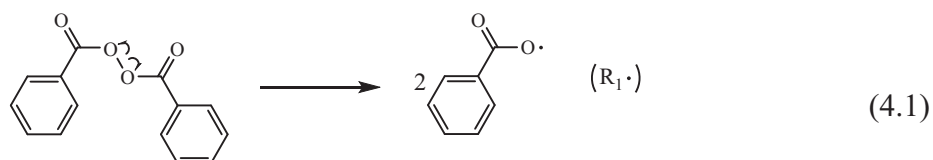
⁽¹⁾ The condition of solution grafting process: NR = 3 g, TFEM = 10-40 phr, BPO = 2 phr, THF = 150 ml at 90°C

⁽²⁾ The condition of melt mixing process: NR = 20 g, TFEM = 10-40 phr, BPO = 2 phr at 90°C

4.1.2 Graft copolymerization mechanism of TFEM onto NR backbone

The graft copolymerization for NR with TFEM was prepared by free radical grafting copolymerization. The grafting mechanism of graft copolymerizations of NR with TFEM could be proposed as shown in Eq. 4.1-4.3.

The abundance of BPO radicals were generated by a hemolytic thermal decomposition (Eq. 4.1). The BPO radical ($R_1\cdot$) then attached to the NR backbone by addition or abstraction of an allylic hydrogen atom from NR to produce polyisoprenyl radicals ($R_2\cdot$) as the reactive sites (Eq. 4.2). For graft copolymerization with TFEM (Eq. 4.3), the free radicals of TFEM could be able to attach with other molecules of TFEM to promote the graft copolymer (Angnanon, Prasassarakich and Hinchiranan, 2011). Eq. 4.3 was the most important step to evaluate the grafting efficiency for graft copolymerization (Yang et al., 2012).



4.1.3 Graft copolymerization of TFEM onto NR via melt mixing process

4.1.3.1 Effect of initiator concentration

The graft copolymerization of TFEM onto NR was initiated by using BPO at 1-3 phr. The effect of BPO concentration on %monomer conversion, %grafting efficiency (%GE) and %gel of the obtained GNR was evaluated after soxhlet extraction. The reaction was performed at 20 phr of TFEM at 90°C for 30 min. The results shown in Figure 4.7 indicated that the increase in the BPO concentration enhanced the amount of free radicals, which was possible to promote the higher grafting sites for providing the %monomer conversion and %GE of the obtained GNR (Tan et al., 1999). The maximum monomer conversion at 65.1 was achieved at 3 phr of BPO concentration. Although the higher BPO concentration gave the higher amount of monomer conversion but the %GE values were very low when compared to the graft copolymerization of TFEM onto silicone rubber by using the similar process (Guo et al., 2010). This could be explained that the methyl group of NR backbone was barrier for the access of monomer onto the grafting sites (Arayaprenee, Presassarakich and Rempel, 2003).

To consider the gelation as shown in Figure 4.8, the results exhibited that the increase in the BPO concentration led the higher amount of gel inside the graft product due to the excess free radicals to promote crosslink resulting to the termination of graft copolymerization. Moreover, the product with the high %gel could not be effectively used in the preparation of the blends due to the phase separation (Nakajima, 2000).

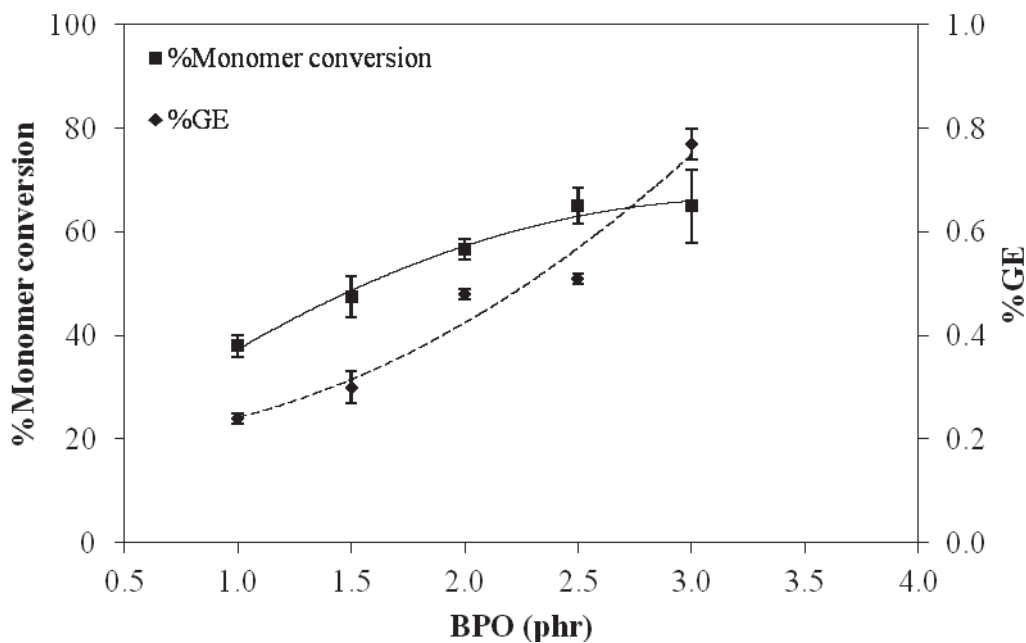


Figure 4.7 Effect of initiator concentration on %monomer conversion and %GE ([TFEM] = 20 phr, reaction time = 30 min at 90°C).

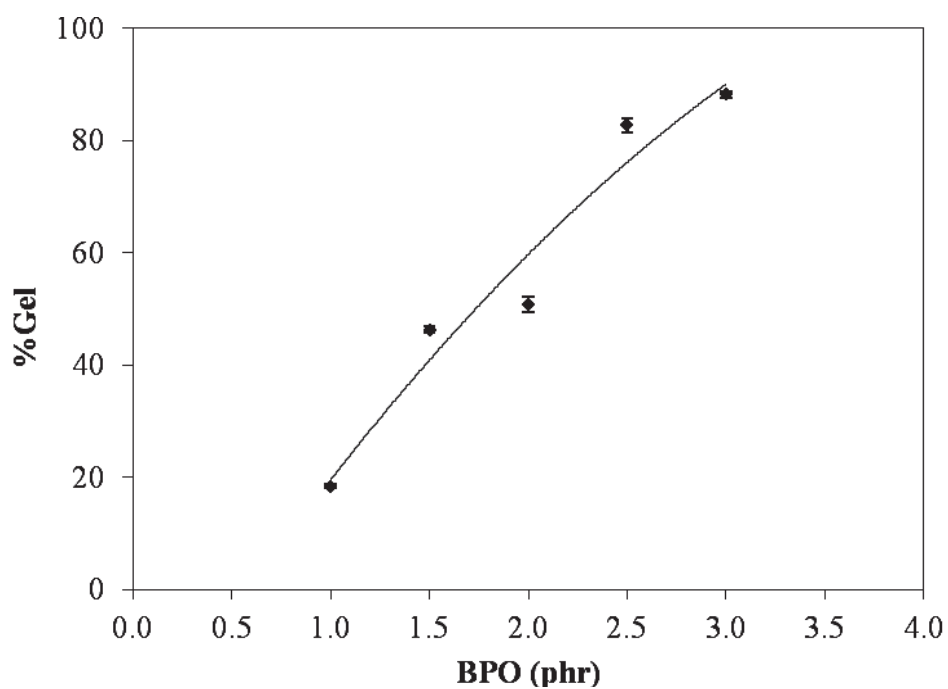


Figure 4.8 Effect of initiator concentration on %gel ([TFEM] = 20 phr, reaction time = 30 min at 90°C).

4.1.3.2 Effect of monomer concentration

The effect of monomer concentration on the %monomer conversion, %GE and %gel of the obtained GNR after soxhlet extraction was presented in Figure 4.9 and 4.10, respectively. The reaction condition was controlled at 2 phr of BPO at 90°C for 30 min. It was found that the increase in the monomer concentration in the range of 10 to 40 phr increased the %GE to 1.34 %. This means that the higher TFEM content promoted the higher possibility to be grafted onto NR backbone (Cheng, Wen and Wu, 2009). However, the increase in the TFEM concentration also induced the recombination of the abundant propagating chains and chains entanglement (Kiilay and Okay, 2002). Since some crosslinking occurred during polymerization, the branch pattern might lead the branched-branches to promote gelation (Nakajima, 2000) as shown in Figure 4.10.

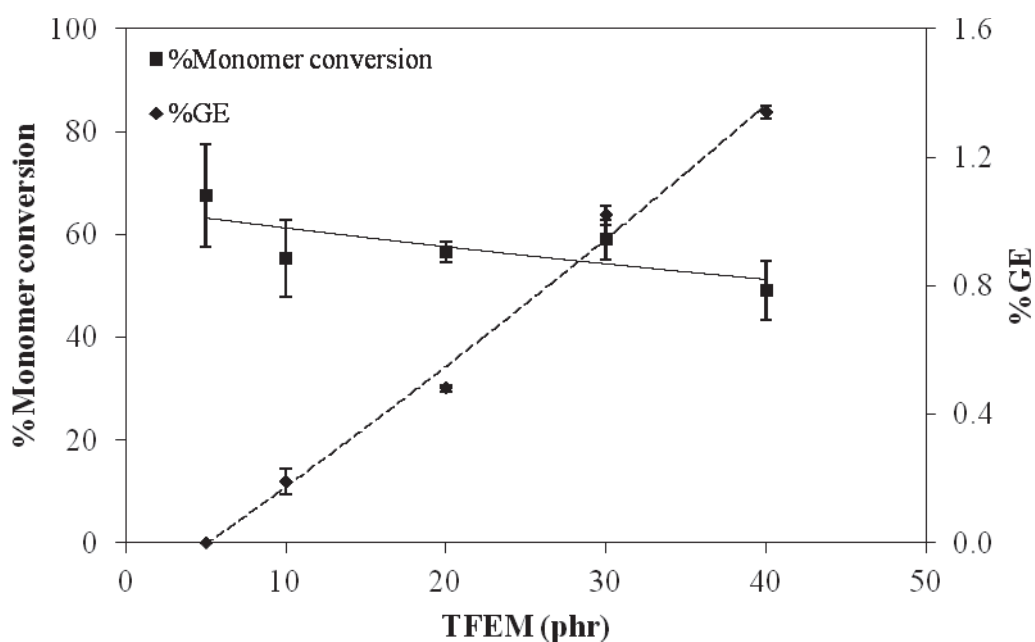


Figure 4.9 Effect of monomer concentration on %monomer conversion and %GE ([BPO] = 2 phr, reaction time = 30 min at 90°C).

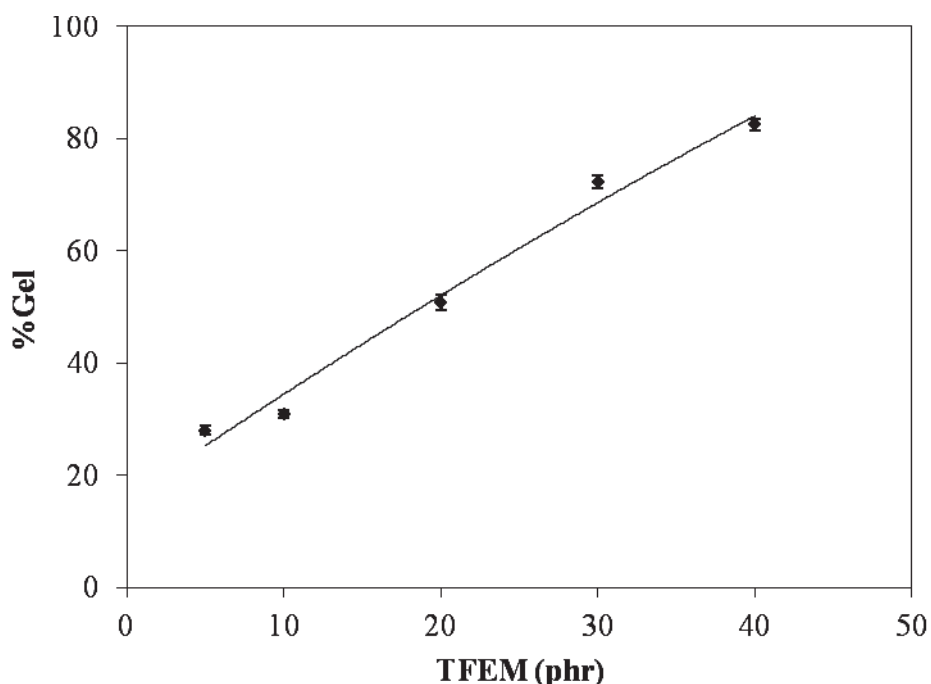


Figure 4.10 Effect of monomer concentration on %gel ([BPO] = 2 phr, reaction time = 30 min at 90°C).

4.1.3.3 Effect of reaction temperature

The effect of reaction temperature was investigated from 70 to 110°C for 30 min with 20 phr of TFEM concentration and 2 phr of BPO loading. The results in terms of the %monomer conversion, %GE and %gel were presented in Figure 4.11 and 4.12, respectively. It indicated that the enhancement of reaction temperature in the range of 70-90°C increased the %monomer conversion, %GE and %gel due to the higher amount of free radicals generated at the higher reaction temperature. The maximum %monomer conversion and %GE were found at 56.6 % and 0.48 %, respectively when the reaction temperature was 90°C. However, the increase in the reaction temperature above 90°C decreased %monomer conversion and %GE due to the thermal degradation of GNR and higher possibility to evaporate TFEM having boiling point at 101-102°C (Raihane and Ameduri, 2006). Moreover, BPO might be decomposed and degraded at high reaction temperature (Russell, 2002).

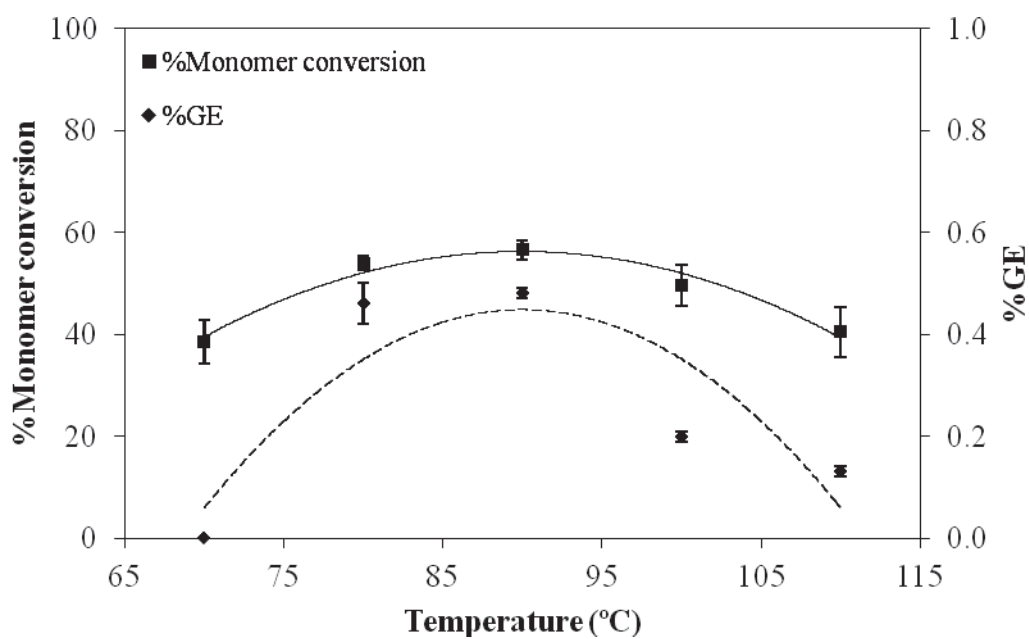


Figure 4.11 Effect of reaction temperature on %monomer conversion and %GE ([BPO] = 2 phr, [TFEM] = 20 phr, time = 30 min).

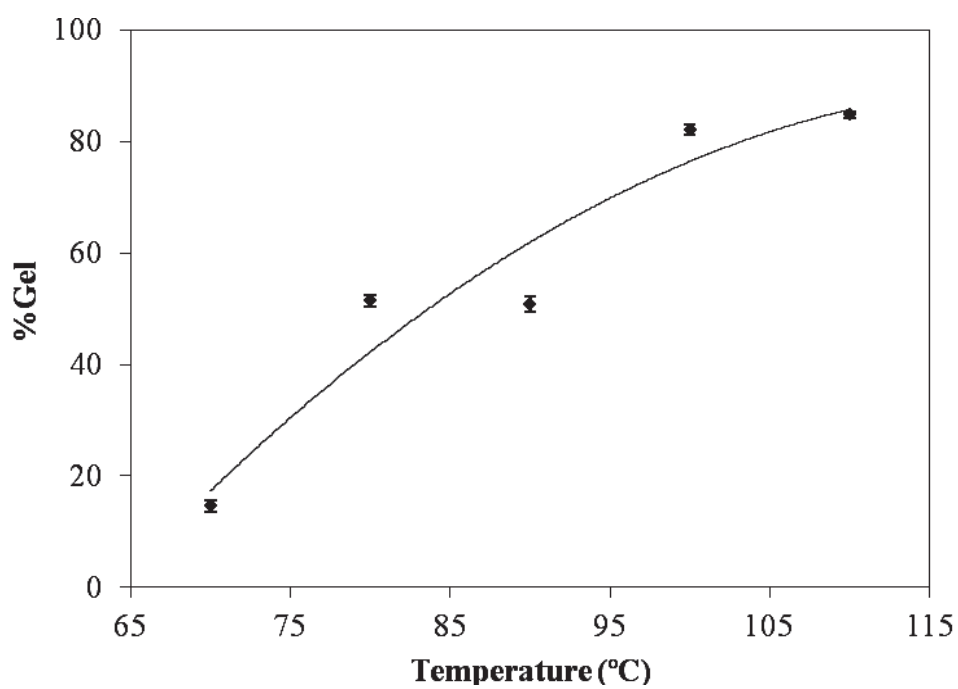


Figure 4.12 Effect of reaction temperature on %gel ([BPO] = 2 phr, [TFEM] = 20 phr, time 30 min).

4.1.3.4 Effect of reaction time

The effect of reaction time on the %monomer conversion, %GE and %gel was studied in the range of 10 – 120 min and presented in Figure 4.13 and 4.14, respectively. The reaction temperature was kept constant at 90°C with 20 phr of TFEM concentration initiated by 2 phr of BPO loading. The results indicated that the longer reaction time to 60 min slightly increased the %monomer conversion and %GE because TFEM required the long reaction time for graft copolymerization due to its low reactivity (Ameduri and Boutevin, 2000). However, the reaction time longer than 60 min decreased the %GE and the gel formation due to the side reactions during the longer mixing including homopolymerization and chain degradation (Tan et al., 1999). Moreover, The longer reaction time also increased the amount of TFEM evaporated during mixing because the melt mixing process conducted at high processing temperature (Yang et al., 2012).

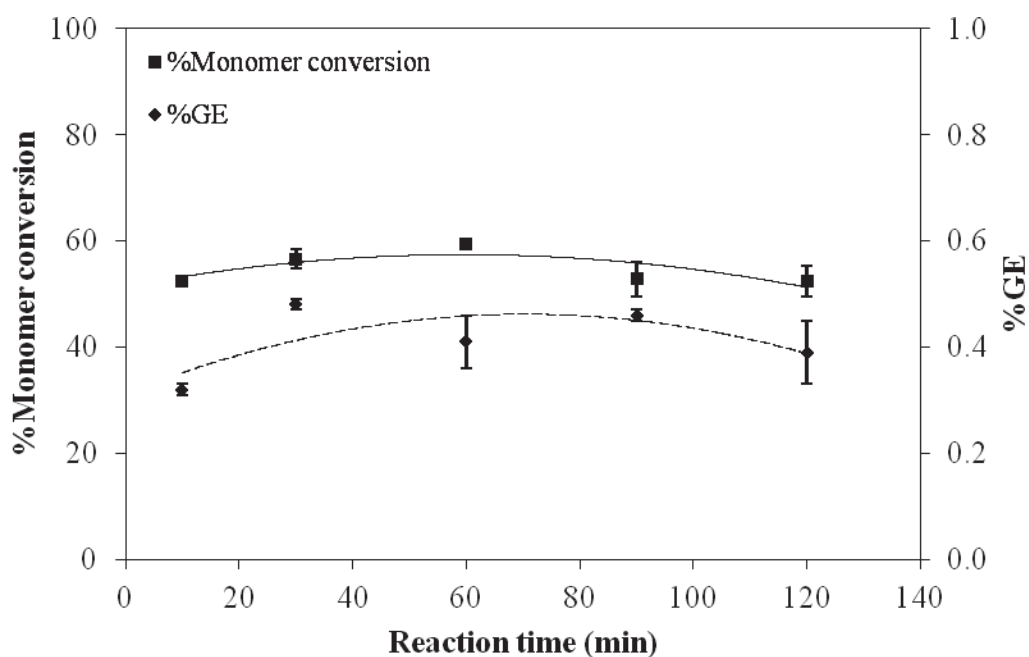


Figure 4.13 Effect of reaction time on %monomer conversion and %GE ([BPO] = 2 phr, [TFEM] = 20 phr at 90 °C).

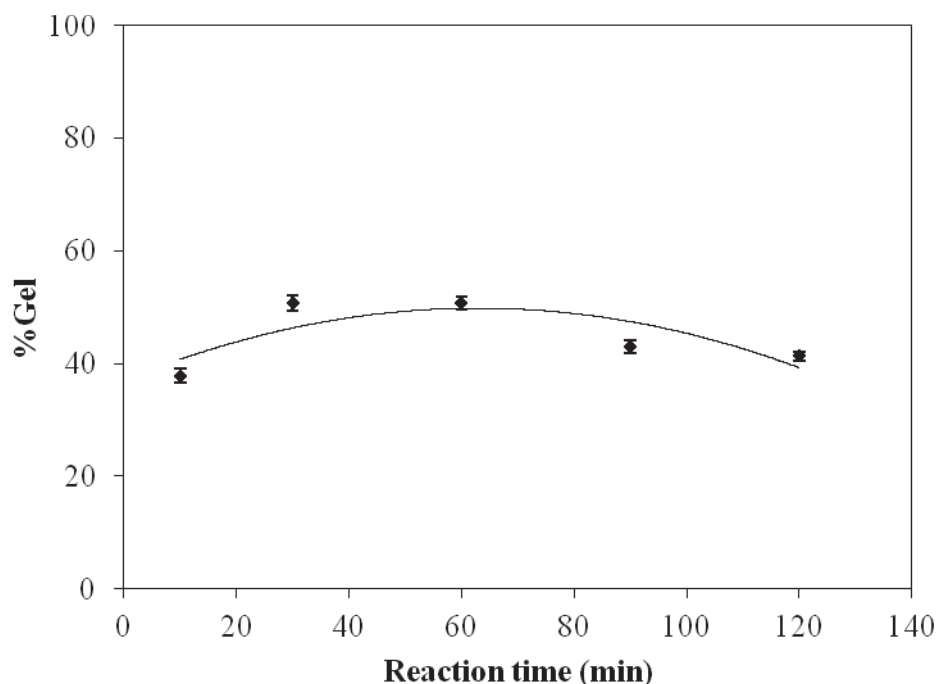


Figure 4.14 Effect of reaction time on %gel ([BPO] = 2 phr, [TFEM] = 20 phr at 90 °C).

The optimum condition of graft copolymerization of TFEM onto NR via melt mixing process was 40 phr of TFEM, 2 phr of BPO at 90°C for 24 h to obtain 1.34 %GE and 82.5 %gel. When the amount of the TFEM loading was overdose, it could induce in the formation of graft copolymers with long grafting chains or the highly gel formation. However, the compatibilizers with high gel formation are not well distributed along two immiscible polymers because of high viscosity and then the poor properties of final product were occurred (Kim et al., 1999). Thus, the GNR obtained from the reaction with 20 phr of TFEM, 2 phr of BPO at 90°C for 30 min was suitable for using as the compatibilizer due to the lower %gel (50.8%) with 0.48 %GE.

4.2 NR/FKM vulcanization

4.2.1 Selection of vulcanization system

Not only the polymeric components affect the properties of blends, but the vulcanization system is also the important factor to assign the performance of the finishing elastomeric blends. Generally, there are two main types of vulcanization system applied for the general elastomers: peroxide and sulfur vulcanization (Siririnha, Phoowakeereewiwat and Saeoui, 2004). For the special elastomers such as fluocarbon elastomers or FKM, they require the specific curing system (Kader and Bhomwick, 2002). Thus, the blending of FKM and NR to provide the cost reduction and improvement of low temperature properties of FKM needed to use the compatibilizer and the adjustment of curing system to reduce the poor properties suffering from phase separation (Wang et al., 2009).

Since the general vulcanization for NR and FKM is sulfur and diamine curing system, respectively, Table 4.3 shows the effect of vulcanization systems on the curing characteristics monitored by using MDR for each rubber. The results indicated that the maximum torques of NR vulcanized by sulfur and FKM vulcanized by diamine showed the highest values at 8.36 and 14.4 dN·m, respectively indicating the crosslink formation during vulcanization. However, the switch of vulcanization system between these rubbers exhibited the low maximum torques and long optimum cure time possibly due to the low crosslink density generated during vulcanization. This implied that both sulfur and diamine vulcanization systems could not be applied for the vulcanization of NR/FKM blends.

To consider the use of peroxide for curing, this system can be used to vulcanize NR for producing products with the good aging resistance (Morrell, 1982). Normally, dicumyl peroxide (DCP) is used as curing agent for peroxide vulcanization of saturated elastomers such as ethylene-propylene diene rubber (EPDM and EPM) and silicone rubber (MVQ). It has also been applied for curing FKM (Ni et al., 2010) and silicone/FKM blends (Guo et al., 2010 and 2012). The peroxide vulcanization system used for vulcanized NR/FKM (20/b0 (w/w)) was consisted of DCP acting as the curing agent cooperated with MgO, Ca(OH)₂ and TAIC. MgO and Ca(OH)₂ were

used as the acid accepters for FKM vulcanization to absorb the hydrofluoric acid (HF) formed during the process, whilst; TAIC played as the co-agent for peroxide curing process of FKM (Taguet, Ameduri and Boutevin, 2005). The results in Table 4.3 and Figure 4.15 exhibited that the peroxide vulcanization was appropriate system for curing NR/FKM blends due to the high value of maximum torques indicating the crosslink formation possibly generated in NR, FKM and their blend.

Table 4.3 The cure characteristics of NR, FKM and NR/FKM vulcanizates

Vulcanization system	Rubber	Minimum torque (dN·m)	Maximum torque (dN·m)	Scorch time (T _s , min)	Optimum cure time (T _{c90} , min)
Sulfur ⁽²⁾	NR	0.20	8.36	2.43	3.35
	FKM	0.86	0.89	n/a ⁽¹⁾	19.0
Diamine ⁽³⁾	NR	0.59	0.07	n/a	24.5
	FKM	1.43	14.4	1.60	12.3
Peroxide ⁽⁴⁾	NR	0.33	5.43	6.46	24.6
	FKM	1.12	2.12	0.53	8.32
	NR/FKM	0.70	4.40	8.02	21.5

⁽¹⁾ Could not be analyzed

⁽²⁾ Sulfur vulcanization: ZnO = 5 phr, steric acid = 1.5 phr, S = 2.5 phr, TMTD = 0.5 phr, CBS = 1 phr cured at 155°C

⁽³⁾ Diamine vulcanization: Ca(OH)₂ = 7.2 phr, MgO = 3.6 phr, DIAK#1 = 5 phr cured at 155 °C

⁽⁴⁾ Peroxide vulcanization: MgO = 2.4 phr, Ca(OH)₂ = 4.8 phr, DCP = 1.5 phr, TAIC = 0.6 phr cured at 155 °C.

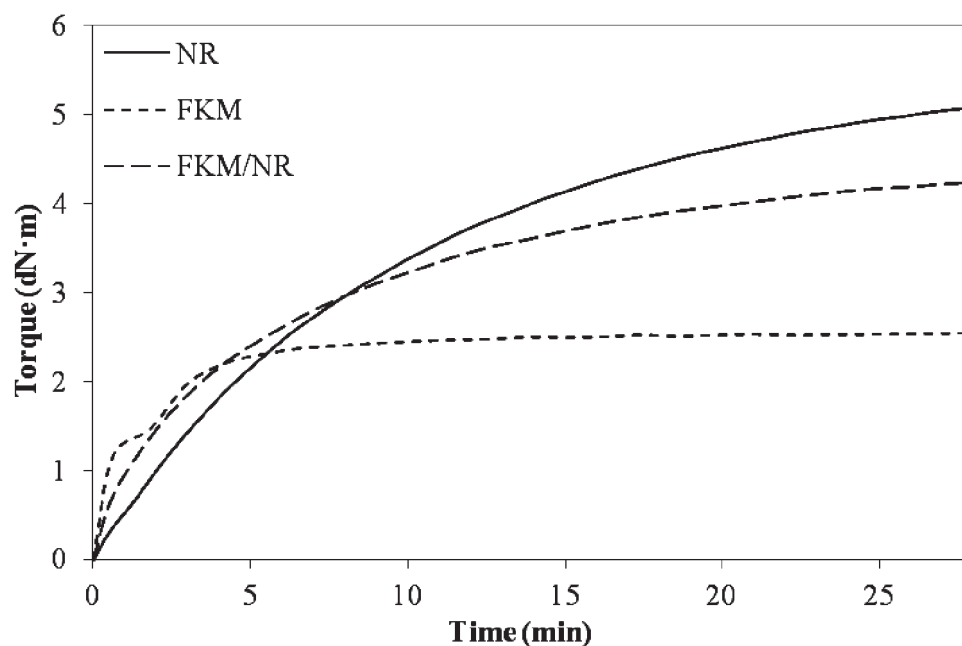


Figure 4.15 Cure characteristics of NR, FKM and NR/FKM blends cured by peroxide system at 155°C.

4.2.2 Effect of GNR on curing characteristics of NR/FKM

This section studied the effect of the addition of GNR produced from graft copolymerization of TFEM onto NR (0.05 phr of PTFEM, 0.48 %GE and 50.8 %gel) on the cure characteristics of NR/FKM blends (20/80 (w/w)) vulcanized by peroxide vulvanization system obtained from the previous section. The amount of GNR in the blends was varied in the range of 3-20 phr. Table 4.4 and Figure 4.16 indicated that the increase in the amount of GNR insignificantly affected the scorch time and the optimum cure time of the blends. However, the increasing of GNR content decreased the minimum torque of the blends due to the higher NR portion. It implied that the processability of the blends was improved (Ismail and Hairunezam, 2001). Moreover, the increasing of GNR up to 9 phr increased the maximum torque. This means that the addition of GNR promoted the crosslink density of NR/FKM blends. Since the GNR compatibilizer might reduce the interfacial energy between NR and FKM phases to obtain finer dispersion during mixing (Ismail and Hairunezam, 2001).

Table 4.4 The effect of GNR content on cure characteristics of the NR/FKM blends cured by peroxide system at 155°C

Rubbers	GNR (phr)	Minimum torque (dN·m)	Maximum torque (dN·m)	Scorch time (min)	Cure time (min)
NR/FKM	0	0.71	4.42	8.02	21.5
	3	0.72	4.85	7.27	22.4
	9	0.60	4.94	6.89	20.7
	15	0.53	4.65	7.82	20.8
	20	0.35	4.62	7.06	21.3

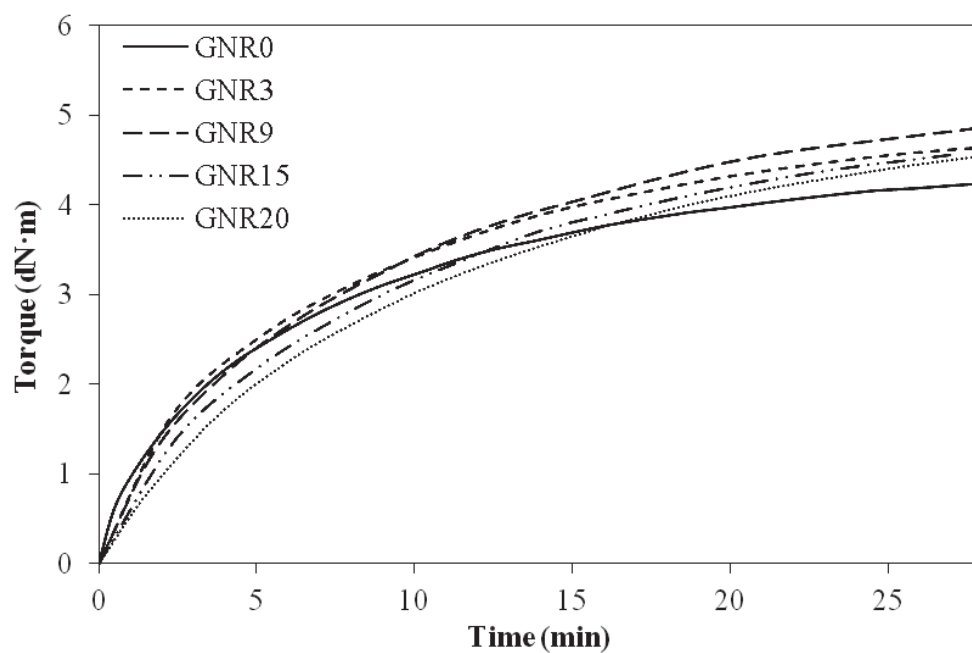


Figure 4.16 Effect of GNR on the rheology characteristics of NR/FKM blends cured by peroxide system at 155°C.

4.2.3 Effect of GNR on glass transition temperature of NR/FKM vulcanizates

The glass transition temperature (T_g) evaluated by different scanning calorimetry (DSC) of NR, poly (2,2,2-trifluoroethyl methacrylate) (PTFEM) and GNR at various amounts of grafted PTFEM prepared by the variation of TFEM loading in the range of 10 to 40 phr was shown and summarized in Figure 4.17 and Table 4.5. The results indicated that NR had T_g value at -62.7 °C, whilst; PTFEM had T_g at 13.2 °C. This indicated that the structure of PTFEM had more rigidity due to the higher interchain interaction with the presence of C-F bonds (Ameduri and Boutevin, 2000). When NR was grafted by PTFEM, the obtained GNR exhibited two region of T_g : -62.7 to -60 °C and 17 to 20 °C. The lower region was attributed to NR segment and the higher region was for PTFEM segment grafted onto NR backbone. It could be observed that the graft copolymerization increased T_g value for both segments indicating the higher rigidity or difficulty for chain movement resulting from the higher crosslink or gel formation during graft copolymerization. (Nakasorn, Kaesuman and Supasanthitikon, 2004).

For the rubber vulcanizates, DSC technique could be applied to monitor the miscibility of the constituents in the blend. The results in Figure 4.18 and Table 4.6 showed the T_g of NR and FKM vulcanizates at -63.3 and -22.6 °C, respectively. The T_g values for NR and FKM in the NR/FKM vulcanizate without the addition of GNR (0.05 phr of PTFEM, 0.48 %GE and 50.8 %gel) were insignificantly changed indicating the immiscibility of two rubber constituents in the blend. However, the addition of GNR slightly increased T_g values of both phases. This was possible that the addition of GNR enhanced the compatibility which was advantage for vulcanization to provide the stronger bonding in the blends.

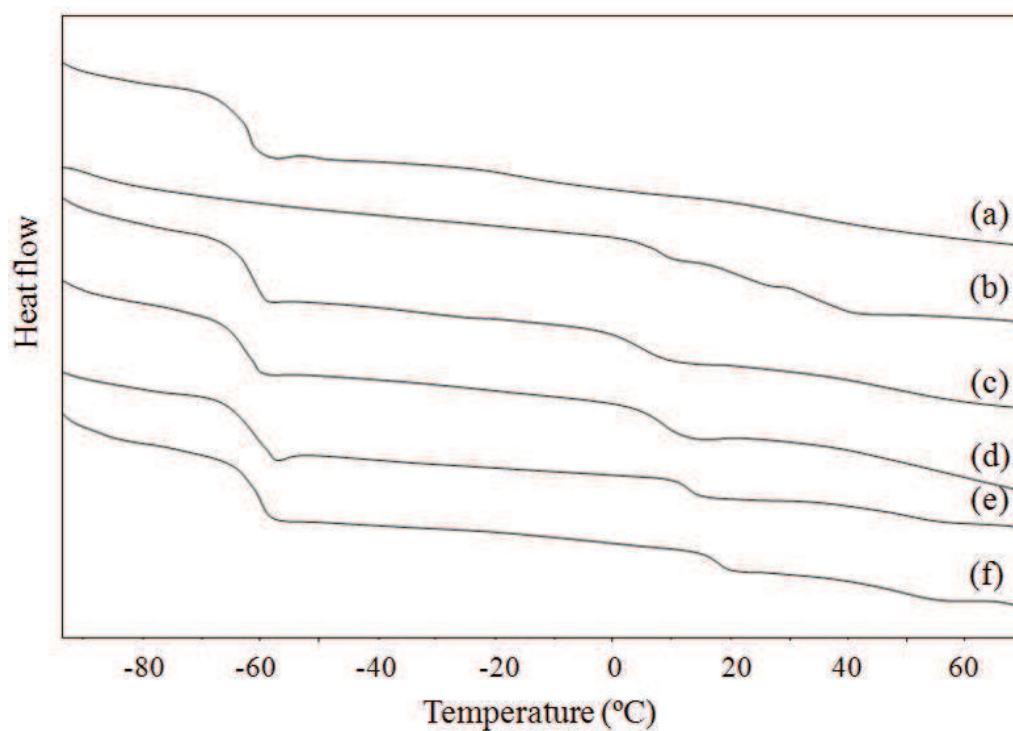


Figure 4.17 DSC thermograms of (a) NR, (b) PTFEM and GNR containing various grafted PTFEM contents: (c) 0.01 phr, (d) 0.05 phr, (e) 0.18 phr and (f) 0.26 phr.

Table 4.5 Glass transition temperatures of NR, PTFEM and GNR at various grafted PTFEM content

Sample	Grafted PTFEM content (phr)	%Gel	T_g (°C)	
			NR segment	PTFEM segment
PTFEM	-	-	-	13.2
NR	-	36.6	-62.7	-
GNR	0.01	38.4	-61.4	12.3
	0.05	49.8	-60.5	18.4
	0.18	74.3	-61.9	17.8
	0.26	81.5	-62.2	19.4

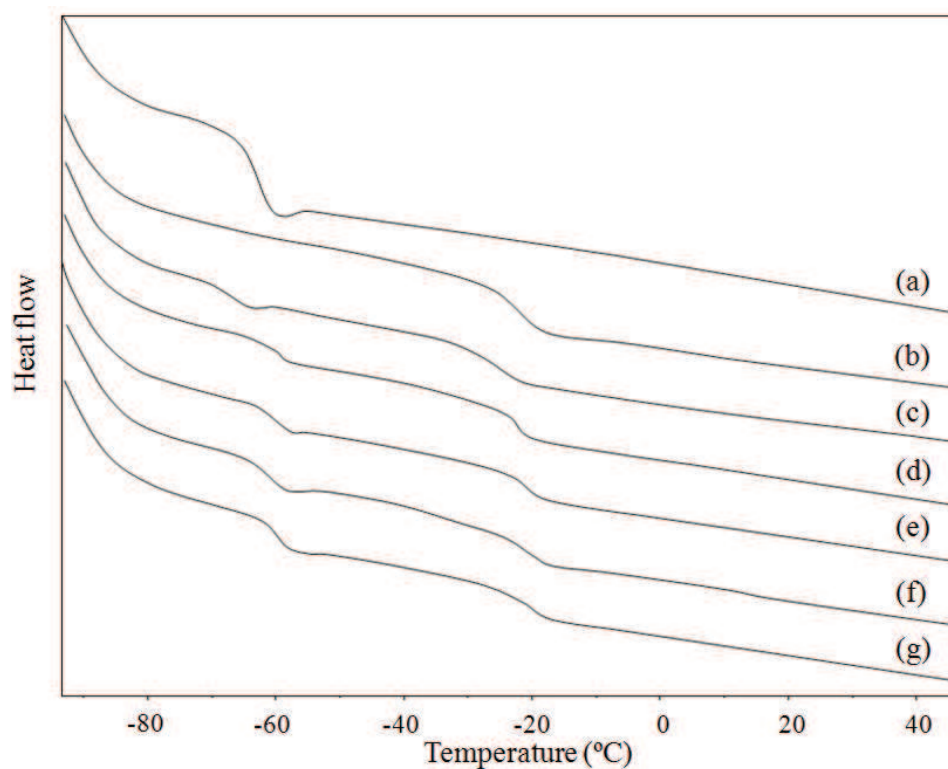


Figure 4.18 DSC thermograms of (a) NR, (b) FKM and NR/FKM vulcanizates (c) without GNR, (d) with 3 phr of GNR, (e) with 9 phr of GNR, (f) with 15 phr of GNR and (g) 20 phr of GNR (0.05 phr of PTFEM, 0.48 %GE and 50.8 %gel).

Table 4.6 Glass transition temperatures of NR, FKM and NR/FKM vulcanizates with and without the addition of GNR

Vulcanizate	GNR content (phr)	T _g (°C)	
		NR phase	FKM phase
NR	-	-63.3	-
FKM	-	-	-22.6
NR/FKM vulcanizate	0	-63.6	-22.8
	3	-60.0	-22.1
	9	-63.0	-22.5
	15	-62.7	-21.8
	20	-61.8	-21.5

4.2.4 Effect of GNR on mechanical properties, thermal stability and morphology of NR/FKM vulcanizates

The mechanical properties in terms of tensile strength, ultimate elongation and hardness of NR/FKM vulcanizates (20/80 (w/w)) with and without compatibilized by using GNR (0.05 phr of grafted PTFEM, 0.48 %GE and 50.8 %gel) were evaluated as shown in Table 4.7. The thermal stability of these vulcanizates was also investigated by thermal aging at 100°C for 24 h. The results were compared to those of NR and FKM vulcanized by using the similar peroxide curing system. The results indicated that NR and FKM vulcanizates cured by peroxide had tensile strength 2.52 and 1.46 MPa with 548 % and 907 % of ultimate elongation respectively indicating that FKM vulcanizates had lower crosslink density than NR. For NR/FKM vulcanizates, it could be noticed that the incompatibilized NR/FKM vulcanizates still showed the low value of tensile strength (1.87 MPa) with high ultimate elongation (747 %). The tensile fracture surface of this vulcanizates examined by SEM as shown in Figure 4.19a exhibited the heterogeneity of the blend providing the low mechanical properties.

For the use of GNR as the compatibilizer, the addition of GNR in the range of 3-15 phr could enhance the tensile strength from 1.87 to 9.93 MPa. Moreover, the ultimate elongation also decreased from 747 % to 632 % with the higher hardness values from 55 to 59. This implied that the addition of GNR promoted higher compatibility between NR and FKM phases in the NR/FKM vulcanizates.

Table 4.7 Mechanical properties and thermal stability of NR, FKM and NR/FKM vulcanizates compatibilized by using GNR

Vulcanizates	GNR (phr)	Tensile strength (MPa)		Ultimate elongation (%)		Hardness	
		Before aging	%Retention	Before aging	%Retention	Before aging	%Retention
NR	-	2.52 (0.1) ⁽¹⁾	N/A ⁽²⁾	548 (5.3)	N/A	32.7 (2.5)	N/A
FKM	-	1.46 (0.1)	106	907 (89)	101	31.5 (6.4)	195
NR/FKM	0	1.87 (0.2)	111	747 (1.8)	78.0	55.3 (0.6)	118
	3	3.49 (0.2)	84.2	606 (36)	108	59.3 (1.5)	113
	9	7.12 (0.6)	82.7	655 (36)	99.2	57.3 (2.0)	109
	15	9.93 (0.2)	58.1	632 (28)	113	59.0 (2.7)	97.2
	20	7.53 (0.4)	56.5	714 (66)	113	51.7 (5.0)	98.0

⁽¹⁾ The standard deviation is in the parenthesis.

⁽²⁾ Could not be analyzed.

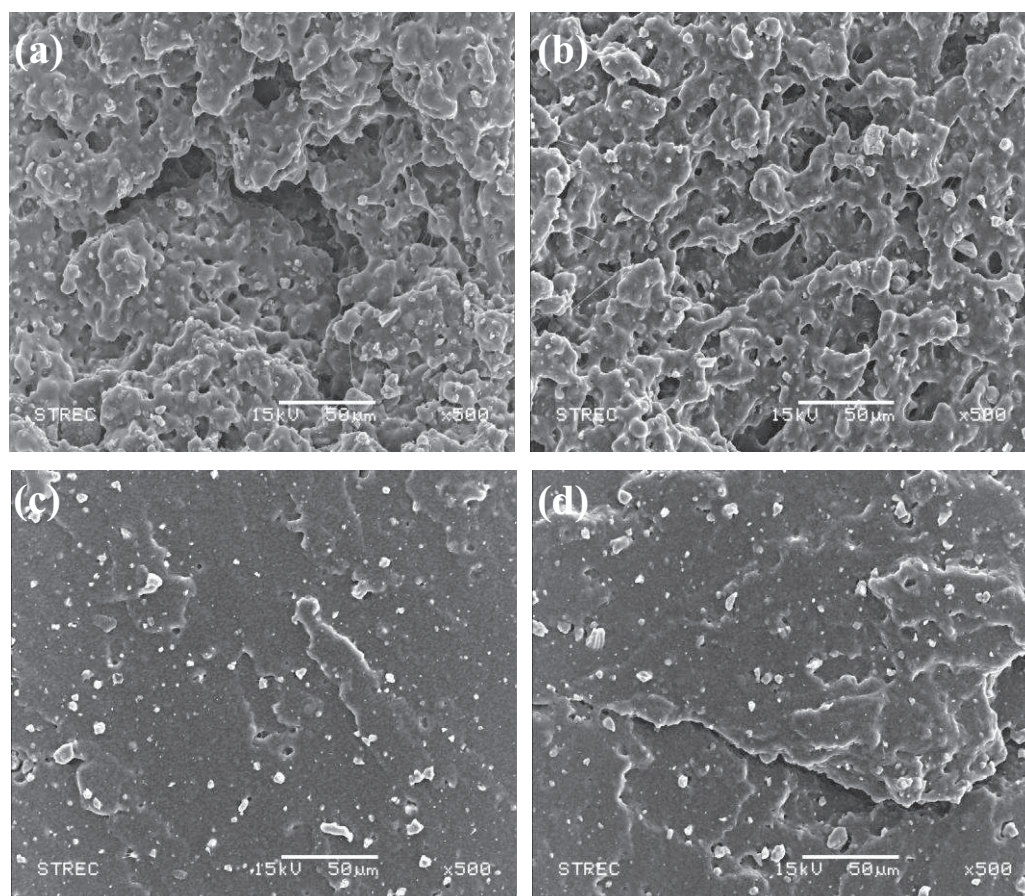


Figure 4.19 SEM micrographs of NR/FKM vulcanizates (a) without GNR, (b) with 3 phr of GNR, (c) with 15 phr of GNR, (d) with 20 phr of GNR.

The SEM micrographs shown in Figure 4.19b and 4.19c also exhibited the higher homogeneity resulting from the higher GNR content from 3 and 15 phr. This was possible that the CF_3 bonds in GNR might reduce the interfacial tension and improve the adhesion between rubber constituent phases (Guo et al., 2010). However, the high loading of GNR above 15 phr caused the reduction of tensile strength and hardness values with higher ultimate elongation. The excess GNR also increased the heterogeneity of NR/FKM vulcanizates as shown in Figure 4.19d due to the imbalance of polarity to provide the formation of phase separation (Angnanon, Prasassarakich and Hinchiranan, 2011).

To consider the thermal stability of NR, FKM and NR/FKM vulcanizates, the results in Table 4.5 showed that the thermal aging process could slightly enhance the tensile strength from 1.46 to 1.55 MPa, the ultimate elongation from 907 % to 916 % and the hardness from 31.5 to 61.5 possibly due to the completion for vulcanization of FKM (Kader and Bhowmick, 2003). However, it was observed that NR was melted after aged at 100°C for 24 h due to its low thermal stability (Derouet et al., 2009). For NR/FKM vulcanizates, the incompatibilized NR/FKM vulcanizate showed the slightly higher tensile strength and hardness with lower ultimate elongation after aging process. This was possible that the thermal aging could improve the mechanical properties of the incompatibilized NR/FKM vulcanizate. The addition of GNR in the range of 3-9 phr could retain the mechanical properties of the NR/FKM vulcanizates. However, the overdose of GNR decreased thermal stability of the NR/FKM vulcanizates. The low retention for tensile strength and higher ultimate elongation indicated lower crosslink density. This could be explained that the excessive addition of GNR induced higher content of low aging resistance NR into the NR/FKM vulcanizates. This might be degraded by chain scission under long term heating (Radhakrishnan, Alex and Unnikrishnan, 2006).

4.2.5 Effect of GNR on oil resistance of NR/FKM vulcanizates

The polar elastomers are generally used for petroleum-based industries since they have high resistance to swelling in the presence of hydrocarbon oils. The general elastomers serving for this activity is nitrile rubber (NBR), chloroprene rubber (CR), acrylate rubber (ACM), hydrogenated NBR (HNBR) and ethylene propylene rubber (EPDM) (Duin and Dikland, 2007).

Nowadays, the alternative liquid fuel named, “gasohol” has become more interesting for the replacement of gasoline used in the transportation due the depletion of the fossil fuels. The presence of alcohol in gasohol enhances the polarity of the oil. Thus, the special elastomers with the higher oil resistance were required to apply for fuel transmission lines and engine parts. From this purpose, FKM is an excellent choice among the general other rubbers (Hazeeb et al., 2011). However, the cost of using only FKM is very expensive. Thus, the preparation of NR/FKM vulcanizates (20/80 (w/w)) compatibilized with using GNR was expected to obtain the resulting product containing both desirable properties with reasonable price. The resistance to gasohol containing 20 % (w/w) (E20) and 85 % (w/w) (E85) of NR, FKM, NR/FKM vulcanizates with and without the compatibilizer were summarized in Table 4.8. The results indicated that NR showed the poor resistance to gasohol E20 (227 %swelling) but FKM had the excellent resistance to E20 (9.60 %swelling). The incompatibilized NR/FKM vulcanizate showed the improved resistance to gasohol E20 (43.4 %swelling). However, this vulcanizate exhibited the low mechanical properties due to the incompatibility of the blend. Although the addition of GNR as the compatibilizer in the range of 3-20 phr could enhance the mechanical properties, the increase in GNR decreased the resistance to gasohol E20 of vulcanizates due to the higher NR portion. However, the compatibilized NR/FKM vulcanizates containing GNR content in the range of 3- 15 phr exhibited the better resistance to gasohol E85 with the higher polarity than gasohol E20. Thus, it was implied that the compatibilized NR/FKM vulcanizates by using GNR might be appropriate for the parts required to be used in the presence of pure alcohol or liquid fuels containing high alcohol content.

Table 4.8 Oil resistance of NR, FKM and NR/FKM vulcanizates in the presence of gasohol E20 and E85

Vulcanizate	GNR content (phr)	%Swelling at 25°C	
		E20	E85
NR	-	227 (2.6)*	11.0 (0.8)
FKM	-	9.60 (2.0)	11.0 (2.4)
NR/FKM (20/80 (w/w))	-	43.4 (1.7)	7.53 (1.3)
	3	53.7 (2.1)	6.57 (0.6)
	9	73.7 (1.9)	6.90 (1.0)
	15	95.0 (1.2)	7.17 (1.2)
	20	116 (1.6)	8.35 (0.4)

*The standard deviation is in the parenthesis.

CHAPTER V

CONCLUSION AND RECOMMENDATION

5.1 Conclusions

5.1.1 Selection of fluorine containing monomer and grafting process

The graft copolymerization of fluorine containing monomers: 2,3,4,5,6-pentafluorostyrene (PFS) and 2,2,2-trifluoroethyl methacrylate (TFEM) onto natural rubber (NR) was prepared by melt mixing and solution grafting processes. The results indicated that TFEM was effectively grafted onto NR due to the higher reactivity. The melt mixing process also yielded products with the higher %GE and the amount of grafted fluorine containing monomer. Thus, the graft copolymerization of TFEM onto NR via melt mixing process was selected to prepare the graft copolymer to be used as the compatibilizer for NR/FKM vulcanizates.

5.1.2 Graft copolymerization of NR with TFEM via melt mixing process

The graft copolymerization of TFEM onto NR via melt mixing process with 40 phr of TFEM, 2 phr of BPO at 90°C for 30 min yielded the maximum level of grafting efficiency as 1.34% with the 0.26 phr of grafted PTFEM. However, this condition promoted the gel formation due to the difficulty for processing of polymer with high gel content, the GNR used for further experiment was prepared by using 20 phr of TFEM, 2 phr of BPO at 90°C for 30 min to obtain the graft product with 0.48 %GE and 0.05 phr of grafted PTFEM with 50.8 %gel.

5.1.3 The preparation of compatibilized NR/FKM vulcanizates

NR/FKM vulcanizates could be effectively prepared by using the peroxide vulcanization system. The GNR was applied as the compatibilizer to promote the compatibilities of NR/FKM vulcanizates (20/80 (w/w)). The results indicated that the incorporation of GNR in NR/FKM vulcanizates did not affect the scorch time and the optimum cure time but improved the processability and the crosslink density of the vulcanizates. The mechanical properties of NR/FKM vulcanizates improved by the introducing of GNR at 15 phr due to the highest compatibility of the two rubber phases. The smoother tensile fracture surface of compatibilized NR/FKM vulcanizate with the increasing of GNR loading up to 15 phr were observed. The thermal properties of NR/FKM vulcanizates indicated that the addition of GNR slightly increased T_g values of both phases due to the strong interaction in the vulcanizates. It was possible that the compatibility of the vulcanizates was promoted. For the oil resistance, the compatibilized NR/FKM vulcanizates had higher resistance to gasohol E85 than E20. This implied that these vulcanizates were appropriated for liquid fuel containing high alcohol content.

5.2 Recommendations

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

- Graft copolymerization of other fluorine containing monomers onto NR should be explored to obtain the graft copolymer with various properties for further applications.
- The graft copolymerization of fluorine containing monomer should be induced by others power resources such as microwave in order to increase the level of grafting efficiency.

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APPENDICES

APPENDIX A

Overall composition of rubbers and monomers

Table A-1 Properties of natural rubber (STR- 5L)

Properties	Content (%)
Dirt	0.04
Ash	0.40
Nitrogen	0.60
Volatil matter	0.80
Initial plasticity	35.0
Plasticity retention index	60.0
Color (Lovibone unit)	6.00

Table A-2 Properties of fluoroelastomer (VITON B70N)

Properties	Reported values
Max condition service temperature (°C)	204
Glass transition temperature (°C)	-30, -17
Tensile strength (MPa)	20
Hardness	55-95

Table A-3 Properties of 2,3,4,5,6-pentafluorostyrene (PFS)

Properties	Reported values
Molecular weight (g/mol)	194.1
Boiling point (°C)	140
Density at 25 °C (g/ml)	1.406
Flash point in closed cup (°C)	34

Table A-4 Properties of 2,2,2-trifluoroethyl methacrylate (TFEM)

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

APPENDIX B

Calculation

B.1. Calculation of grafted fluorinated monomer content and %GE

The amount of grafted fluorine containing monomer in GNR can be determined by using the $^1\text{H-NMR}$ of GNR as shown in Figure B-1. The grafted fluorinated monomer in GNR was calculated by the following equations (Oliveira et al., 2005).

$$\% \text{mol of graft PTFEM in GNR (C)} = \left[\frac{\left(\frac{S_1}{2} \right)}{\left(S_0 + \frac{S_1}{2} \right)} \right] \times 100$$

$$\% \text{mass composition of grafted PTFEM in GNR (C')} = \left[\frac{(C \times M_F)}{(C \times M_F) + ((1 - C) \times M_{NR})} \right]$$

$$\text{Grafted PTFEM (g)} = \frac{(C' \times \text{Gross GNR})}{100}$$

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

Integrated peak area at 5.1 ppm of unsaturated methylene proton of NR = S_0 .

Integrated peak area at 4.4 ppm of methylene proton of PTFEM = S_1 .

For example: $S_0 = 1.00$ and $S_1 = 0.25$

$$\% \text{molar of monomer in GNR (C)} = \left[\frac{\left(\frac{0.25}{2} \right)}{\left(1.00 + \frac{0.25}{2} \right)} \right] \times 100$$

$$= 11.1 \%$$

$$\text{Molecular weight of TFEM (M}_F) = 168.11 \text{ g/mol}$$

$$\text{Molecular weight of NR (M}_{NR}) = 68 \text{ g/mol}$$

$$\begin{aligned} \text{\%mass composition of PTFEM in GNR (C')} &= \left[\frac{(11.1 \times 168.11)}{((11.1 \times 168.11) + ((100 - 11.1) \times 68))} \right] \\ &= 0.236 \% \end{aligned}$$

$$\text{Weight of gross GNR} = 24.25$$

$$\text{Grafted PTFEM} = \frac{(0.236 \times 24.25)}{100} \text{ g}$$

$$= 0.057 \text{ g}$$

Converted The content of grafted PTFEM into phr unit

$$= \frac{(0.057 \times 100)}{20} \text{ phr}$$

$$= 0.286 \text{ phr}$$

$$\text{Weight polymer grafted} = \text{Grafted PTFEM} = 0.057 \text{ g}$$

$$\text{Weight total polymer formed} = \text{Weight of gross GNR} - \text{Weight of initial NR}$$

$$= 24.25 - 20.00$$

$$= 4.25 \text{ g}$$

$$\text{\%Grafting efficiency (\%GE)} = \frac{0.057}{4.25} \times 100$$

$$= 1.35$$

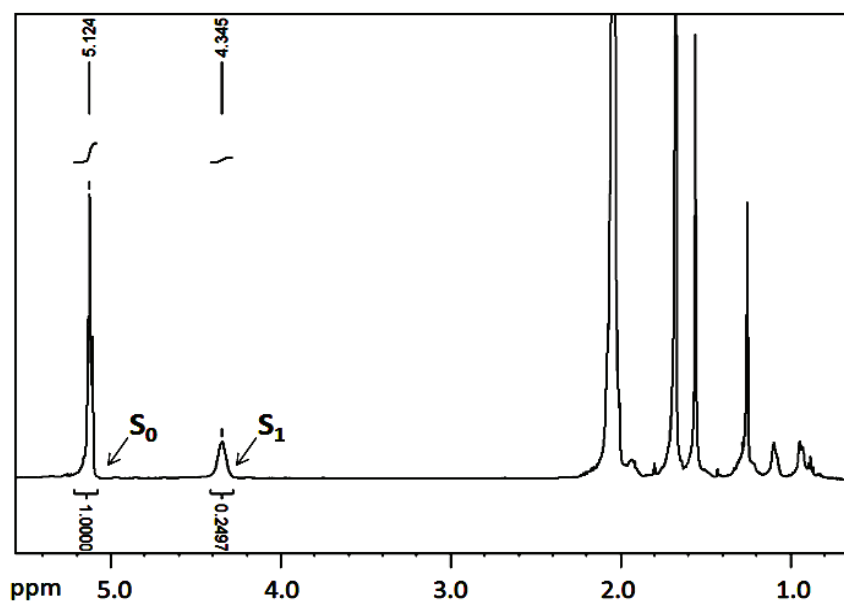


Figure B-1 ^1H NMR spectra of GNR (condition : NR 20 g, TFEM 40 phr, BPO 2 phr, Time 30 min at 90°C).

B.2. Calculation of grafting properties

For example: all obtained data from GNR

(condition : NR 20 g, TFEM 40 phr, BPO 2 phr, Time 30 min at 90°C).

Weight of NR (A)	=	20.0
Weight of TFEM charged (B)	=	8.00
Weight of obtained product (C)	=	24.2
Weight of sample (D)	=	2.75
Weight of sample after extraction with PE (E)	=	1.66
Weight of sample after extraction with acetone (F)	=	1.59

1. %Conversion

$$\begin{aligned}
 \% \text{Conversion} &= (C-A)/B \times 100 \\
 &= (24.2 - 20.0)/8.00 \times 100 \\
 &= 53.13
 \end{aligned}$$

2. %Graft natural rubber, GNR

$$\begin{aligned}
 \% \text{GNR} &= F/D \times 100 \\
 &= 1.59/2.75 \times 100 \\
 &= 57.82
 \end{aligned}$$

3. %Free NR

$$\begin{aligned}
 \% \text{Free NR} &= (D-E)/D \times 100 \\
 &= (2.75 - 1.66)/2.75 \times 100 \\
 &= 39.64
 \end{aligned}$$

4. %Free poly(2,2,2-trifluoroethyl methacrylate), PTFEM

$$\begin{aligned}
 \% \text{Free PTFEM} &= (E-F)/D \times 100 \\
 &= (1.66 - 1.59)/2.75 \times 100 \\
 &= 2.55
 \end{aligned}$$

B.3. Calculation of %gel

For example: all obtained data from GNR

(condition : NR 20 g, TFEM 40 phr, BPO 2 phr, Time 30 min at 90 °C).

Weight of 25 ml of rubber solution after drying (A)	=	0.0169
Weight of total dried solution (B)	=	0.0676
Initial weight before dissolving in the solvent (C)	=	0.4023

$$\begin{aligned}
 B &= 4A \\
 &= 4(0.0169) \\
 &= 0.0676
 \end{aligned}$$

$$\begin{aligned}
 \text{Gel}(\%) &= \frac{(C - B)}{C} \times 100 \\
 &= \frac{(0.4023 - 0.0676)}{0.4023} \times 100 \\
 &= 83.2
 \end{aligned}$$

APPENDIX C

Data of graft copolymerization

Table C-1 The effect of parameters on graft copolymerizations of TFEM on to NR via melt mixing process

Exp.	BPO (phr)	TFEM (phr)	Temperature (°C)	Time (min)	Graft product (g)	%Conv.	Grafting properties			%GE	%Gel	Grafted PTFEM (phr)
							%Grafting	%Free NR	%Homopolymer			
GNR01	1	20	90	30	21.6	39.5	83.4	15.1	1.5	0.25	18.5	0.020
	1	20	90	30	21.5	36.5	81.4	17.6	1.1	0.23	17.9	0.017
GNR02	1.5	20	90	30	22.0	50.3	82.6	16.3	1.1	0.29	46.7	0.025
	1.5	20	90	30	21.8	44.8	75.3	23.8	0.9	0.25	45.8	0.022
GNR03	2	20	90	30	22.3	58.0	73.0	25.1	1.9	0.49	49.8	0.057
	2	20	90	30	22.2	55.3	68.2	30.0	1.8	0.47	51.7	0.052
GNR04	2.5	20	90	30	22.7	67.5	68.5	30.8	0.7	0.51	83.7	0.069
	2.5	20	90	30	22.5	62.8	66.5	32.3	1.2	0.50	81.9	0.063
GNR05	3	20	90	30	22.8	70.0	76.3	20.1	3.6	0.75	87.9	0.105
	3	20	90	30	22.4	60.0	75.0	20.4	4.6	0.79	88.7	0.095
GNR06	2	5	90	30	20.8	75.0	83.2	14.2	2.6	0	28.5	0
	2	5	90	30	20.6	60.0	81.4	15.5	3.1	0	27.4	0
GNR07	2	10	90	30	21.2	60.5	84.3	12.5	0.7	0.16	30.4	0.008
	2	10	90	30	21.0	50.0	81.0	18.4	0.6	0.21	31.4	0.011
GNR08	2	30	90	30	23.4	56.3	69.2	29.7	1.1	1.04	71.5	0.168
	2	30	90	30	23.7	61.7	65.5	33.1	1.4	1.00	73.1	0.186

Table C-1 (Cont.)

Exp.	BPO (phr)	TFEM (phr)	Temperature (°C)	Time (min)	Graft product (g)	%Conv.	Grafting properties			%GE	%Gel	Grafted PTFEM (phr)
							%Grafting	%Free NR	%Homopolymer			
GNR09	2	40	90	30	24.3	53.1	62.0	35.2	2.8	1.35	83.2	0.286
GNR10	2	40	90	30	23.6	45.0	57.7	39.7	2.6	1.32	81.7	0.237
	2	20	70	30	21.4	35.5	70.8	28.5	0.7	0	13.9	0
GNR11	2	20	70	30	21.7	41.5	70.8	28.2	1.0	0	15.3	0
	2	20	80	30	22.1	53.0	75.1	22.9	2.1	0.43	50.7	0.026
GNR12	2	20	80	30	22.2	55.0	74.9	23.4	1.9	0.48	52.2	0.029
	2	20	100	30	22.1	52.5	79.3	19.7	1.1	0.20	82.7	0.021
GNR13	2	20	100	30	21.9	46.8	74.2	24.6	1.2	0.19	81.4	0.018
	2	20	110	30	21.8	44.0	65.0	33.8	1.1	0.12	84.4	0.011
GNR14	2	20	110	30	21.5	37.0	76.2	22.6	1.2	0.14	85.1	0.013
	2	20	90	10	22.1	52.0	77.5	22.1	0.6	0.31	38.7	0.036
GNR15	2	20	90	10	22.1	52.8	75.1	24.6	0.3	0.33	36.9	0.035
	2	20	90	60	22.4	59.8	79.9	19.5	0.6	0.44	49.8	0.052
GNR16	2	20	90	60	22.4	59.0	79.3	19.8	0.9	0.37	51.5	0.044
	2	20	90	90	22.2	55.0	86.4	12.3	1.3	0.45	42.1	0.050
GNR17	2	20	90	90	22.0	50.5	80.0	18.6	1.4	0.46	43.7	0.047
	2	20	90	120	22.0	50.3	82.7	13.5	3.8	0.34	41.9	0.034
	2	20	90	120	22.2	54.5	86.5	10.4	3.1	0.43	40.7	0.042

APPENDIX D

Thermal aging properties

Table D-1 The effect of thermal aging on tensile strength of NR, FKM and NR/FKM vulcanizates

vulcanizates	GNR content (phr)	Tensile strength (MPa)			
		Unaged	S.D.	Aged	S.D.
FKM	-	1.46	0.11	1.55	0.07
NR	-	2.52	0.05	-	-
GNR0	0	1.87	0.22	2.07	0
GNR3	3	3.49	0.21	2.94	0.3
GNR6	6	4.95	0.48	3.27	0.38
GNR9	9	7.12	0.61	5.89	0.05
GNR12	12	7.77	0.02	4.78	0.14
GNR15	15	9.93	0.20	5.77	0.95
GNR20	20	7.53	0.44	4.26	0.35

Table D-2 The effect of thermal aging on ultimate elongation of NR, FKM and NR/FKM vulcanizates

vulcanizates	GNR content (phr)	Ultimate elongation (%)			
		Unaged	S.D.	Aged	S.D.
FKM	-	907	88.5	916	9
NR	-	548	5.29	-	-
GNR0	0	747	1.82	583	4.84
GNR3	3	606	36.0	656	67.3
GNR6	6	674	2.81	796	8.52
GNR9	9	655	36.2	650	0.07
GNR12	12	632	16.3	728	28.4
GNR15	15	632	27.8	712	74.3
GNR20	20	714	66.1	807	126

Table D-3 The effect of thermal aging on hardness of NR, FKM and NR/FKM vulcanizates

vulcanizates	GNR content (phr)	Hardness			
		Unaged	S.D.	Aged	S.D.
FKM	-	31.5	6.36	61.5	0.71
NR	-	32.7	2.52	-	-
GNR0	0	55.3	0.58	65.0	2.00
GNR3	3	59.3	1.53	67.0	2.65
GNR6	6	56.7	2.08	59.0	1.00
GNR9	9	57.3	2.08	62.7	2.89
GNR12	12	57.3	1.15	58.7	3.79
GNR15	15	59.0	2.65	57.3	3.79
GNR20	20	51.7	5.03	50.7	3.06

APPENDIX E

Oil resistance properties

Table E-1 Weight before and after immersion in gasohol E20 and %swelling of NR, FKM and NR/FKM vulcanizates

Vulcanizates	GNR content (phr)	Weight (g)						%Swelling
		1		2		3		
		Before	After	Before	After	Before	After	
NR	-	0.63	2.04	0.68	2.23	0.56	1.84	227 (2.6)*
FKM	-	1.53	1.64	1.50	1.67	1.39	1.53	9.60 (2.0)
NR/FKM	-	1.11	1.61	1.01	1.43	1.10	1.58	43.4 (1.7)
	3	1.15	1.74	1.10	1.71	1.07	1.65	53.7 (2.1)
	6	1.13	1.87	1.12	1.86	1.11	1.80	64.6 (2.1)
	9	0.97	1.68	1.01	1.74	1.03	1.81	73.7 (1.8)
	12	1.22	2.27	1.17	2.22	1.22	2.26	87.0 (2.4)
	15	0.93	1.82	0.96	1.86	1.00	1.96	95.0 (1.2)
	20	1.21	2.64	1.18	2.55	1.19	2.56	116 (1.6)

*The standard deviation is in the parenthesis.

Table E-2 Weight before and after immersion in gasohol E85 and %swelling of NR, FKM and NR/FKM vulcanizates

Vulcanizates	GNR content (phr)	Weight (g)						%Swelling
		1		2		3		
		Before	After	Before	After	Before	After	
NR	-	0.70	0.78	0.70	0.78	0.70	0.77	11.0 (0.8)
FKM	-	1.45	1.65	1.50	1.65	1.50	1.64	11.0 (2.4)
NR/FKM	-	1.16	1.26	1.14	1.21	1.15	1.24	7.53 (1.3)
	3	1.10	1.18	1.13	1.20	1.12	1.19	6.57 (0.6)
	6	1.24	1.32	1.16	1.22	1.18	1.27	6.42 (1.2)
	9	1.02	1.10	1.00	1.07	1.05	1.11	6.90 (1.0)
	12	1.20	1.29	1.19	1.27	1.13	1.21	7.10 (0.4)
	15	1.02	1.08	1.00	1.07	1.01	1.09	7.17 (1.2)
	20	1.12	1.21	1.10	1.19	1.12	1.22	8.35 (0.4)

*The standard deviation is in the parenthesis.

VITA

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