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GRAFT COPOLYMERIZATION OF STYRENE ONTO HYDROGENATED
NATURAL RUBBER LATEX

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science

Faculty of Science

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ศิริพร สาคร : กราฟต์โคพอลิเมอร์ไฮโดรเจนของสไตรีนบนเลเทกซ์ยางธรรมชาติไฮโดรจิเนต.
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ยางธรรมชาติเป็นหนึ่งในวัสดุที่สามารถย่อยสลายได้ทางชีวภาพที่ถูกนำไปใช้ในหลายอุตสาหกรรม แต่อย่างไรก็ตามยางธรรมชาติมีความต้านทานต่อความร้อนและปฏิกิริยาออกซิเดชันต่ำ เนื่องจากมีปริมาณพันธะคู่อยู่มากในโครงสร้างจึงเป็นสาเหตุให้มีข้อจำกัดในการนำไปใช้งานในภาวะที่รุนแรง ดังนั้นโครงสร้างทางเคมีของยางธรรมชาติควรถูกปรับปรุงด้วยไฮโดรจิเนชันและกราฟต์โคพอลิเมอร์ไฮโดรเจนสำหรับการขยายขอบเขตการนำยางธรรมชาติไปใช้งาน ในงานวิจัยนี้ น้ำยางธรรมชาติถูกไฮโดรจิเนตผ่านปฏิกิริยาไดอิมิตรีคชันและจากนั้นถูกกราฟต์ด้วยสไตรีนหรือสไตรีน/เมทิลเมทาคริเลตโดยใช้ตัวริเริ่มปฏิกิริยาแบบบริดจิ้ง การรายงานการเปลี่ยนแปลงของมอนอเมอร์และสมบัติการกราฟต์เป็นฟังก์ชันของระดับไฮโดรจิเนชัน ความเข้มข้นของมอนอเมอร์และตัวริเริ่มปฏิกิริยา อุณหภูมิและเวลาในการทำปฏิกิริยา ยางธรรมชาติไฮโดรจิเนตกราฟต์ที่ได้ถูกนำไปผสมกับเรซินอะครีโลไนไทรล์-บิวทาไดอีน-สไตรีน (เอบีเอส) โดยมีอัตราส่วนระหว่างยางธรรมชาติไฮโดรจิเนตกราฟต์ต่อเอบีเอส 10/90 โดยน้ำหนัก ผลการทดลองแสดงให้เห็นว่าเอบีเอสที่มียางธรรมชาติไฮโดรจิเนตกราฟต์ด้วยสไตรีนหรือสไตรีน/เมทิลเมทาคริเลตมีความแข็งแรงต่อการค้ำโค้ง (96.9 และ 99.8 เมกกะปาสกาล) มากกว่าเอบีเอสที่ผสมยางธรรมชาติไฮโดรจิเนต (78.5 เมกกะปาสกาล) ผลการทดลองนี้ยืนยันด้วยการวิเคราะห์สัณฐานวิทยาของพื้นผิวรอยแตกด้วยกล้องจุลทรรศน์อิเล็กตรอนแบบส่องผ่านซึ่งแสดงให้เห็นความเป็นเนื้อเดียวกันและความเข้ากันได้ดีขึ้นของเอบีเอสผสมที่มียางธรรมชาติไฮโดรจิเนตกราฟต์ นอกจากนี้อุณหภูมิคล้ายแก้วของเอบีเอสลดลงเมื่อผสมยางธรรมชาติไฮโดรจิเนตกราฟต์ด้วยสไตรีนหรือยางธรรมชาติไฮโดรจิเนตกราฟต์ด้วยสไตรีนและเมทิลเมทาคริเลตซึ่งมีอุณหภูมิลายแก้วต่ำกว่าเนื่องจากมีความเป็นไปได้ที่จะเกิดความเข้ากันได้บางส่วนของยางธรรมชาติไฮโดรจิเนตกราฟต์ในภูมิภาคของเอบีเอส

สาขาวิชา...ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์...ลายมือชื่อนิสิต

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SIRIPORN SAKORN: GRAFT COPOLYMERIZATION OF STYRENE ONTO HYDROGENATED NATURAL RUBBER LATEX. ADVISOR: ASST. PROF. NAPIDA HINCHIRANAN, Ph.D., CO-ADVISOR: PROF. PATTARAPAN PRASASSARAKICH, Ph.D., 95 pp.

Natural rubber (NR), one of biodegradable materials is normally applied in many industries. However, NR has poor thermal and oxidative resistance due to its highly carbon-carbon double bonds in structure caused to limitation in severe conditions. Thus, the chemical structure of NR should be improved via hydrogenation and graft copolymerization for extending its application. In this research, the NR latex was hydrogenated via diimide reduction and then grafted with styrene (ST) or ST/methyl methacrylate (MMA) by using redox initiator. The monomer conversion and grafting properties of hydrogenated NR latex (HNRL) were reported as functions of hydrogenation level, monomer and initiator concentrations, reaction temperature and reaction time. The resulted grafted HNR (GHNR) was then blended with acrylonitrile-butadiene-styrene (ABS) resin with a ratio of GHNR/ABS=10/90 (w/w). The results indicated that the ABS containing HNR grafted with ST (GHNR(ST)) or ST/MMA (GHNR(ST/MMA)) had higher flexural strength (96.9 and 99.8 MPa, respectively) than HNR (78.5 MPa). This result confirms by using a scanning electron microscopy (SEM) of the fractural surfaces exhibited the more homogeneity and compatibility in the ABS containing grafted HNRs. Moreover, the glass transition temperature (T_g) of ABS decreased when GHNR(ST) or GHNR(ST/MMA) with lower T_g values were applied possibly due to the partial miscibility of grafted HNRs in the ABS phase.

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LIST OF ABBREVIATIONS

ABS	:	Acrylonitrile butadiene styrene
ACN	:	Acrylonitrile
CHPO	:	Cumene hydroperoxide
DMAEA	:	Dimethylaminoethyl acrylate
DRC	:	Dry rubber content
DSC	:	Differential scanning calorimetry
FT-IR	:	Fourier Transform Infrared spectroscopy
GE	:	Grafting efficiency
GHNR	:	Graft hydrogenated natural rubber
HD	:	Hydrogenation level
HNR	:	Hydrogenated natural rubber
HSNR	:	Hydrogenated skim natural rubber
INT	:	Initiator concentration
M	:	Monomer concentration
MMA	:	Methyl methacrylate
MW	:	Molecular weight
NBR	:	Nitrile-butadiene rubber
Ni	:	Nickel
NMR	:	Nuclear Magnetic Resonance spectroscopy
NR	:	Natural rubber
NR- <i>g</i> -ST	:	Natural rubber grafted with styrene
phr	:	Parts per hundred of rubber by weight
PB	:	Polybutadiene
PI	:	Polyisoprene
PMMA	:	Poly(methyl methacrylate)
PS	:	Polystyrene
PVC	:	Poly(vinylchloride)
SBR	:	Styrene-butadiene rubber
SAN	:	poly(styrene- <i>co</i> -acrylonitrile)

SDS	:	Sodium dodecyl sulfate
SEM	:	Scanning electron microscopy
SNR	:	Skim natural rubber
ST	:	Styrene
T_g	:	Glass transition temperature
T_{id}	:	Initial decomposition temperature
T_{max}	:	Maximum decomposition temperature
TBHP	:	<i>t</i> -Butyl hydroperoxide
TEPA	:	Tetraethylene pentamine
TEM	:	Transmission Electron Microscope
Temp.	:	Temperature
TGA	:	Thermogravimetry analysis
XSBR	:	Carboxylic styrene-butadiene rubber

CHAPTER I

INTRODUCTION

1.1 The statement of problem

Currently, the rising of environmental consciousness and concept of green products innovation has approached significant attention in the global. This concept concentrates on finding the methodologies and consumption of natural materials that are friendly for environment and human health. Natural rubber (NR), one of biodegradable and renewable materials, has outstanding mechanical and dynamic properties due to its ability to crystallize under stretching with high impact resilience and tear strength. It also exhibits low heat build-up property with good formability (Morton, 1973). In the rubber and plastic industries, NR is totally or partially replaced the conventional petroleum-based plastics or elastomers. However, it is deteriorated by thermal and oxidative degradation due to its unsaturated carbon-carbon double bonds in isoprene units to limit NR for outdoor application (Pruttisirikul et al., 2010; Tobing, 1988). Thus, the chemical modification of NR gives advantage to improve its properties for extending utilizations. To improve the thermal properties, hydrogenation is simple chemical modification by reducing the unsaturated carbon-carbon double bonds to enhance stability against thermal and oxidative degradation of diene-based elastomer such as acrylonitrile-butadiene rubber (NBR) (Lin, Pan and Rempel, 2004), styrene-butadiene rubber (SBR) (Sarkar, De and Bhowmick, 2000; Pan and Rempel, 2004; Singha and Sivaram, 1995) including NR (Hinchiranan, Prasassarakich and Rempel, 2006; Inoue and Nishio, 2007).

Hydrogenation of diene-base elastomers is normally performed in both polymeric solution and latex forms. According to the emphasis in the green product, the NR latex is milky colloidal. The hydrogenation via diimide reduction has been more attractive for the green process due to nonessential the organic solvent, no requirement of high cost specific equipment and precious transition metal catalysts.

Moreover, the resulting hydrogenated product is still in the latex form which is ready to be further applied in next process (Mahittikul, Prasassarakich and Rempel, 2007). The diimide reduction is the redox reaction between hydrazine hydrate (N_2H_4) and hydrogen peroxide (H_2O_2) catalyzed by metal catalyst such as boric acid (Zhuo, Bai and Wang, 2004) or copper sulfate (Mahittikul, Prasassarakich and Rempel, 2007). The hydrogenated polymers were reviewed that have excellent high thermal stability with resistance to oxygen, ozone and UV radiation.

As the hydrogenated NR (HNR) has been reported that it had better thermal stability resulting to the attempt to blend HNR with various polymers. For example, Thawornvisit, Prasassarakul, Charmondusit and Rempel (2010) reported that the addition of 1% (w/w) of HNR (56% hydrogenation) increased thermal stability and impact resistance of modified acrylic sheets. Nevertheless, HNR with higher hydrogenation level could not be applied due to difference in polarity of constituents. Normally, the blending of elastomer and plastics occurred phase separation due to the inferior interfacial tension between the component phases yielding poor mechanical properties. To increase the compatibility of HNR in the polymer blends, the graft copolymerization is a general technique to modify HNR and avoid a such problem. The graft copolymers exhibit the combination properties of polymeric backbone and grafting vinyl monomers. Thus, graft copolymers are normally applied as compatibilizers for increasing the homogeneity of the rubber and thermoplastics phase with dissimilar properties in the thermoplastic elastomers production such as NR/MMA (Thiraphattaraphum et al., 2001) or NR/PVC (Arayapranee, Prasassarakich and Rempel, 2004).

Acrylonitrile–butadiene–styrene (ABS) copolymer is one of the most common used engineering plastics containing rubber. It is widely applied in various industries due to its good mechanical properties, chemical resistance and processing advantages (Owen and Harper, 1999). ABS has three major components: acrylonitrile (ACN), styrene (ST) and polybutadiene (PB). A glassy poly(styrene-*co*-acrylonitrile) (SAN) copolymer acts as the continuous phase; whereas a rubberic polybutadiene (PB) acts as the dispersive phase (Kao and Duh, 2002; Ho, Chen and Duh, 2005). It is

usually produced by two techniques: blending process and graft copolymerization. The blending is conventional method which prepared from mixing the SAN and PB in both solid or latex. For graft copolymerization, styrene (ST) and acrylonitrile (ACN) are grafted onto the PB latex in the second emulsion polymerization step to enhance the steric stability and impact resistance (Hua, Kaob and Duha, 2008). The elastomeric segment of PB is a rubber phase and exists as spherical particles dispersed in the glassy matrix of SAN. However, ABS is drawback in thermal properties result to limit in outdoor application because of it has PB as elastomeric segment which easier expose to thermal and oxygen when using long time.

In order to the trend of green polymer, the industries using the synthetic rubbers as raw materials have attempted to partially or fully replace them by using HNR. This research started with the partial saturation of NR latex by diimide hydrogenation to improve its thermal and oxidative properties. Then, the HNR latex was grafted with ST or ST/MMA via emulsion polymerization initiated by redox system. The effect of hydrogenation level, monomer and initiator concentrations on grafting properties of HNR was investigated. The obtained grafted HNR (GHNR) was then applied into the ABS blends. The mechanical properties in terms of flexural strength and their stability after thermal aging were also investigated. Moreover the thermal properties such as glass transition temperature and decomposition temperature were also examined.

1.2 Objectives of the research work

The objectives of this research were stated as follow:

1. To prepare HNR latex with various hydrogenation levels via diimide reduction.
2. To study the graft copolymerization of ST or ST/MMA onto HNR latex initiated by redox system
3. To investigate the mechanical properties and thermal stability of ABS blended with GHNR.

1.3 Scope of the research work

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

1. Surveyed the previous literatures and related research works.
2. Prepared HNR latex via diime reduction.
3. Studied the graft copolymerization of ST or ST/MMA onto HNR latex via emulsion polymerization initiated by cumene hydroperoxide (CHPO)/tetraethylene pentamine (TEPA) redox system.
4. Characterized the structure of HNR and grafted HNR (GHNR) latexes by using nuclear magnetic resonance spectroscopy ($^1\text{H-NMR}$) and fourier transform infrared spectroscopy (FT-IR).
5. Studied the morphology of HNR and GHNR latexes by using a transmission electron microscope (TEM).
6. Investigated the effect of the addition of GHNR latex on the morphology, mechanical properties and thermal stability of ABS blends before and after thermal aging
7. Summarized the experimental results.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Natural rubber

In spite of the commercial existence of synthetic rubbers for more than 50 years, natural rubber (NR) is still used as general proposed elastomer which is irreplaceable by other synthetic rubbers due to its unique mechanical properties such as high tensile strength with high flexibility and low heat build-up. Thus, NR is normally applied in various industries such as tire industry, medical equipments and engineering thermoplastic materials.

NR latex is obtained from the milky secretion which is largely produced from tapping the para rubber or “*Hevea Brasiliensis*”, which is an original native of the tropical rain forest in the Amazon Basin in Brazil. Nowadays, the most NR source in the world is supplied from Southeast Asia, mainly Thailand, Malasia and Indonesia (Brydson,1978). NR latex contains rubber particles suspended in an aqueous serum phase. The latex exuded from cutting is called as the fresh NR latex or fresh latex. The chemical structure of NR latex is mainly consists of isoprene unit (C_5H_8) higher than 94% (Figure 2.1) with its molecular weight of 100,000 to 1,000,000.

The fresh latex composes of approximately 30 – 40% of dry rubber content (DRC) and 5 – 10% of non-rubber such as proteins, lipids, carbohydrates and inorganic salt. The composition is depended on the clones and age of the rubber tree including the tapping method. A typical fresh latex composition is shown in Table 2.1

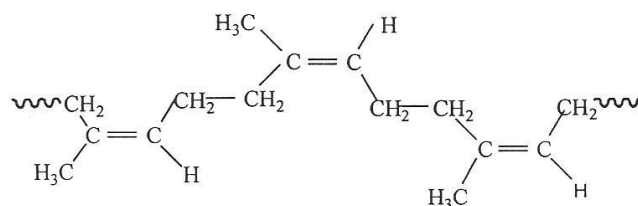


Figure 2.1 Natural rubber or *cis*-1,4-polyisoprene (Tanaka, 2001).

The rubber particles are believed to be covered by some phospholipids and proteins which influence on the colloidal stability of the NR latex. Phospholipids are strongly adsorbed on the surfaces of the rubber particles. It might act as an intermediate by which the proteins are anchored on the rubber particles as shown in Figure 2.2. The particle size of the rubber particles in the fresh latex depends on the age and clone of rubber trees. NR latex from the mature trees contains both large and small rubber particles. The average size of large rubber particles is ca. 0.04 – 4 μm with average diameter of 1.03 μm . However, the size distribution of small rubber particles in the serum phase is in the range of 0.05 – 0.3 μm . The particle size distribution of the rubber particles in the NR latex is shown in Figure 2.3 (Tanaka, 1999).

Table 2.1 Typical fresh stituent rubber latex composition (Morton,1999)

Constituents	Composition (% w/v)
Total solid content	36.0
Dry rubber content	1.4
Neutral lipids	1.6
Proteins	1.0
Phospholipids	0.6
Inorganic constituents	0.5
Water	58.5

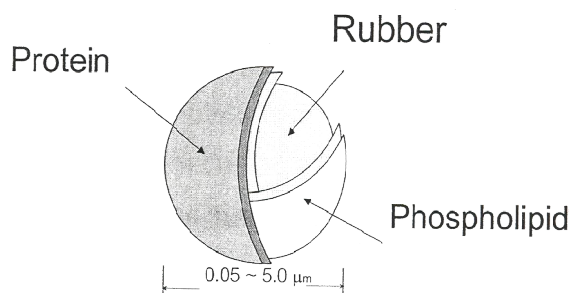


Figure 2.2 Presumed structure of a rubber particle (Venharr, 1959).

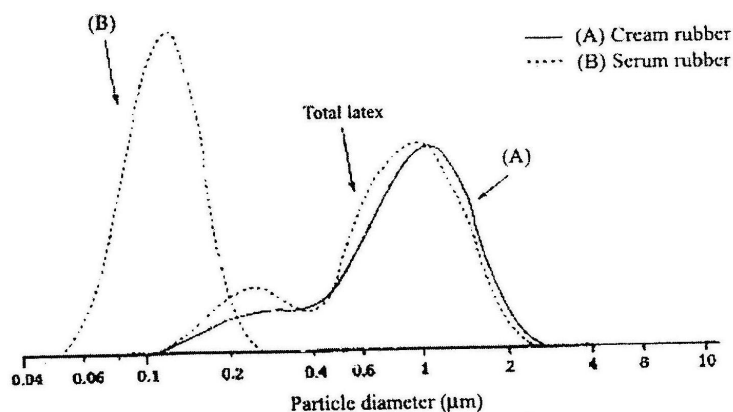


Figure 2.3 Particle size distribution of NR latex (Tanaka, 1999).

2.2 Chemical modification of natural rubber

Although NR is classified as an eco-material with high mechanical properties which could be applied in the various industries such as vehicle tire, dipping goods and a lot of products obtained from blending with various synthetic rubbers, it is deteriorated when it is exposed to sunlight, ozone and oxygen. It also has poor resistance to weathering and chemical reagents. This limits the use of NR for high performance applications or using under critical conditions. Therefore, it is necessary to improve the structure of NR to enhance thermal and chemical resistance properties in order to extend its application and also compete with synthetic elastomers in the world market. Therefore, the modification is important for NR to improve its properties. The chemical modification methods for diene-based elastomers can be classified as followed (Sroysom, 1999):

- Modification by bond rearrangement without introducing new atoms such as carbon-carbon cross-linking, cyclization, *cis*, *trans*-isomerization and depolymerization.
- Modification by attachment of new chemical groups (like chlorine

and epoxy) through addition or substitution at the olefinic double bonds such as chlorination, hydrogenation and epoxidation.

- Grafting short or long chains of different polymer types onto the polymer backbone. This type of chemical modification is mostly carried out using vinyl monomer such as methyl methacrylate (MMA) and styrene (ST).

The chemical modification of diene-based polymers has been an interesting method to improve or produce new materials, which are inaccessible or difficult to prepare by conventional polymerization processes such as thermoplastic elastomers or resinous materials. The modification of diene-based polymers can be carried out by synthesis of new polymers, by new polymerization process, or by blending of existing polymers having various properties.

2.2.1 Hydrogenation of diene-based polymers (Hashim et al., 2002)

According to the lower thermal and oxidative resistance of diene-based polymers due to their unsaturated C=C bonds, the chemical modification of diene-based polymers via hydrogenation is alternative way to enhance their thermal stability reducing the amount of carbon-carbon double bonds. The hydrogenation process has been commercially utilized and developed in the rubber industry such as hydrogenated styrene-butadiene rubber (HSBR) produced by Shell and hydrogenated acrylonitrile-butadiene rubber (HNBR) manufactured by Zeon Chemicals and Lanxess Inc. Both of these hydrogenated rubbers have excellent thermal stability and resistance to oxygen, ozone and ultraviolet radiation, which are far superior to those of the parent rubbers (McManus and Rempel, 1995).

The hydrogenation process of diene-based polymers can be classified as three methods: homogeneous catalytic, heterogeneous catalytic and non-catalytic hydrogenation. The comparison of these methods is summarized as shown in Table 2.2. The hydrogenation of diene-based polymers can be performed using a variable methods such as solution hydrogenation (Martin, McManus and Rempel, 1997),

Table 2.2 Comparison of hydrogenation methods (Hashim et al., 2002)

Methods of hydrogenation	Yield	Side reaction	Catalyst poisoning and removal
Homogeneous hydrogenation	High yield of saturated products can be obtained with hydrogenation level up to 100%.	Degradation of NR occurs, but can be overcome by using nickel (Ni) catalyst.	Ni catalyst is easily poisoned by impurities and difficult to be removed.
Heterogeneous hydrogenation	Yields with purer products.	Degradation does not occur and foreign groups are present.	Catalyst can cause poisoning.
Non-catalytic hydrogenation	Low level of hydrogenation with (< 70% of conversion).	Isomerization, attachment of hydrazine fragments (this reaction can be minimized with the addition of antioxidant), depolymerization and cyclization occur.	No poisoning or catalyst removal issue.

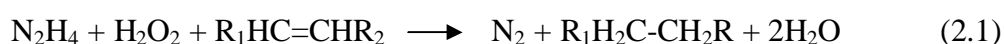
latex hydrogenation (Guo and Rempel, 1997) and solid state hydrogenation (Gilliom, 1989). It is depended on the physical state of elastomers at the time of hydrogenation. For the solution hydrogenation, this method was carried out via catalytic hydrogenation. The substrate polymer is normally dissolved in an appropriate solvent followed by the addition of specific catalyst at the desired reaction temperature and pressure. For the latex hydrogenation, the polymer particles are suspended in aqueous solution. The hydrogenation is carried out with an oil-soluble catalyst dissolved in organic solvent used as co-solvent or with a water-soluble catalyst. For the solid state

hydrogenation, the catalyst is impregnated into the polymer sheet and hydrogenation is then performed under a particular pressure and temperature (Budiman, 2002).

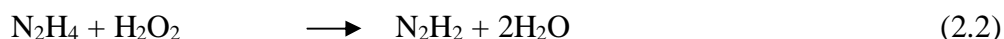
Catalytic hydrogenation can be carried out by using heterogeneous or homogeneous catalytic processes. The homogeneous catalytic process is more favored than heterogeneous one for hydrogenation of unsaturated polymers due to its higher selectivity without involvement of a macroscopic diffusion problem. Moreover, the role of the homogeneous catalyst can be explained and understood at the molecular level (Bhaduri and Mukesh, 2000). However, the drawback of this technique is the requirement of precious transition metal as the catalyst, high hydrogen pressure, organic solvents and specific equipment resulting the expensive operating cost. This process is also difficult to remove or separate the spent catalyst from the obtained product. Since the catalytic hydrogenation is carried out in the presence of organic solvent, this is also claimed as a non-environmental friendly system. To avoid the use of organic solvents, the hydrogenation of diene-based polymers in the latex form via diimide reduction would be more advantage. This also reduced the steps for preparation of solid rubber from latex and re-dissolution of the obtained solid rubber in the organic solvent for using as the starting material for hydrogenation.

2.2.2 Hydrogenation of latex by diimide reduction (Wideman, 1984; Parker, Robert and Schiessl, 1992 and 1993)

The non-catalytic hydrogenation applied for unsaturated latex polymers is carried out via diimide reduction. This technique was firstly discovered to saturate the latex of polybutadiene by treating with hydrazine, an oxidant and a metal catalyst (Wideman, 1984). Therefore, the re-dissolving and solvent-removing steps are not necessary for diimide reduction since this technique does not require an organic solvent. Moreover, the hydrogenated products is still in the latex form. The overall mechanism of this reaction can be presented in Eq. 2.1 (Lin, Pan and Rempel, 2004)



Diimide hydrogenation is consisted of two steps. Firstly, hydrazine (N_2H_4) is reacted with hydrogen peroxide (H_2O_2) to produce diimide (N_2H_2) and water (Eq. 2.2). This reaction can be performed at the interface of the rubber particles and the bulk aqueous phase. The N_2H_2 is then reacted with carbon-carbon double bonds to form hydrogenated polymer as shown in Eq. 2.3.



However, the undesired side reactions such as chain scission, cyclization, crosslinking and gel formation are normally occurred (Schulz, Turner and Goiub, 1982; Nang, Katabe and Minoura, 1976). Moreover, N_2H_2 can be further reacted with H_2O_2 (Eq. 2.4) to generate nitrogen gas (N_2) mostly occurring at the interface as nitrogen which is dissolved in the water phase. The another side reaction is the reaction between two N_2H_2 molecules to release one molecule of N_2H_4 and nitrogen gas as shown in Eq. 2.5 at the rubber phase. Moreover, this reaction can induce the crosslinking formation.

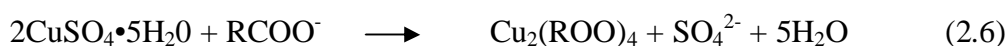


Diimide is consumed by Eq.2.4 either at the interface or in the aqueous phase before diffusing into the rubber particles. There are three competing parallel processes in the reaction mechanism:

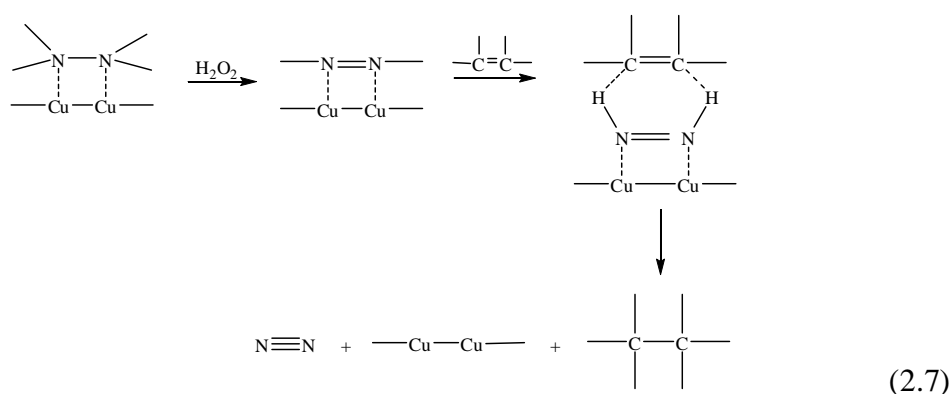
1. The reaction of Eq. 2.2 may occur at the interface and also in the bulk aqueous phase. Diimide generated in the aqueous phase would not be available for hydrogenation in the organic phase. Therefore, this competition influences the efficiency of the diimide utilization in the aqueous phase.

2. The reaction of Eq. 2.4 competes with the diimide diffusion process into the rubber particles. This competition affects the efficiency of diimide utilization at the interface.
3. The reaction in Eq. 2.5 also competes with Eq. 2.2 for diimide production. This competition involves the diimide utilization efficiency in the rubber phase, and also produces the platform for radical generation and crosslinking.

The copper ion (Cu^{2+}) is able to greatly accelerate the formation of diimide from the $\text{N}_2\text{H}_4/\text{H}_2\text{O}_2$ redox system. When Cu^{2+} is added into the system, it can be distributed over the surface of latex particle by means of a strong complex with carboxylate group (RCOO^-) at outer surface of carboxylated NBR (Sarkar, De and Bhomwick, 2000). This reaction can be shown as



From the above equation, it is seen that the active site is actually bimetallic copper which resides within the surface layer of polymer particles as the bridge species (Parker et al., 1992). When copper resides at the latex particle surface, where it comes across a large excess of hydrazine in aqueous phase, it is likely that hydrazine bound between copper centers through lone electron pairs on nitrogen. Subsequently, the oxidation of bound hydrazine with hydrogen peroxide then directly produces diimide and water whereas the active copper site is regenerated. Diimide is the actual hydrogenating species for reducing the carbon-carbon double bonds. The overall reaction mechanism is presented in Eq. 2.7



Although the hydrogenated polymers are well known to have higher ozone and heat resistance, the functionalization via graft copolymerization can extend the application of hydrogenated polymer to have higher compatibility with other constituents in the rubber-rubber blends or thermoplastic elastomer production.

2.2.3 Graft copolymerization (O dian, 2004)

The chemical modification of polymer via graft copolymerization is the way to modify and improve the polymers to have desirable properties. The advantage of graft copolymerization is improvement of the inferior properties without sacrificing the superior properties. The graft copolymers contain a long sequence of one monomer (often referred as the backbone polymer) with one or more branches (grafts) with a long sequence of a second monomer (O dian, 2004). The simplest case of graft copolymer can be represented by the following structure as shown in Figure 2.4, where a sequence of A units is referred as the main chain or backbone and the sequence of B units is the side chain of grafting polymer.

In graft copolymerization, the polymer side chains are formed and attached to perform macromolecules of different chemical composition and the chain are randomly distributed (Calvin, 1977). The graft copolymerization involves the radical polymerization. The necessary requirements for the synthesis of graft copolymer are (1) chain transfer to a saturated or unsaturated polymer, (2) activation by photochemical or radiation, and (3) introduction and subsequent activation of peroxide and hydroperoxide groups.

The technique for the graft copolymerization can be divided into three method. The first method to prepare graft copolymers is named as “grafting onto”. The growing chain B attacks the polymer backbone A with formation of a long branch.

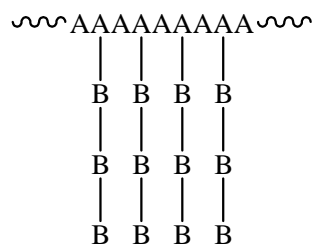


Figure 2.4 Graft copolymer (Odian, 2004).

The second method is called as “grafting from”. This means the active sites are generated at the polymer backbone A, which then initiates the polymerization of monomer B. The third method which is called “grafting through” involves the homo and copolymerization of macromonomer, usually a vinyl macromonomer. The pathways for graft copolymerization are shown in Figure 2.5. For this purpose, macromolecules with only one polymerization end group are needed. The final product of the graft copolymerization usually contains the following three species:

1. Homopolymer B, resulted from homopolymerization of monomer B.
2. Homopolymer A, which is the original backbone polymer A. This is not reacted by free radicals and therefore not involve in graft copolymerization.
3. Graft copolymer which is the graft of poly-B branching out from poly-A.

The grafting efficiency is depended on the competition of the reaction between monomer and backbone for initiator radicals, growing polymer radicals and termination processes. For rubber modification, the polymer backbone can be NR, polybutadiene (PB), styrene-butadiene rubber (SBR) and acrylonitrile-butadiene rubber (NBR) due to the presence of C=C bonds which can be initiated grafting site for polymerization with various monomers such as MMA, ST, acrylonitrile, ethyl methacrylate, maleic anhydride, 2-hydroxyethylmethacrylate (Huang and Sundberg, 1995).

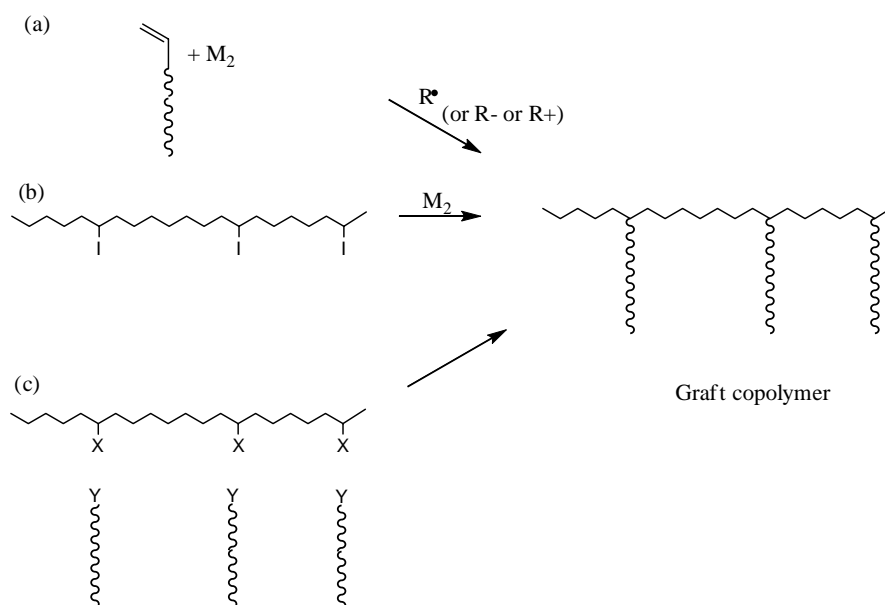


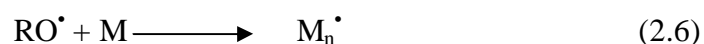
Figure 2.5 Pathway of graft copolymerization: (a) homo- and copolymerization of macromonomers route, (b) "grafting from" route and (c) "grafting onto" route (M = monomer, R = radicals, I = azo or peroxy group, X and Y = reactive side groups).

To explain the reaction mechanism for graft copolymerization of vinyl monomers onto NR latex, the graft copolymerization of NR has been performed in solution, solid rubber and latex phase. However, the latex is most economical and practical method, since the latex particles are ready for grafting in the further polymerization step. The mechanism of graft copolymerization of monomer onto the NR backbone consists of three steps: initiation, propagation and termination. For the initiation step, the radicals produced by oxidation-reduction can be used to initiate polymerization. For the redox initiation system, the hydroperoxide is induced by decomposition of amine activator to yield alkoxy radicals (RO^\bullet). Cumene hydroperoxide (CHPO) and tetraethylene pentamine (TEPA) are normally used as the redox initiators for graft copolymerization. The alkoxy radicals interact with either the applied monomer (M) (Eq. 2.6) or the rubber molecule (Eq. 2.7) to produce monomer radicals (M_n^\bullet) and polyisoprene radicals (NR^\bullet), respectively. The NR^\bullet can then initiate monomer for producing graft copolymer radicals ($NR-M_n^\bullet$) (Eq. 2.8). In the

propagation step, NR- M_n^\bullet attacks M to form graft copolymer (NR- M_{n+1}^\bullet) (Eq. 2.9). Moreover, M_n^\bullet can also attack M to propagate the chain of free copolymer radicals (M_{n+1}^\bullet) (Eq. 2.10). Then, the M and NR- M_n^\bullet will either combine with NR $^\bullet$ to terminate the process or transfer to NR via chain transfer agent (A) to form NR- M_n^\bullet (Eq. 2.11 – 2.15). Finally, the NR- M_n^\bullet can also terminate the process by reacting with free copolymers (Eq. 2.6-2.18) on the surface of latex particle (Arayapranee, Prasassarakich and Rempel, 2003).

Initiation:

Attacking monomer:



Attacking rubber:



Reinitiation:

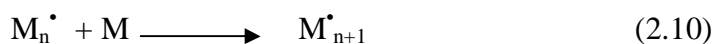


Propagation:

Propagation of graft polymerization:



Propagation of free polymerization:

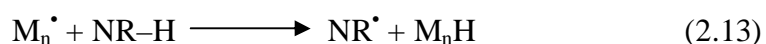


Chain transfer to macromolecules:

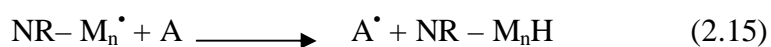
Transfer to monomer:



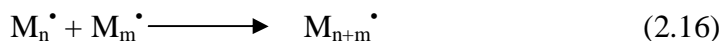
Transfer to rubber:



Transfer to chain-transfer agent:



Termination by combination:



The mechanism of the graft copolymerization of monomer onto the NR backbone normally involves with free radicals. The grafting of the secondary polymer onto polyisoprene could be induced by two pathways:

1) Direct attack of rubber by initiator radicals

The method is occurred through a grafting site which the initiator-derived radicals either add across the double bond or abstract hydrogen from polyisoprene backbone by polymeric radicals as shown in Figure 2.6. (Kochthongrasamee, Prasassarakich and Kiatkamjornwong, 2006).

2) Chain transfer with polymer *via* abstraction

This pathway relates to the growing long chain radicals (RO-polymer \bullet) which undergo chain transfer with the polymer by hydrogen abstraction, leading the initiator for grafting (Oliveira et.al, 2005) as shown in Figure 2.7.

2.2.3.1 Radical graft copolymerization (Odian, 2004)

Graft copolymers can be synthesized via radical polymerization. There are various routes to graft copolymers via radical polymerization such as chain transfer and copolymerization, ionizing radiation, redox initiation and living radical polymerization.

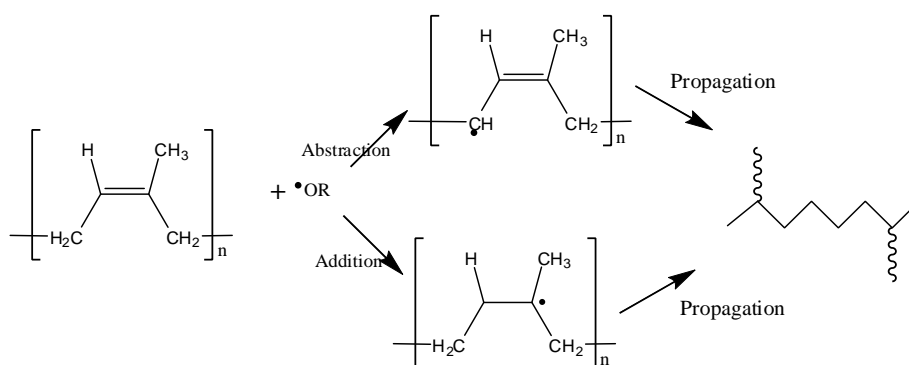


Figure 2.6 Illustration of graft copolymerization via direct attachment of rubber by initiator radicals (Kochthongrasamee et al., 2005).

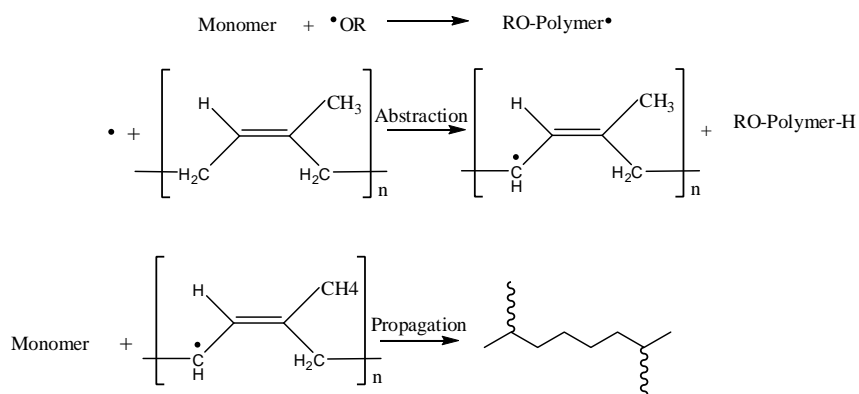


Figure 2.7 Illustration of graft copolymerization via chain transfer with polymer by abstraction (Oliveira et.al, 2005)

1) Chain transfer and copolymerization

The chain transfer is considerable reaction. This reaction can be occurred as chain transfer to a monomer, solvent or other growing chain. For this route, it generates the radicals which act as active sites for chain growth and grafting when the chain transfer reaction to another chain. Firstly, the polymer radicals are formed by chain transfer between the propagating radicals of vinyl monomer and polymer backbone (1), and then initiate the graft copolymerization of vinyl

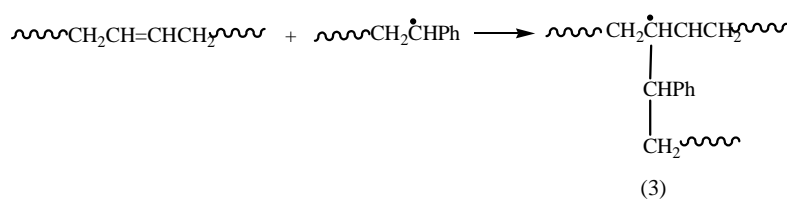
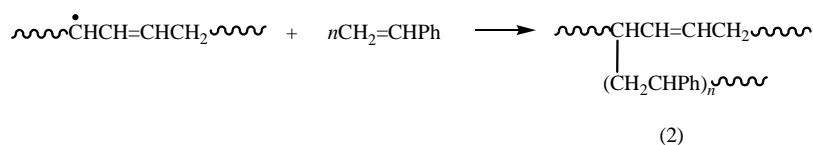
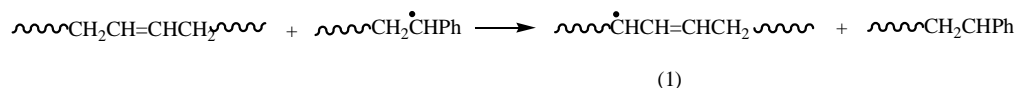


Figure 2.8 Scheme of chain transfer reaction (Odian, 2004).

monomer (2). This grafted product (2) consists of polyvinyl grafted on the backbone polymer. Moreover, polymer radicals are also provided from the attack on the polymer by primary radicals from initiator. The chain transfer usually concerns hydrogen abstraction and generates a radical on polymer chain as the grafting sites for fresh monomer. For polymers containing double bonds such as 1,4-poly- or 1,3-polybutadiene, graft polymerization also involves copolymerization between the polymerizing monomer and the double bonds of the polymer in addition to grafting initiated by chain transfer (3).

2) Ionizing radiation

The polymer radicals can also be produced by the irradiation of a polymer-monomer mixture with ionizing radiation. The radiation graft copolymerizations are mostly carried out as heterogeneous reaction. The interaction of ionizing radiation produces radical center on backbone polymer (1), and continuously initiates graft copolymerization vinyl monomer to generate graft copolymer (2) as followed in Figure 2.9. This method has been used chemically active polymers for adsorption and separation processes. The polymer is swollen by monomer, but it is not dissolved

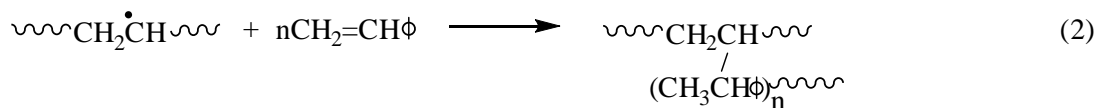
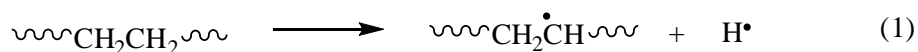


Figure 2.9 Scheme of ionizing radiation (Odian, 2004).

in monomer. For the semicrystalline polymer, it was only swollen and initiated grafting in the amorphous regions. The typical reaction involves equilibration of polymer with monomer followed by irradiation of the monomer-swollen polymers, which are immersed in excess monomer. Whether graft copolymerization generates uniformly throughout the volume of the polymer or mainly at its surfaces, it depends on the rate of monomer diffusion into the polymer relative to the grafting rate.

3) Redox initiation

Many oxidation-reduction produce radicals that can be used to initiate polymerization. This type of initiation is referred as redox initiator, redox catalysis or redox activation. Redox initiation is often sufficient way for graft copolymerization, since the radical production occurs at reasonable rate over every range of temperature of 0-50°C and even lower. In the addition, some redox polymerization can be photocally initiated as well as thermally. It includes both inorganic or organic components either wholly or in part. Some redox systems involve direct electron

transfer between reductant and oxidant, while others involve the intermediate formation of reductant-oxidant complexes. In this system, hydroperoxide or similar group is reduced to a free radical plus an anion, while the metal ion is oxidized and monomer was added in the same time. The reducible group was attached to a polymer chain, the free radical grafting site was formed on the macromolecular backbone as well as initiator for grafting. Hydroxyl polymers can be grafted by redox polymerization by using water soluble peroxide such as hydrogen peroxide in conjugation with ferrous ion. It was produced by abstraction of hydrogen atoms from the hydroxyl groups in the polymer to get free radical grafting sites on the backbone

polymer which are converted as R-O radical. Thus, homopolymer slightly occurred while pure graft copolymer is provided.

4) Living radical polymerization

Living radical polymerization has been extensively investigated for synthesis of graft copolymers using both the grafting-from and grafting-through methods. It is potential way to produce graft copolymers in which the lengths of the graft chains are controlled better than other radical polymerizations. Moreover, it is unlike the other method of radical polymerization. It is possible to have the more graft chains than the block copolymer by using a sequential addition of different monomers.

Although, the type of graft copolymerization is classified by using of route for generation of the radical polymerization. It is also classified by (1) type of initiator such as thermal decomposition initiator, redox initiator, persulphate initiator system and ionizing radiation and (2) process condition of graft copolymerization such as bulk or mass polymerization, solution polymerization, suspension polymerization and emulsion polymerization.

2.2.3.2 Bulk polymerization (Odián, 2004)

Bulk or mass polymerization of pure monomer offers the simplest method with a minimum of contamination of the product. However, it is difficult to be controlled since the radical polymerization provides highly exothermic, high activation energy and the tendency toward the gel effect combination to be difficult for heat dissipation. Further, it also requires the strong stirring equipment due to the enhancement of viscosity in reaction system at relative low conversion. Moreover, the increase in the temperature in system induces the degradation and coloration of the resulting polymer with boardened molecular weight distribution resulting from chain transfer to polymer. For this process, the monomers and initiators are mixed in a reactor consisting of heating or cooling unit. Many reactions are performed by addition one monomer into the reactor and/or slowly addition the second monomer.

According to control the temperature, the special steps must be taken to remove heating during polymerization. It can be differentiated between quiescent and stirred bulk polymerization. Both methods are applied to system which polymer is stable in monomer and gradually increases viscosity with conversion. For quiescent systems normally occurred gel formation or infinity of viscosity. However, the reaction rate of system is difficult to be controlled due to the released heat during reaction.

2.2.3.3 Solution polymerization (Odian, 2004)

Solution polymerization is carried out in the presence of solvent to overcome many the disadvantages of the bulk polymerization. The solvent was used as diluents to dissipate the heat generated from the polymerization. The solvent also enhances the ease of stirring due to the lower viscosity of system. The control of reaction temperature is easier in solution polymerization than the bulk process. Nevertheless, the presence of solvent in system may give new drawbacks. Unless the appropriate solvent was selected, chain transfer to solvent can become a problem. Moreover, the purity of the resulting polymer may be affected if the solvent is not properly removed.

2.2.3.4 Suspension polymerization (Odian, 2004)

Suspension polymerization is used to control the thermal and viscosity problems. It is carried out by suspending the monomer (discontinuous phase) as droplets (50-500 μM diameter) in water (continuous phase). Most monomer such as styrene, acrylic and methacrylic ester, vinyl chloride, vinyl acetate and tetrafluoroethylene are polymerized by suspension process. The monomer droplets (subsequently converted to polymer particles) are prevented from coalescing by agitation and the presence of suspension stabilizer (also referred as dispersants or surfactant). The stabilizer is classified as two types including water-soluble polymers (often in the presence of electrolyte or buffer) and water-insoluble inorganic

compounds. The amount of stabilizer for suspension process is typically less than 0.1 % (w/w) of the aqueous phase. The initiators of this method are soluble in the monomer droplets. Such initiators are often referred as oil-soluble initiators. Each monomer droplet in a suspension polymerization is considered to be a miniature bulk process system. The kinetics of polymerization within each droplet are same as those for corresponding bulk polymerization. The suspension process has many advantages such as ability to control the heat of polymerization and suspension or resulting granular polymer may be directly usable. However, it has some problems including contamination by stabilizer, requirement of continuous agitation, washing and drying process.

2.2.4 Emulsion polymerization (Odian, 2004)

Emulsion polymerization is unique process for some radical chain polymerization. It involves the polymerization of monomers in the form of emulsion (colloidal dispersion). The process is similar to suspension polymerization but it is different in mechanism and reaction characteristics. Emulsion process is small size of the particle than suspension process. The emulsion polymerization has many distinct advantages such as the ease of temperature and viscosity control. The resulting product is in latex or colloidal form which can be directly used in many application without separation or coagulation. Moreover, the advantage of this process is high rate of polymerization to give resulting product with high molecular weight and narrow distribution.

2.2.4.1 Core shell mechanism

The couple redox initiator of CHPO/TEPA could be used to prepare NR-based core-shell latex particles. CHPO is soluble in organic phase (NR particle phase and monomer), whereas the amine activator (TEPA) is soluble in aqueous phase. For Figure 2.10, the TEPA transfers into the surface of rubber particle (1) and

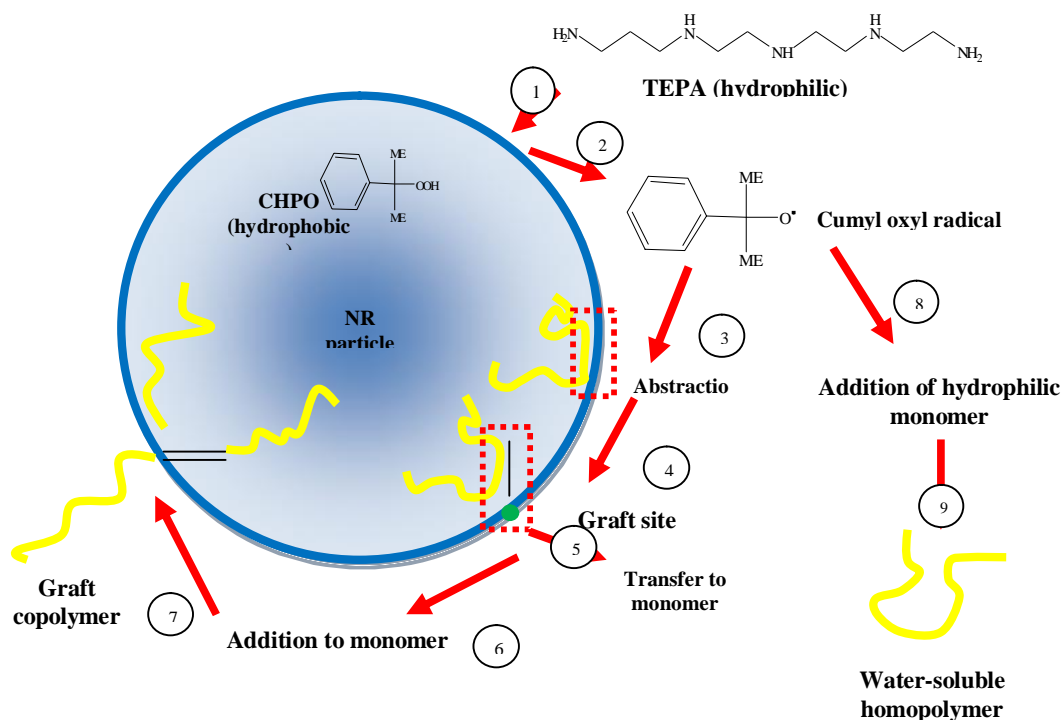


Figure 2.10 Schematic of the possible grafting reaction by using the bipolar redox initiator (CHPO/TEPA) system via seeded emulsion polymerization (Oliveira et al., 2005).

then is reacted with the CHPO to form cumyl oxyl radicals (2). The cumyl oxyl radicals transferred to NR particles at the surface and then created the grafting sites by abstraction over addition to allylic double bond at the interface of NR particles to form graft copolymer (3-7). The further addition of hydrophilic monomer will extend the grafted chain into the aqueous phase (8-9). Therefore, the free radicals are mostly generated only at the surface of NR particle resulting to higher grafting efficiency (Oliveira et al., 2005).

2.3 Polymer blends

The utilization of polymer blends for industrial applications has become more prevalent over the past few decades. Nowadays, polymer blends are widely applied in many applications such as tire, mechanical goods, and adhesive

industries. It has played a very important role in the commercialization of polymers. The practice of polymer blending is as old as the polymer industry itself with early examples involving NR (Banker, 2001). Polymer blending products are frequently formulated by blending two or more polymers. In general, a miscible blend of two polymers exhibits the combination properties obtained from those polymers (Folkes and Hope, 1993). The common applications require materials having some properties from one polymer and other properties from different ones. Polymer blends can be used to prepare a new polymer with all desired properties, with more practicality and economization. The rationale for this development involves one or more of the following points: (1) develop new properties, (2) improve properties, (3) reduce material costs, (4) improve processibility, (5) modified polymeric materials, and (6) reuse of plastic scrap. Therefore, the recent industrial efforts have directed towards development of: (1) blends for high performance polymers, (2) multiphase blends with several polymers, and/or reinforcement, (3) reactive processing, (4) blends with controlled morphology and (5) blends from recycled materials.

For the preparation method, there are many processes to produce the polymer blends such as mechanical blending, mechano-chemical blending, latex blending and chemical blending (Malcolm, 1999). Mechanical process is mostly used in the industry due to its convenience for large scale production.

2.3.1 Effect of factors on morphology of blends

The morphology of polymer blends is important to determine their physical and mechanical properties. The morphology of polymer blends is dependent on the following factors:

2.3.1.1 Polymer proportion (Fayt, 1985)

For the immiscible blends from two polymers (polymer A and polymer B), the small amount of polymer B indicated as small spherical globs, which are separated and dispersed in the larger phase of polymer A (continuous phase) as shown

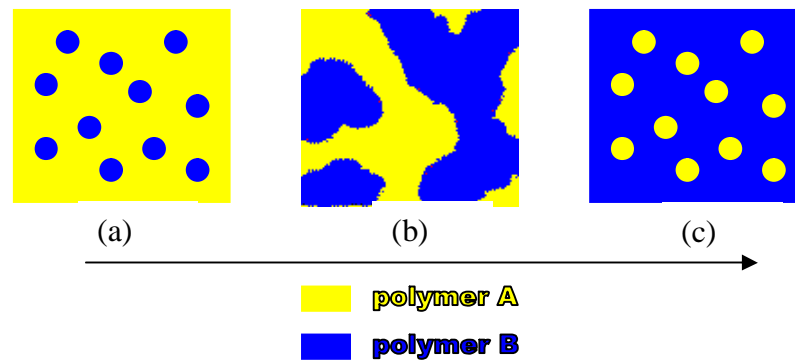


Figure 2.11 Effect of various polymer B contents in the immiscible blends (Fayt, 1985).

in Figure 2.11a. Therefore, polymer B is called as the dispersed phase. When the content of polymer B increases, it becomes as the continuous phase whereas the polymer A acts as the dispersed phase in the polymer B as present in Figure 2.11c. For the partially miscible blend containing higher content of polymer B, the spherical globs of polymer B become larger than polymer A and they partially join together with the continuous phase to form a co-continuous as shown in Figure 2.11b.

2.3.1.2 Polymer viscosity (Corish, 1974)

Polymers with lower viscosity tend to form a continuous phase whereas one with higher viscosity can be formed as a dispersed phase. Furthermore, the difference in viscosity between each polymeric component also affects the morphology of polymer blends.

2.3.1.3 Blend method

The method for blending is one factor to significantly affect the morphology of polymer blends. There are many processes to blend the different polymers such as mechanical blending, mechano-chemical blending, latex blending, chemical blending and solution blending (Malcolm, 1999). Each process carries out different shear forces resulting to the dissimilarity of morphology of the polymer blends. Normally, the size of dispersed polymer is reduced with increasing the mixing

time and severity of mixing. In addition, the types of mixing instrument must be considered because it provides the different shear stress and polymer flow rate during a mixing process (Hess, Scott and Callan, 1967).

2.3.2 Rubber toughening plastic (Keith, 1996; Jar et al., 1999)

There are many types of polymer blends such as two thermoplastics (plastics blend), two rubbers (rubber blend), a thermoplastic resin filled with rubber as the dispersed phase (rubber-modified plastics), or a rubber with a plastic as the dispersed phase (polymer-filled elastomer) (Elias, 2003).

The application of brittle polymers such as poly(vinyl chloride), poly(methyl methacrylate) (PMMA) and polystyrene (PS) was limited prior to the development of rubber toughened polymers in 1930s and 1940s. The technique to improve the fracture toughness of brittle polymers by adding a small quantity of rubber particles was discovered. The rubber-toughened polymer is provided by the addition of a small amount of rubber (typically between 5 and 20% (w/w)) to be incorporated as a dispersed phase into the rigid plastic matrix (Martuscelli, Musto and Ragosta, 1996). The toughness improvement is mainly attributed to the presence of rubber particles to enhance the energy absorption capacity of matrix. For brittle polymers that on their own failed by crazing, the rubber particle can act as the craze initiator to decrease the craze flow stress. Thus, the number of crazes in the deformation zone is effectively increased. To prepare the rubber-toughened plastic, it can be approached in several ways. One is to synthesize new homo-or copolymer based on the novel monomers such in the cases of polycarbonates, polysulphones and polyether-ketones. The second way is considered as the modification of the existing polymers through the addition of the second polymeric component by usually blending. This leads the distinctive advantages such as more economical attraction with lower production cost. For example, the preferred toughening additive for PS is a styrene-butadiene rubber (SBR). Copolymers of styrene such as styrene-acrylonitrile

and styrene-maleic anhydride have been also toughened by addition of acrylonitrile-butadiene rubber (NBR).

Rubber toughened plastics are composite materials, consisting of a rigid matrix with a high glass transition temperature (T_g) and a rubbery dispersed phase with a low T_g . The adhesion between these phases should be strong and the rubber should be broken down into small particles without becoming too finely dispersed for effective toughening the rigid polymer. It is necessary to produce and maintain phase separation between the rubber and rigid polymer in order to make a product having combination of stiffness and toughness. However, it is important to ensure that the two thermoplastics are completely compatible (Bucknall, 1997).

Grafting is an important method for obtaining a strong bond between rubber particles and the surrounding resin. For this reason, it is an essential feature in the manufacture of ABS. Locatelli and Riess have made an extensive study of acrylonitrile-butadiene-styrene (ABS) polymerization, in which ST and ACN are grafted onto PB, ungrafted SAN is also formed. (Kim, Keskkula and Pual, 1990).

2.4 Acrylonitrile-butadiene-styrene copolymer (ABS)

Acrylonitrile-butadiene-styrene copolymer (ABS) is an attractive engineering thermoplastic, for use in various fields and particularly in many aspects of daily life. ABS is normally used in the electrical industry and wide range of injection molding products such as general purpose, high flow, high gloss, paintable and plating grades as well as sheet extrusion products. Because of its excellent mechanical, electrical, optical and processing properties, the main applications are toys, automotive parts, electrical appliances, telephone sets, business machine housings and refrigeration.

ABS is a two-phase system consisting of styrene-acrylonitrile copolymer (SAN) acting as the continuous phase and polybutadiene (PB) acting as the rubber phase. The characteristic properties of ABS are strongly affected by

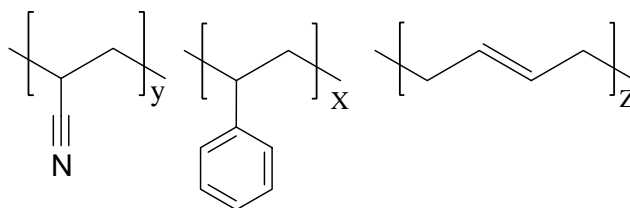


Figure 2.12 Structure of acrylonitrile-butadiene-styrene rubber (ABS) (Hosseini, Madaeni and Khodabakhshi, 2010).

characteristics of monomer. Acrylonitrile provides the chemical resistance and heat stability, butadiene gives the toughness and the styrene component provides the rigidity and easy processability. The ABS is a balance of strength, toughness, high gloss, processability, high dimensional accuracy and stability. It has good electrical insulating properties, resistance to many aggressive media, which is partly due to the amorphous structure of the polymer. Finished parts of ABS can be made by injection molding, extrusion, thermoforming and other techniques. In addition, ABS lends itself to secondary processing such as plating, painting and large a number of other secondary processing forms.

The general ABS manufacture can be divided as two methods. The first method is related to the blending of SAN copolymer with PB. Whereas, the later one is involved with the grafting of SAN onto PB backbone. This technique increase the adhesion between SAN matrix and SAN-graft rubber particles to improve the mechanical properties. The composition can be varied from 15-35% of acrylonitrile, 5-30% of PB and 40-60% of ST. ABS is a long chain of polybutadiene criss-crossed with shorter chains of poly(styrene-*co*-acrylonitrile) (SAN) (Jin et al., 2009). The structure of ABS is presented in Figure 2.12.

2.4.1 Production of ABS (Saunders, 1988)

The properties of ABS are strongly affected by the rubber particle size and properties of SAN matrix. ABS is commercially prepared via two techniques; blending and grafting method. These processes give rise the resulting materials which

are rather different to each other. However, the grafting is more important and favored for preparation.

2.4.1.1 Blending process

NBR and SAN are mixed in the solid form by using a two-roll mill. In this method, a non-crosslinking NBR may be used as a starting material. The rubber is firstly crosslinking by milling with a peroxide and then SAN is added. A wide range of products is possible depending on the composition of each copolymer and the relative amounts of each employed. It has been found that a non-crosslinking NBR is compatible with SAN. The mixture shows a little improvement for impact strength and has low softening points. Although, the copolymer with sufficient crosslinking degree can not be completely soluble, it has high impact strength and high softening points. The convenient method for preparation of the suitably crosslinking NBR is synthesized via emulsion polymerization to give high conversion. Alternatively, a small amount of divinylbenzene can be added into the emulsion recipe. When the SAN and NBR is mixed, the acids or salts are added to coagulate resulting product. The crumb is then wash, filtered, extruded and chopped as granules.

2.4.1.2 Grafting process (Scheirs and Priddy, 2003)

The commercial manufacturing of ABS is accomplished by a number of different methods based on free radical polymerization. The two main methods based on the emulsion polymerization or solution polymerization. Most of ABS is prepared by using the emulsion process. Due to the more complication for solution polymerization, the emulsion polymerization is more favorite to be used because of its greater flexibility. The scheme of emulsion method is showed in Figure 2.13. The rubber latex was firstly synthesized by using emulsifier. The crosslinking of the rubber occurs simultaneously during polymerization and it is controlled by initiator level, chain transfer agent and process condition. The particle size of rubber particles are increased by agglomeration.

Next, ACN and ST are polymerized in the presence of polybutadiene latex. Part of the polymerized styrene-acrylonitrile is grafted onto the rubber. This grafted rubber concentrate is then either mixed with styrene-co-acrylonitrile (SAN) copolymer and then coagulated. Otherwise, it was firstly isolated and then compounded with SAN. The product properties are depended on the relative quantities of reactants. The reaction is carried out at about 50° C. A typical recipe is shown in Table 2.3 (Rodriguez, 1970). ABS obtained from grafting process consists of a continuous matrix of SAN with polybutadiene particles acted as the dispersed phase. The boundary layer of polybutadiene is grafted with acrylonitrile and ST.

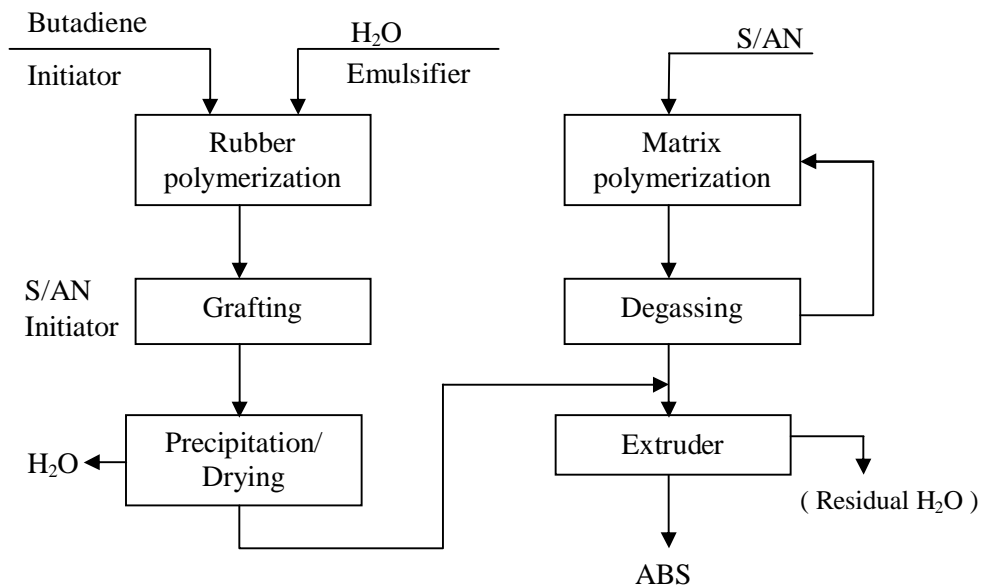


Figure 2.13 Scheme of manufacturing ABS by using emulsion polymerization

(Scheirs and Priddy, 2003)

Table 2.3 A typical recipe of ABS preparation (Rodriguez, 1970)

Ingredients	Parts by weight
Polybutadiene latex	34
Acrylonitrile	24
Styrene	42
Water	200
Sodium disproportionated resin (surfactant)	2.0
Mixed tertiary mercaptans (transfer agent)	1.0
Potassium persulphate (initiator)	0.2

2.4.2 Characteristics of ABS resins

The factors affecting the properties of ABS are described below:

- 1) Molecular weight (MW) and MW distribution of the polymer chains and copolymer chains.
- 2) Proportions of acrylonitrile, butadiene and styrene in each phase of the polymer.
- 3) Size and size distribution of rubber particles.
- 4) Degree of grafting of SAN copolymer on the rubber particles.
- 5) Degree of adhesion between the rubber particles and the SAN matrix.
- 6) Addition of modifiers to one or both phases.

The rigid SAN phase correlated to molecular weight, can also have a significant effect on ABS resin properties. Generally, the longer polymer chain results the higher strength properties, including impact/ductility with the lower flow. The ratio of the rigid SAN phase to the rubber phase affects the flow/impact balance of the

ABS resin. For example, the increases in the rubber content enhances the impact/toughness properties of ABS material and provides the lower flow. This balance between the flow and impact properties of ABS material is necessary to distinguish the grade of ABS for applications.

2.5 Literature reviews

The modification, particularly the hydrogenation of diene-based polymers, has been studied for many years. The hydrogenation is a very useful method to decrease the level of unsaturation of diene rubbers (Mohammadi and Rempel, 1987). The hydrogenation of diene polymer is normally carried out via catalytic hydrogenation. However, this method requires the use of solvent, high hydrogen pressure and precious transition metals in a specific expensive equipments. Moreover, the catalytic hydrogenation of diene polymers is usually performed in solution phase; whereas many polymers are inherent latex form. To reduce the step of the rubber dissolution in the organic solvents with no requirement of any special instruments for reaction, the hydrogenation using diimide reduction generated from the redox reaction between H_2O_2 and N_2H_4 is energetically favorable. The diimide reduction technique can directly convert elastomers in latex form to its saturated structure in the similar form. There are many previous literatures working on the diimide reduction of diene-based polymers.

Wideman (1984) studied the use of the diimide reduction method to hydrogenate NBR latex. The N_2H_4/H_2O_2 (or oxygen) redox system was used to generate an *in situ* diimide (N_2H_2). The copper ion (or ferric sulfonate) was applied as a catalyst to give 80% hydrogenation.

Parker et al. (1992) provided more refined results and a detailed process for the preparation of highly saturated NBR latex. The diimide hydrogenating agent was generated from N_2H_4/H_2O_2 system at the surface of polymer particle. Carboxylated surfactants, which were adsorbed at the latex particle surface, played an

important role by forming hydrazinium carboxylates with hydrazine and copper ions. Then, the generated N_2H_2 intermediates were stabilized by copper ion (Cu^{2+}) to effectively reduce the carbon-carbon double bonds as shown in Figure 2.14. The anionic soap was indispensable for the hydrogenation because the soap could retain the copper ion at the surface of the rubber particles.

Belt et al. (2000, 2003) explained patent of hydrogenation for NBR latex, catalyzed by boric acid. It was reported that the addition of some compounds such as primary or secondary amine, hydroxylamine, imines, azines, hydrazones, oximes and so on during or after hydrogenation could break crosslinking formation. An emulsion form of n-1,4-dimethylphenyl (n'-phenyl)-p-phenylenediamine was also suggested to reduce gel formation.

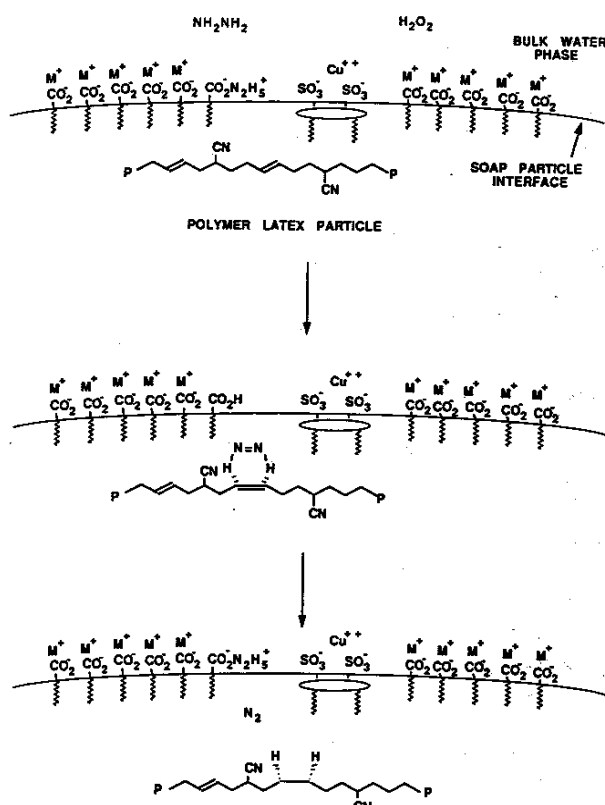


Figure 2.14 Proposed mechanism of diimide reduction for hydrogenation of NBR latex (Parker et al., 1992).

Xie et al. (2003) investigated the hydrogenation of NBR latex by using N_2H_4 and H_2O_2 using CuSO_4 as a catalyst. A hydrogenation degree of 87% was achieved after 6 h at 40°C for a mole ratio of N_2H_4 to carbon–carbon double bonds of 2.5:1. However, a problem for this process was gel formation. When *p*-tert-butylprocatechol was used as a gel inhibitor, it could reduce the gel formation from 94.3 to 21.7%.

He et al. (1997) studied the diimide hydrogenation of styrene-butadiene rubber (SBR) latex as a function of different particle sizes. It was found that the hydrogenation of carbon–carbon double bonds was depended on the latex particle size and the extent of crosslinking in the particles. The SBR latex with a diameter of 50 nm could be hydrogenated as 91% using 1 of $\text{N}_2\text{H}_4/\text{H}_2\text{O}_2$ mole ratio per a mole of carbon–carbon double bond. For the SBR latex with a diameter of 230 nm, the

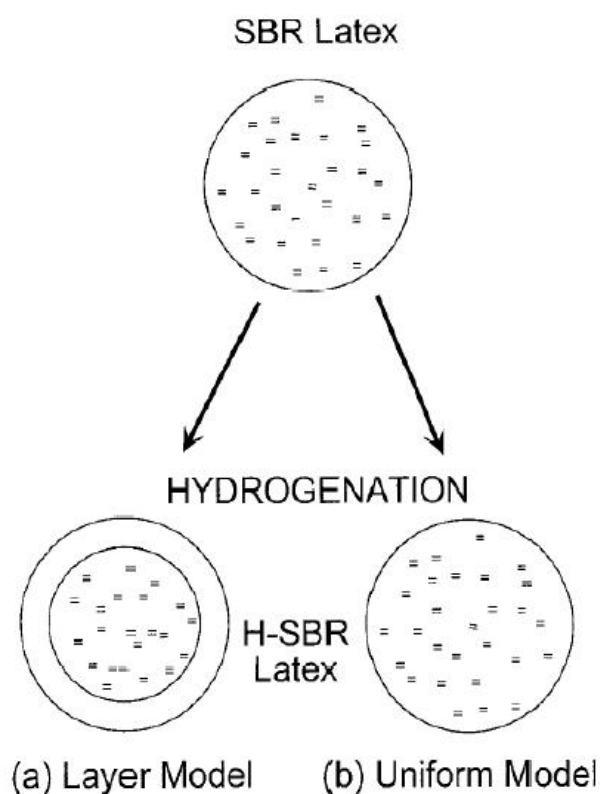


Figure 2.15 Two models for the distribution of double bonds in hydrogenated SBR latex particle: (a) layer model and (b) uniform model (He et al., 1997).

hydrogenation degree was only 42%. The effect of particle size on %hydrogenation could be explained according to a “layer model” as shown in Figure 2.15. The copper ion catalyst was postulated as staying at the surface of the latex particles. By modulating the concentration of copper ions at the particle surface, the higher degree of hydrogenation could be attained. However, the gel fraction of SBR latex was increased after the hydrogenation.

Xie et al.(2002) studied the diimide reduction conditions for hydrogenation and crosslinking. It was found that a ferrous sulfate was better than cupric sulfate for catalyzing the diimide hydrogenation of carboxylic styrene-butadiene rubber latex (XSBR). The hydrogenation level reached over 90% when sodium *N,N*-dimethyldithiocarbonate and *p*-tert-butyl-pyrocatechol were used as a gel inhibitors.

Mahittikul et al. (2007) investigated the diimide hydrogenation of NR latex with diimide reduction catalyzed by CuSO_4 . It was found that 67.8% hydrogenation was achieved within 6 h at 55°C. The low rubber concentration ($\text{C}=\text{C}$) and high N_2H_4 concentration provided the optimum condition. The cupric acetate was also a highly active catalyst for the reaction. The addition of a controlled amount of gelatin demonstrated a beneficial effect on the degree of hydrogenation. Whereas, the use of stabilizer sodium dodecyl sulfate (SDS) decreased the degree of hydrogenation. Moreover, the system containing SDS required the longer reaction time and higher amount of N_2H_4 . However, the gel formation during the hydrogenation did not significantly affect the degree of hydrogenation. The hydroquinone used as the gel inhibitor also decreased the degree of hydrogenation.

Simma et al. (2009) studied the diimide hydrogenation of skim NR (SNR) latex using N_2H_4 and H_2O_2 catalyzed by CuSO_4 . It was found that 64.7% hydrogenation was achieved with 2.68 M of $[\text{N}_2\text{H}_4]$, 3.53 M of $[\text{H}_2\text{O}_2]$, 49.4 μM of $[\text{CuSO}_4]$ and 0.55 M of rubber concentration $[\text{C}=\text{C}]$ within 6 h at 60 °C. The kinetics of diimide hydrogenation using SNR latex exhibited a first order behavior with respect to the $[\text{C}=\text{C}]$. The apparent activation energy of the catalytic and non-catalytic hydrogenation of SNR latex were calculated as 9.5 and 21.1 kJ/mol, respectively. For

the thermal properties, the decomposition temperature of SNR latex increased after hydrogenation. It indicated that the thermal stability of SNR latex was improved. Furthermore, the hydrogenated SNR (HSNR)/NR vulcanizates at all blend ratios exhibited the highest retention of mechanical properties after aging due to the higher saturation level and the formation of zinc-dimethyldithiocarbamate acting as an efficient antioxidant. The HSNR/NR vulcanizates at various blend ratios had also high resistance to surface cracking caused by ozone.

To extend the application of NR, graft copolymerization is one of modification methods to improve the chemical properties of parent polymer. Graft polymerization of NR can be carried out in solution, solid, and latex phases. The graft copolymerization of vinyl monomers such as methyl methacrylate (MMA) (Schneider, Pith and Lamble, 1996; Oommen and Thomas, 1997) and ST (Schneider et al., 1996; Asaletha et al., 1998), which are the most suitable monomers onto NR has been reported. The graft NR-based composite latex particles have some properties which are better than those of inherent ones and can be used as impact modifiers in thermoplastics (Schneider, Pith and Lambla, 1996; Arayapranee et al., 2004; Braun et al., 1998). Many investigators have reported the influence of various process parameters on the modification of NR by grafting reactions in both latex and solution.

Kangwansupamonkon et al. (2005) studied the modification of NR by grafting with hydrophilic vinyl monomers. The CHPO/TEPA, *tert*-butylhydroperoxide(*t*-BHP)/TEPA and potassium persulfate/potassium metabisulfite ($K_2S_2O_8/K_2S_2O_5$) were used as initiators for grafting of dimethylaminoethyl acrylate (DMAEA) and dimethylaminoethyl methacrylate (DMAEMA) onto NR latex. It was found that the CHPO/TEPA was the most effective initiator for this system and followed by *t*-BHP/TEPA and $K_2S_2O_8/K_2S_2O_5$.

Arayapranee et al. (2003) investigated the preparation of graft copolymerization of ST and MMA mixtures onto NR seed latex using the redox initiator system. The influence of process variables such as the amounts of initiator, emulsifier, chain-transfer agent, monomer-to-rubber ratio, and temperature on the

grafting properties was studied. The increase in the initiator concentration up to 2 phr increased the both grafting efficiency and grafting level. The grafting yield increased with increasing temperature up to 70°C and then decreased, suggesting that a large amount of free radicals produced at higher temperature might combine themselves. The amount of emulsifier did not significantly affect the grafting properties. The grafting efficiency decreased when monomer to rubber ratio increased, indicating that graft copolymerization occurred on the surface of the latex particles. The grafting properties also decreased when the amount of chain-transfer agent increased because of the reduction of macroradical formation.

Chujajit et al. (2005) studied the use of natural rubber-g-polystyrene (NR-g-PS) as a compatibilizer in casting NR/PS blends. NR/PS blend ratio (w/w) was varied as 70/30, 60/40 and 50/50. The graft copolymer with various grafting properties by controlling the NR/ST ratios was prepared by emulsion polymerization initiated by *t*-BuHPO/ TEPA. The obtained graft copolymers (0-30 phr) was then added into the NR/ST blends. The film containing NR-g-ST prepared from 80/20 of NR/ST had higher tensile and tear strength with finer domain size of the dispersed phase. However, the mechanical properties of the films were decreased at overdose of graft copolymer.

Arayaprane and Rempel (2008) prepared the grafting of vinyl, methyl methacrylate (MMA) or styrene (ST) onto NR, which exhibited a core-shell structure. The reaction was depended on the main process factors: reaction time, initiator concentration, and content and type of monomer. It was found that a long reaction time was favorable for the grafting reaction. Grafting efficiency (GE) firstly increased and then decreased with increasing the content of initiator. GE decreased with increasing the monomer concentration. It was also confirmed that the graft copolymerization of NR latex exhibited a surface-controlled process. The results indicated the use of ST monomer showed the higher GE value than of MMA monomer due to the higher different polarity of MMA from NR backbone.

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

3.1.1 Preparation of hydrogenated natural rubber (HNR) latex

The natural rubber (NR) latex with 60% (w/w) of dry rubber content (DRC) was provided by Thai Rubber Latex Co.Ltd. (Bangkok, Thailand) Public Company Limited. Hydrazine monohydrate ($\text{N}_2\text{H}_2\cdot\text{H}_2\text{O}$), 30% aq. solution of hydrogen peroxide (H_2O_2), copper sulfate (CuSO_4) and *d*-chloroform (CDCl_3) were all purchased from Merck Co. Ltd. (Bangkok, Thailand). Silicone oil and ethanol (95% purity) were received from Ajax Finechem (Auckland, New Zealand) and Earth chemical (Bangkok, Thailand), respectively. Commercial grade nitrogen gas (N_2) (95% purity) was provided from Praxair (Samutprakan, Thailand). De-ionized water was used for all diimide hydrogenation experiments.

3.1.2 Preparation of graft copolymer of styrene or styrene/methyl methacrylate onto HNR latex

The NR latex used as the starting material for this step had a degree of hydrogenation at 54.3%. The commercial grade of N_2 with 95% purity was supplied by Praxair, (Samutprakarn, Thailand). Potassium hydroxide (KOH) was obtained from Ajax Finechem (Seven Hills, Australia). Sodium dodecylsulfate (SDS) and isopropanol were received from Fisher Scientific (Loughborough, UK). Styrene (ST) monomer (99% purity) was purchased from Aldrich. Methyl methacrylate (MMA) monomer (99% purity) was purchased from MERCK (Hohenbrunn, Germany). 80% Cumene hydroperoxide (CHPO) solution and tetraethylene pentamine (TEPA) were obtained from ACROS ORGANICS (New Jersey, USA). Anhydrous sodium sulfate (Na_2SO_4), petroleum ether (PE) and methyl ethyl ketone (MEK) were obtained from

Fisher Scientific (Loughborough, UK), Mallinckrodt Chemicals (New Jersey, USA) and QReCTM (New Zealand), respectively. Sodium hydroxide (NaOH) was also purchased from QReCTM.

3.1.3 Preparation of modified NR/acrylonitrile-butadiene-styrene (ABS) blends

After coagulation of HNR latex before and after graft copolymerization, the crumbed modified rubber products was then blended with acrylonitrile butadiene styrene (ABS) resin supplied from Liack Seng trading CO., LTD. (Bangkok, Thailand).

3.2 Diimide hydrogenation procedure of NR latex

Hydrogenation via diimide reduction of NR latex was typically carried out following a previous literature (Mahitikul et al., 2007). NR latex was charged into a 500 mL four-necked round bottom flask equipped with a condenser, a thermometer, a mechanical stirrer and a N₂ tube inlet. The reactor was immersed in a temperature-controlled water bath to maintain the desired reaction temperature. After stirring for 30 min and degassing by using N₂ to remove oxygen, 49.4 μM of CuSO₄ and N₂H₂·H₂O were added and stirred for 60 min. The mixture was then heated to 60 °C. 3.53 M of H₂O₂ was gradually dropped. During the addition of H₂O₂, the small amount of silicone oil used as an anti-forming agent was added when a lot of bubbles were formed. After 6 h of reaction time, the mixture was further post-reacted under stirring for 60 min during cooling down to room temperature to obtain HNR latex. The small amount of HNR latex was sampled and coagulated in ethanol and dried under vacuum to evaluate the chemical structure and degree of hydrogenation. The apparatus for diimide reduction of NR latex was shown in Figure 3.1.

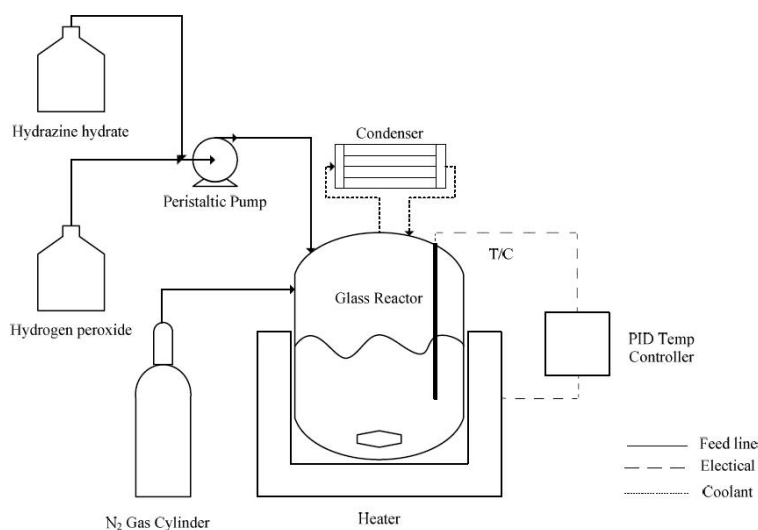


Figure 3.1 Diagram of experimental apparatus for diimide reduction of NR latex.

3.3 Graft copolymerization of ST or ST/MMA onto HNR latex

The ST and MMA monomers were prior purified by washing with 10% (w/v) aq. NaOH and followed by deionized water until neutral. Then, they were dried over Na_2SO_4 , and distilled under reduced pressure. The graft copolymerization of ST onto HNR latex was prepared by emulsion polymerization. The HNR latex (54.3% hydrogenation) was transferred into a 500 ml three-necked round bottom flask. Then, 0.5 part per hundred of dry rubber content (phr) of KOH and 1.0 phr of SDS were added into the reactor under stirring. The mixture was purged with N_2 for elimination of oxygen for 15 min at room temperature. The 5 phr of isopropanol was then added to stabilize the mixture. After 10 min, ST monomer was slowly added into the mixture and stirred at 200 rpm for 30 min. The mixture was then heated up to 50°C following the addition of CHPO (1 phr) used as an initiator. After 15 min, TEPA (1 phr) used as an activator was added. The reaction was allowed under stirring for 8 h in the presence of N_2 atmosphere. The grafted HNR (GHNR) latex was precipitated using 5% (w/v) of formic acid, washed with deionized water until neutral and then dried to get a constant weight in vacuo at 40°C . The gross grafted product was purified by soxhlet extraction using petroleum ether and 2-butanone to remove free HNR and free polystyrene, respectively before evaluation of grafting properties and structure

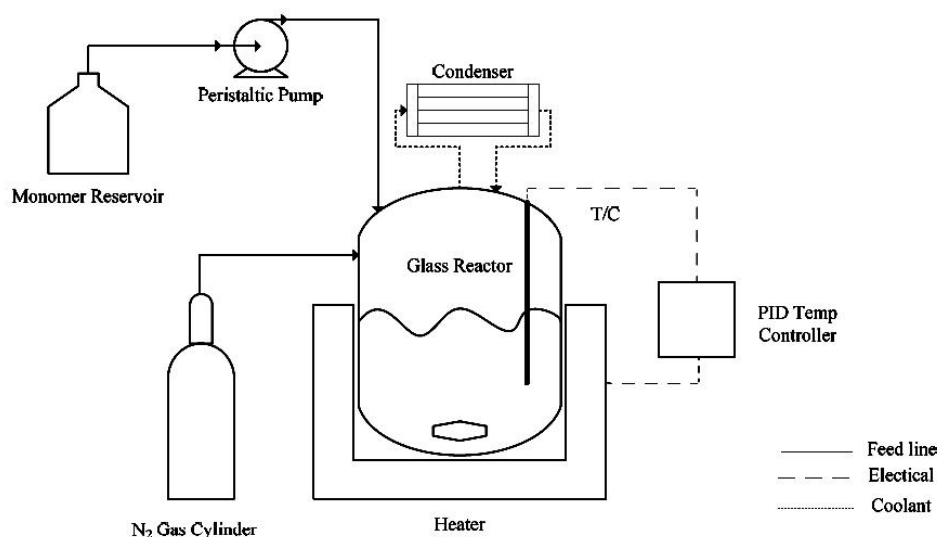


Figure 3.2 The apparatus of graft copolymerization of ST or ST/MMA onto HNR latex

characterization. The set of experimental equipments for graft copolymerization of HNR latex was presented in Figure 3.2.

For graft copolymerization of ST/MMA onto HNR latex, the procedure was similar to the explanation in the graft copolymerization of ST onto HNR latex. The condition for synthesis was performed by using the 0.5 phr of KOH, 1.0 phr of SDS, 5 phr of isopropanol, 1/1 (w/w) ratio of CHPO/TEPA (1phr) and 100 phr of mixture monomer (ST/MMA = 75/25 (w/w)) at 50°C for 8 h.

3.4 Determination of grafting properties

The obtained GHNR latex consisted of three parts: graft copolymer, free HNR (ungrafted HNR) and homopolymer (polystyrene or poly(ST-*co*-MMA)). The free HNR and free homopolymer were removed by using soxhlet extraction with petroleum ether and MEK, respectively. The dried final residue was the graft copolymer of ST or ST/MMA onto HNR. The different weight between initial and extracted samples obtained from soxhlet extraction was used to determine the contents

of graft copolymer, free HNR and homopolymer. All calculations are presented as Eqs. 3.1-3.5 and shown in Appendix A.

$$\% \text{Total conversion} = \frac{\text{Weight of gross polymer products} - \text{weight of NR}}{\text{Weight of monomer charged}} \times 100 \quad (3.1)$$

$$\% \text{Free HNR} = \frac{\text{Weight of free NR}}{\text{Weight of gross polymer products}} \times 100 \quad (3.2)$$

$$\% \text{homopolymer} = \frac{\text{Weight of homopolymer}}{\text{Weight of gross polymer products}} \times 100 \quad (3.3)$$

$$\% \text{Graft copolymer} = \frac{\text{Weight of graft copolymer}}{\text{Weight of gross polymer products}} \times 100 \quad (3.4)$$

$$\% \text{Grafting efficiency (\%GE)} = \frac{\text{Weight of monomer grafted}}{\text{Weight of monomer polymerized}} \times 100 \quad (3.5)$$

3.5 Characterization of HNR and GHNR latex

3.5.1 Fourier Transform Infrared (FT-IR) spectroscopy

For the FT-IR analysis, the samples were dissolved in toluene and casted as films on NaCl plates. The FT-IR spectra of samples were recorded on a BIO-RAD Merlin FTS 3000X spectrometer.

3.5.2 Nuclear magnetic resonance (NMR) spectroscopy

The final degree of olefin conversion of HNR latex was calculated by NMR spectroscopic analysis. The samples were dissolved in CDCl_3 at 1% (w/v) at atmospheric pressure and room temperature. The ^1H -NMR spectra were obtained on Bruker 400 MHz spectrometer using tetramethyl silane (TMS) as the internal standard. The chemical shift (δ) reported was given in part per million (ppm) down field from TMS.

Integration of spectra was used to determine the amount of characteristic protons of each structure in the polymer. The integration peak area for the saturated protons ($-\text{CH}_2-$ and $-\text{CH}_3$) in the range of 0.8-2.3 ppm and the unsaturated protons peak area at 5.2 ppm were measured in order to calculate the degree of hydrogenation by using Eq. 3.6 (Hinchiranan, 2004).

$$\% \text{Hydrogenation} = \frac{A - 7B}{A + 3B} \times 100 \quad (3.6)$$

where A is the integration peak area of saturated protons and B is the integration peak area of unsaturated protons. The example for calculation of hydrogenation level is presented in Appendix B.

For graft copolymer, the chemical structure of graft copolymers after Soxhlet extraction was evaluated. The graft copolymer sample was swollen in CDCl_3 . 0.01 g of sample in 3-4 mL of CDCl_3 was analyzed by using $^1\text{H-NMR}$.

3.5.3 Transmission electron microscopy (TEM)

The morphology of the latex samples before and after chemical modifications was examined by using a transmission electron microscope (TEM) (JEM-2100) with accelerating voltage in the range of 160-200 kV. The sample was diluted for 400 times with distilled water to a concentration of 0.05 % (w/w). In 1 mL of this solution, 2% aq of osmium tetroxide (OsO_4) solution was added and allowed to stain the existing C=C bonds in the samples for overnight. The stained samples were then placed on a grid and dried before evaluation.

3.6 Blending method

After precipitation of modified NR latexes in the presence of 95% ethanol, the hydrogenated and grafted rubber-crumbed products were blended with

ABS resin at 10/90% (w/w) of crumbed rubber/ABS by using an internal mixer (HAAKE Polydrive) with two counter-rotating rotors. The ABS resin was firstly warmed in the mixing chamber at 180 °C for 3 min. Then, the rubber with or without modification was added into the mixing chamber with a roter speed of 60 rpm at 180 °C for 7 min. The resulting blends were sheeted by using a compression molder at the same melting temperature.

3.6.1 Flexural strength of modified NR/ABS blends

The flexural strength of modified NR/ABS blends was measured according to the standard method ASTM D790. The specimens were cut from the compressed sheets with a thickness of 3 mm. The flexural strength of the blends before and after thermal aging at 165°C for 25 min was investigated by using a Universal Testing Machine (LLOYD model LR5K) at a cross-head speed of 1 mm/min. Stress was applied until fracture by a centrally located rod connected to a 50 kgF load cell.

3.6.2 Morphology of modified NR/ABS Blends

The fracture surfaces of modified NR/ABS blends were detected by using scanning electron microscope (SEM). The fracture zone of specimens after flexural testing was cut and stitched on a SEM stub using double-side tape. The samples were then sputter-coated with gold and examined by an electron microscope, JEOL model JSM-6480 LV operated at 15 kV with a magnification of 1,000x.

3.7 Thermal properties of modified NR and modified NR/ABS blends

3.7.1 Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) of the modified NR and

modified NR/ABS blends was performed on Mettler Toledo DSC 822. The instrument signal was derived from the temperature difference. The sample in a crimped aluminium pan was cooled down to -100°C by using liquid nitrogen and then heated up to 25°C with a constant heating rate of $20^{\circ}\text{C}/\text{min}$ under N_2 atmosphere. The glass transition temperature (T_g) of samples was calculated from the midpoint of base-line shift of DSC thermogram.

3.7.2 Therogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) of the crumbed rubber/ABS blends was performed on Perkin-Elmer Pyris Diamond TG/DTA. The temperature was raised under N_2 atmosphere from room temperature to 800°C with a constant heating rate of 2.5, 5.0 and $10^{\circ}\text{C}/\text{min}$. The flow rate of N_2 was $50 \text{ mL}/\text{min}$. The initial decomposition temperature (T_{id}) and the final decomposition temperature (T_f) were obtained from the intersection of two tangents at the initial and final stage of decomposition, respectively. The maximum decomposition temperature at maximum of mass loss rate (T_{max}) for each specimen was also evaluated.

The overall kinetics of the thermal decomposition of samples were evaluated by using the Kissinger method (differential method) for determination of the activation energy (E_a) of the solid state transformation without a precise knowledge of any mechanism of thermal decomposition, as presented in Eq. 3.7:

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\frac{AR}{E_a} + \ln[n(1-\alpha_p)^{n-1}] - \frac{E_a}{RT_p} \quad (3.7)$$

where β is the heating rate, T_p and α_p are the absolute decomposition temperature and weight loss at the maximum weight – loss rate $(d\alpha/dt)_p$, respectively, R is the gas constant, A is the pre-experiment factor and n is the reaction order. E_a was calculated from the slope of the straight line obtained from a plot of $\ln(\beta/T_p^2)$ versus $1/T_p$.

CHAPTER IV

RESULTS AND DISCUSSION

In this chapter, the results have been divided into three parts. The first part is concentrated on the synthesis and characterization of hydrogenated natural rubber (HNR) latex prepared by diimide reduction. The concentration of hydrazine hydrate ($[N_2H_4]$) was varied to control the desired hydrogenation level. For the second part, the HNR latex with 54.3% hydrogenation was grafted with styrene (ST) or ST/methyl methacrylates (MMA) by using emulsion polymerization initiated by redox initiator. Cumene hydroperoxide (CHPO)/tetraethylene pentamine (TEPA) was selected as a couple-redox initiator due to its high efficiency for graft copolymerization (Kangwansupamonkon et al., 2005). To study the effect of grafting parameter, ST was selected as the grafting monomer onto HNR latex. The effect of hydrogenation level, initiator concentration ($[INT]$), monomer concentration ($[M]$), reaction temperature and reaction time on grafting properties was investigated. The structure of samples was characterized by FTIR and degree of hydrogenation was evaluated by 1H -NMR spectroscopy. For the last section, the GHNR latex was coagulated in 5% of formic acid as a crumbed product for blending with ABS. The flexural strength of grafted HNR (GHNR)/ABS blends (10/90% (w/w)) was investigated and fracture surfaces of these blends were observed by SEM. The thermal properties such as glass transition temperature and decomposition temperature of GHNR and GHNR/ABS blends were also reported and compared to ABS containing NR and HNR at similar rubber content.

4.1 Proposed overall reaction mechanism

The overall reaction mechanism for chemical modification of NR latex via hydrogenation and graft copolymerization to produce GHNR is proposed as shown in Figure 4.1. Firstly, NR latex was partially hydrogenated via the reduction of

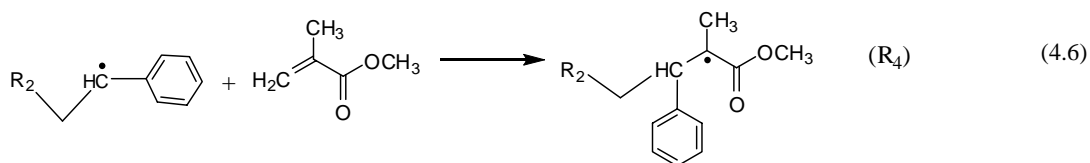
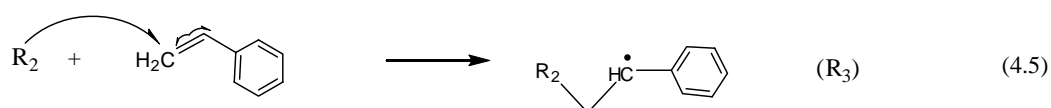
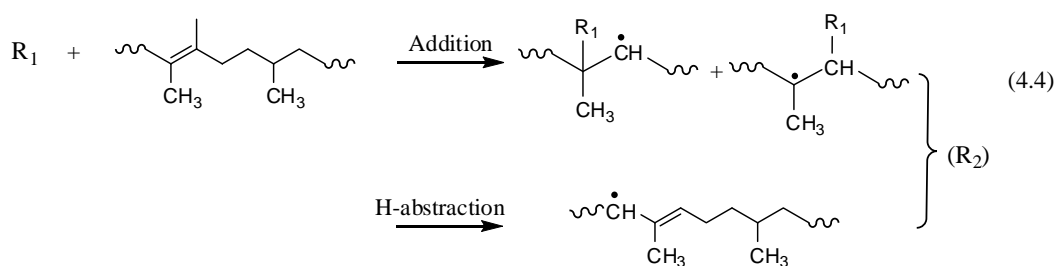
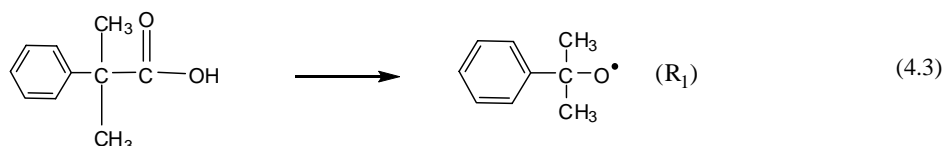
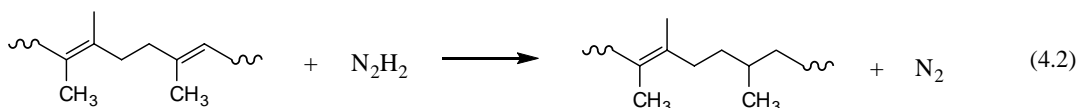
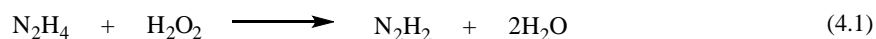


Figure 4.1 The mechanism propose for chemical modification of NR latex via diimide reduction and graft copolymerization.

diimide reduction. This reaction is redox reaction between N_2H_4 and H_2O_2 catalyzed by CuSO_4 to generate the diimide (N_2H_2) (Eq.4.1). Then, the N_2H_2 reacted with $\text{C}=\text{C}$ bonds in isoprene unit to form HNR latex (Eq.4.2) (Mahittikul, Prasassarakich, Rempel, 2007; Simma, prasassarakich, Rempel, 2009). The HNR latex was continuously grafted with ST or ST/MMA monomer initiated by CHPO/TEPA redox system. Since the CHPO/TEPA is quite different in the partitioning ability of initiator between the monomer-swollen rubber phase and aqueous phase, this initiator system could give high grafting efficiency for graft copolymerization at rubber particle/water interface in the rubber latex system (Kochthongrasamee, Prasassarakich,

Kiatkamjornwong, 2006). The cumyloxyl radicals (R_1) were generated by decomposition of CHPO induced by TEPA (Eq.4.3) at the rubber particle/water interface. Then, R_1 might attack the residual C=C bonds of HNR backbone by addition to produce the secondary and tertiary polyisoprenyl radicals (R_2) (Eq.4.4) or abstraction of allylic-hydrogen atoms from HNR backbone (Eq.4.4). These macroradicals might initiated ST monomer to form styryl radicals (R_3) (Eq.4.5) and then might be further reacted with either ST monomer to produce the longer grafted chains for polystyrene (PS-*g*-HNR) or styryl radicals (R_3) copolymerized with MMA monomer to yield poly(ST-*co*-MMA)-*g*-HNR (Eq.4.6) (Angnanon, Prasassarakich and Hinchiranan, 2011; Lin, Pan and Rempel, 2005).

4.2 Structure characterization by using FT-IR and $^1\text{H-NMR}$

The graft copolymer section of GHNR was isolated by using soxhlet extraction to remove all free HNR and homopolymer. The chemical structure of NR before and after modification via hydrogenation and graft copolymerization was characterized by using FT-IR and confirmed by using $^1\text{H-NMR}$ spectroscopy.

4.2.1 FT-IR spectroscopic characterization

The functional groups analyzed by FT-IR spectroscopy of NR, HNR (54.3% hydrogenation), GHNR(ST) (54.3% hydrogenation; 19.2% GE) and GHNR(ST/MMA) (54.3% hydrogenation; 27.3% GE) are shown in Figure 4.2. The FT-IR spectrum of NR (Figure 4.2a) exhibits the absorption peak of aliphatic C-H stretching at $2,970\text{ cm}^{-1}$, C=C stretching at $1,664\text{ cm}^{-1}$, CH_2 bending vibration at $1,473\text{ cm}^{-1}$ and C=C bending vibration at 837 cm^{-1} . After diimide reduction (Figure 4.2b), the structure of NR latex become more saturated as seen from the reduction of the C=C stretching absorption bands around $1,664\text{ cm}^{-1}$ and C=C vibration at 837 cm^{-1} and the new characteristic peak at 737 cm^{-1} corresponded to the $-(\text{CH}_2)-$ groups was appeared in the structure of HNR latex.

After graft copolymerization with ST and ST/MMA, the structure of graft copolymer after isolation showed the new signals assigned as benzene ring at 700 cm^{-1} (Figure 4.2c), C=O stretching at $1,732\text{ cm}^{-1}$ and C-O-C stretching at $1,147\text{ cm}^{-1}$ (Figure 4.2d).

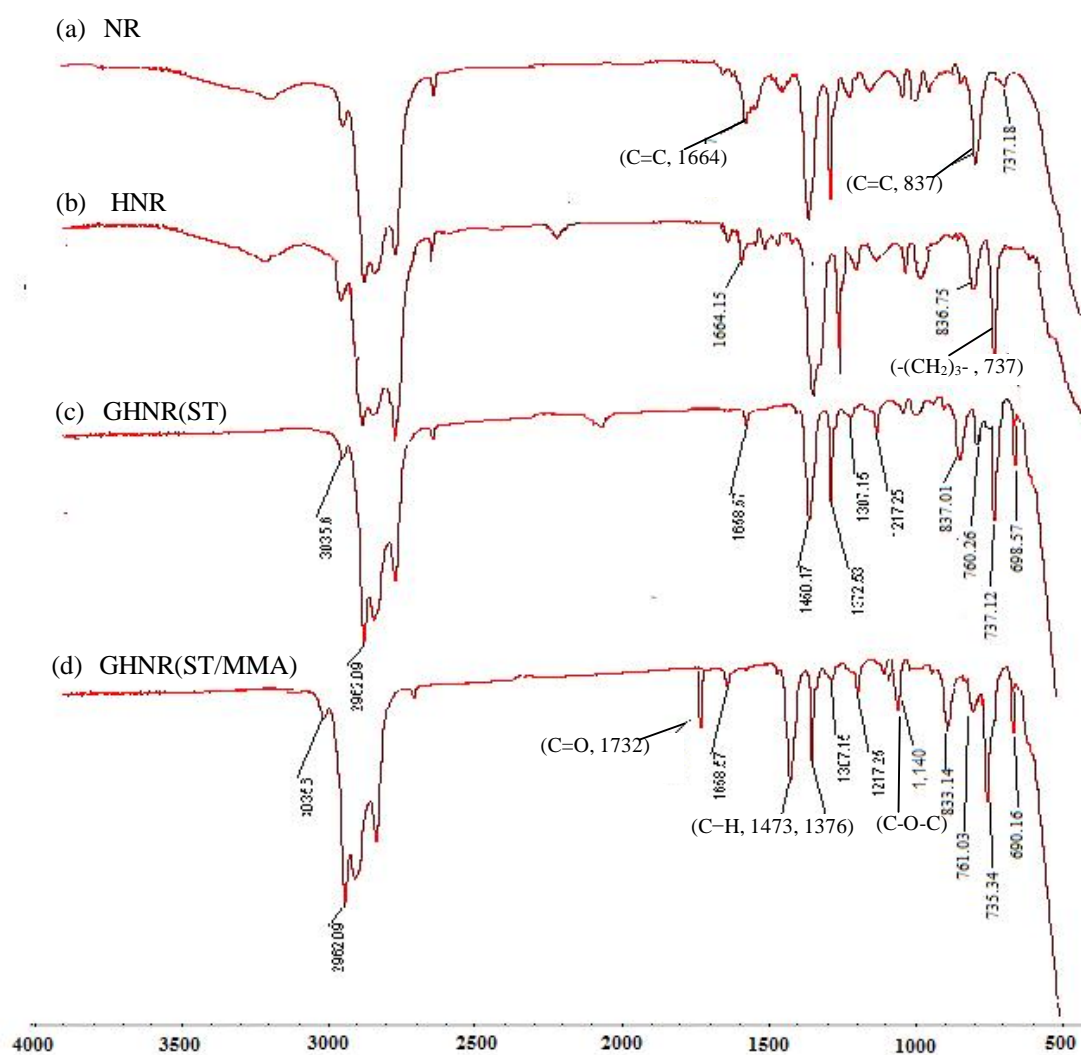


Figure 4.2 FT-IR spectra of (a) NR, (b) HNR (54.3% hydrogenation), (c) GHNR(ST) (54.3% hydrogenation; 19.2% GE) and (d) GHNR(ST/MMA) (54.3% hydrogenation; 27.3% GE).

4.2.2 $^1\text{H-NMR}$ spectroscopic characterization

To confirm the FT-IR result, the structure of modified NRs were analyzed by using $^1\text{H-NMR}$ spectroscopy. Before modification (Figure 4.3a), the $^1\text{H-NMR}$ signals of NR appear at 1.7 and 2.2 ppm corresponded to aliphatic proton. The peak at 5.1 ppm attributed to the *cis*-olefinic proton. After diimide reduction (Figure 4.3b), the peak at 5.1 ppm tended to be decreased and the peaks at 1.7 and 2.2 ppm also shifted to the new signals at 0.8 and 1.2 ppm, which were the regions of saturated $-\text{CH}_3$ and saturated $-\text{CH}_2-$ units, respectively. The extent of hydrogenation was calculated from the change in the integral area of peaks representing protons for HNR as presented in Appendix B.

When HNR latex grafted with ST, the $^1\text{H-NMR}$ spectra of graft copolymer showed the signal of aryl proton of ST in the range of 6.5-8.0 ppm as shown in Figure 4.3c. When ST/MMA mixture monomer (Figure 4.3d) was grafted onto HNR latex, the $^1\text{H-NMR}$ signals also appeared at 6.5-8.0 ppm for aryl protons of ST and 3.53 ppm corresponding to methoxyl proton ($-\text{OCH}_3$) of MMA.

4.3 Preparation of HNR latex

The HNR latex was prepared by using diimide reduction catalyzed by CuSO_4 . The level of hydrogenation was controlled by adjustment of N_2H_4 content ($[\text{N}_2\text{H}_4]$) in the range of 0.6 to 3.14 M when the concentration of $\text{C}=\text{C}$ bonds in the NR latex was kept constant at 0.55 M in the presence of $49.4 \mu\text{M}$ of CuSO_4 and 3.53 M of H_2O_2 at 60°C for 6 h. The results shown in Figure 4.4. indicated that the degree of hydrogenation increased with increasing $[\text{N}_2\text{H}_4]$ due to the higher diimide (N_2H_2) formation which could produce the large amount of hydrogen for hydrogenation of the $\text{C}=\text{C}$ bonds (Mahittikul et al., 2007; Simma et al., 2009). The maximum hydrogenation level at 54.3% was obtained when the N_2H_4 concentration was 2.68 M. However, the increase in the $[\text{N}_2\text{H}_4]$ above this point decreased the hydrogenation level since some diimide species could self-react at high N_2H_4 concentration.

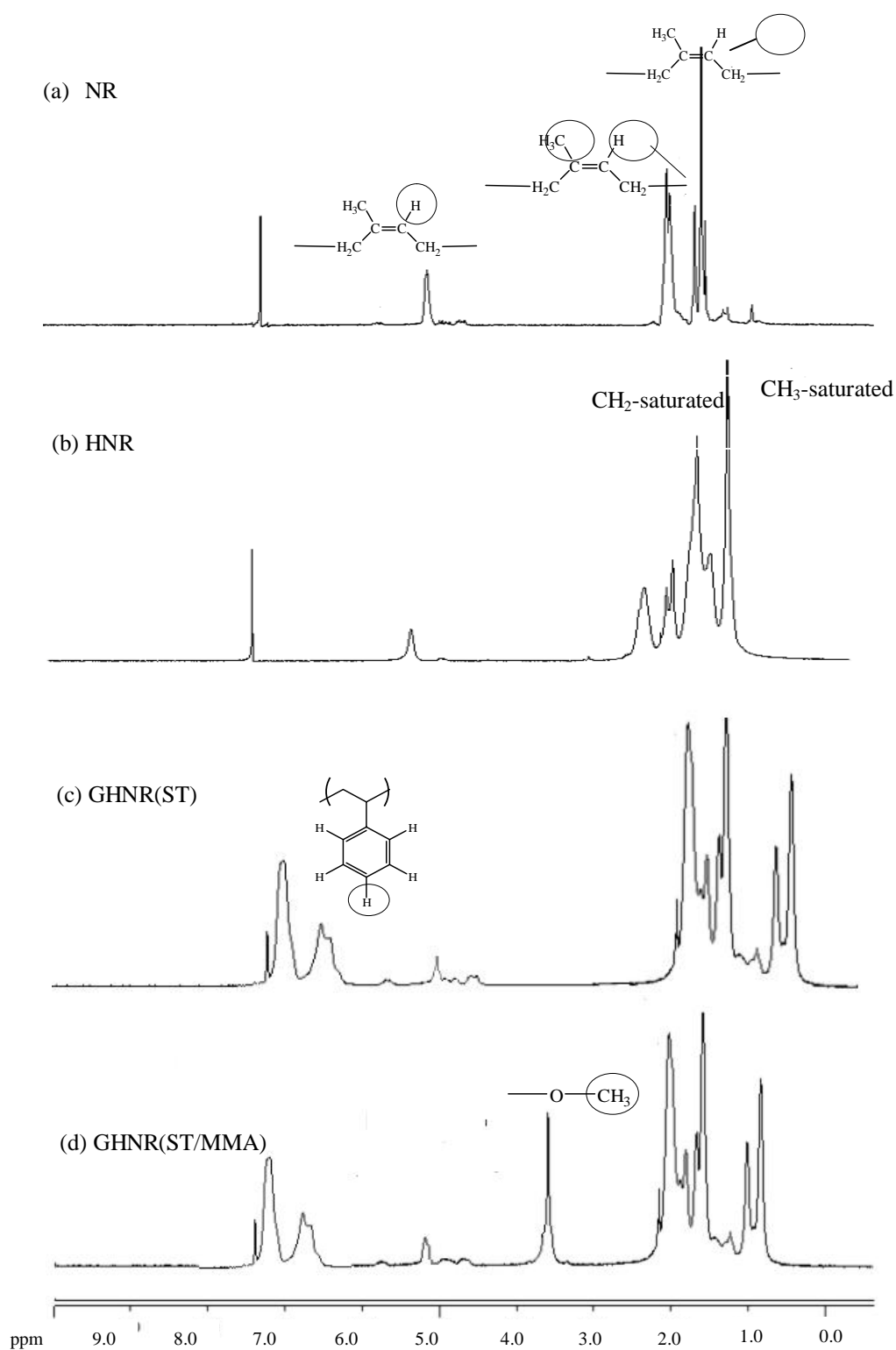


Figure 4.3 $^1\text{H-NMR}$ spectra of (a) NR, (b) HNR (54.3% hydrogenation), (c) GHNR(ST) (54.3% hydrogenation; 19.2% GE) and (d) GHNR(ST/MMA) (54.3% hydrogenation; 27.3% GE).

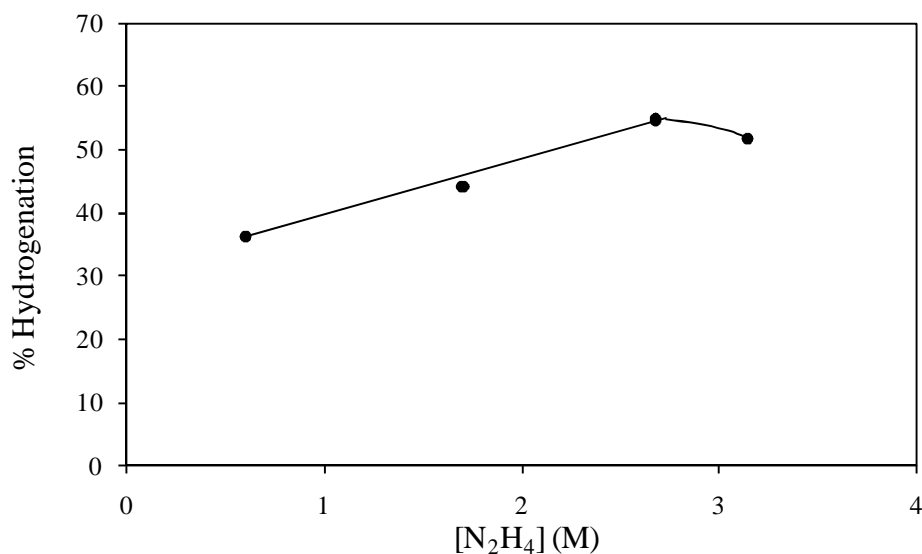


Figure 4.4 Effect of hydrazine concentration on NR latex hydrogenation: [CuSO₄] = 49.4 M; [H₂O₂] = 3.54 M; [C=C] = 0.55 M at 60 °C for 6 h.

Moreover, the excess content of N₂H₂ in this system might also diffuse into the aqueous phase resulting the reduction of the hydrogenation efficiency (Mahittikul et al., 2007; Xie et al., 2002).

4.4 Graft copolymerization of HNR latex

To study the effect of reaction parameters on the graft copolymerization of HNR latex, the ST monomer was selected as the grafting monomer. The graft copolymerization was carried out by emulsion polymerization initiated by CHPO/TEPA (1/1 (w/w)) redox system. The effect of reaction variables such as %hydrogenation, monomer concentration, initiator loading, reaction time and reaction temperature on the %conversion, %grafting efficiency (%GE) and grafting properties was investigated.

4.4.1 Effect of hydrogenation level

The effect of hydrogenation level on grafting properties, %conversion and %GE of GHNR latex was investigated. The graft copolymerization of ST onto HNR latex was carried out by varying the degree of hydrogenation in the range of 36.3 to 54.3% initiated by using 1 phr of CHPO/TEPA (1/1 (w/w)) at 50 °C for 8 h. The monomer concentration was kept at 30 phr. The results shown in Figure 4.5 indicated that the increase in the %hydrogenation of HNR latex from 0 to 54.3% decreased % conversion, %GE and %graft copolymer from 55.2, 39.6 and 38.8% to 26.4, 11.1 and 18.7%, respectively. This could be explained that HNR latex with higher %hydrogenation has lower unsaturated C=C bonds acting as grafting sites. Moreover, HNR latex produced from diimide reduction is normally occurred gel or crosslinking formation during reaction (Mahitikul et al., 2007). This might inhibit the accessibility of monomer to grafting sites resulting in the lower % conversion and %GE.

The effect of chemicals for HNR preparation on graft copolymerization of ST was also individually investigated on NR latex as shown in Table 4.1. The concentrations of N_2H_4 , H_2O_2 and $CuSO_4$ were controlled as similar to those used in the diimide reduction. The results indicated that the small amount of $CuSO_4$ did not affect the %conversion and %GE for graft copolymerization of NR latex and %graft copolymer decreased due to the $CuSO_4$ might be still adsorbed onto the surface of rubber particles to inhibit the graft copolymer. The styryl radicals were higher propagated long chains than grafting onto surface of rubber particles. However, the addition of N_2H_4 and H_2O_2 significantly decreased the %conversion and %GE of graft copolymerization of NR latex. For H_2O_2 , it was postulated that H_2O_2 could induce the overdose of free radicals to promote the termination of graft copolymerization (Bakar, Mat and Isnin, 2008; Jideonwo and Adimula, 2006). For the N_2H_4 , the N_2H_4 and H_2O_2 to produce the diimide normally occurred at the surface of rubber particles (Mahittikul et al., 2007). Thus, N_2H_4 could not be transformed as diimide in the absence of H_2O_2 and it might be still adsorbed onto the surface of rubber particles to inhibit the graft copolymerization.

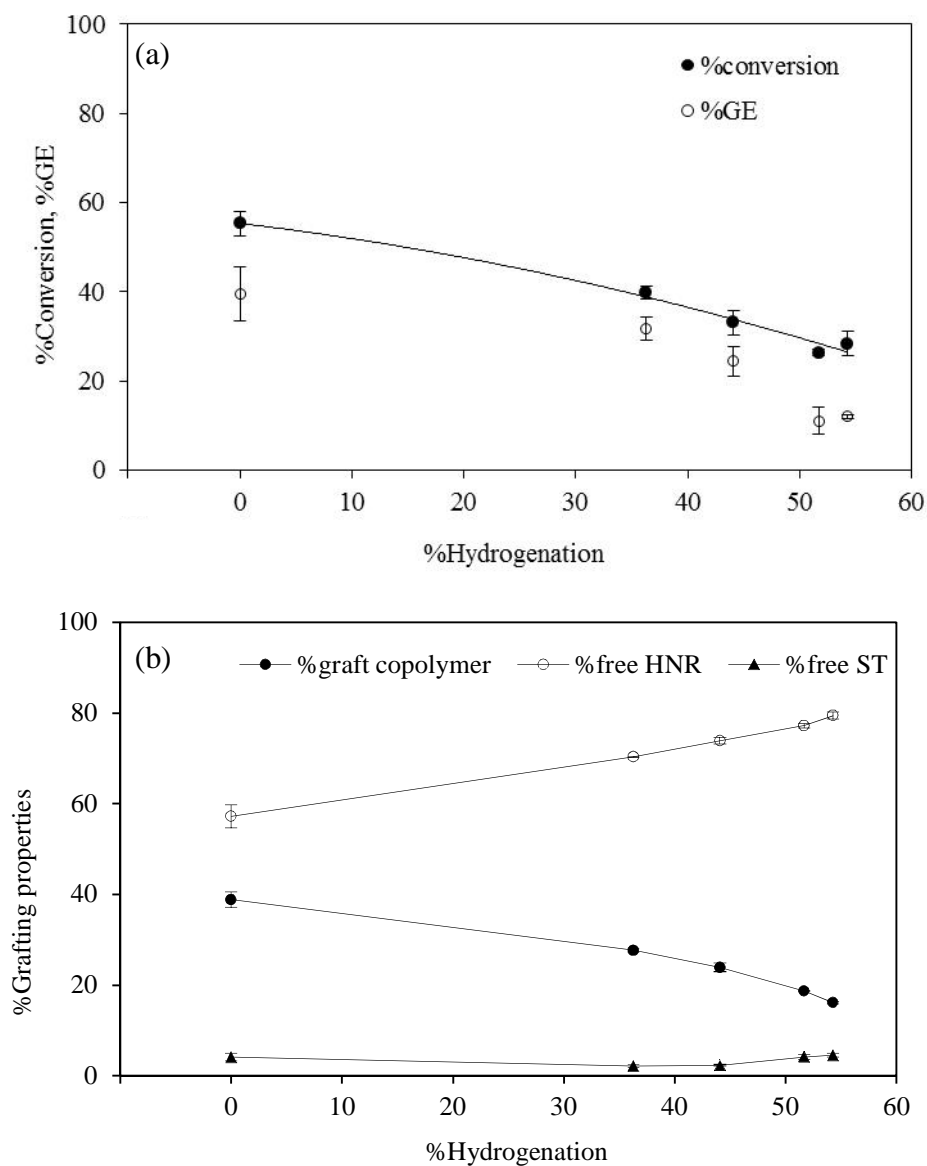


Figure 4.5 Effect of %hydrogenation on grafting properties: (a) %conversion and %GE and (b) %graft HNR, %free HNR and %free ST. Condition: %hydrogenation = 54.3, [CHPO/TEPA] = 1 phr, [ST] = 30 phr at 50°C for 8 h.

Table 4.1 Effect of chemicals for diimide reduction on graft copolymerization of ST onto NR latex.

Exp.	%Conv.	Grafting properties			
		%Graft NR	%Free NR	%Free ST	%GE
-	66.7 (3.08)	62.0 (1.70)	18.0 (6.56)	20.0 (4.86)	52.8 (1.49)
N ₂ H ₄	44.8 (0.00)	18.0 (0.71)	80.2 (0.23)	1.78 (0.95)	41.9 (1.54)
H ₂ O ₂	32.4 (5.69)	26.3 (11.1)	71.2 (11.5)	2.57 (0.40)	26.3 (7.65)
CuSO ₄	62.7 (2.76)	45.0 (0.73)	51.7 (0.75)	3.30 (1.48)	56.7 (0.01)

Condition: [N₂H₄] = 2.68 M, [H₂O₂] = 3.53 M, [CuSO₄] = 42.4 μM, [CHPO/TEPA] = 1.5 phr, [ST] = 100 phr at 50 °C for 8 h.

4.4.2 Effect of monomer

The HNR latex with highest degree of hydrogenation at 54.3% was selected as the backbone polymer for grafting with ST monomer. The effect of the monomer concentration on the grafting properties was investigated by varying the monomer concentration in the range of 30 to 125 phr. The reaction condition was controlled at 1 phr of CHPO/TEPA ((1/1 (w/w))) at 50 °C for 8 h. The results shown in Figure 4.6 indicated that the %conversion, %GE and %graft copolymer increased with increasing of monomer concentration and reached to a highest value at 40.2, 33.2 and 20.8%, respectively when 100 phr of monomer concentration was applied. However, the increase in the monomer concentration higher than 100 phr decreased the %GE and %graft copolymer. It might be explained that the overload of monomer concentration increased the possibility to form homopolymer and promoted the more concentration on grafting was described as illustrated in Figure 4.7. At low monomer

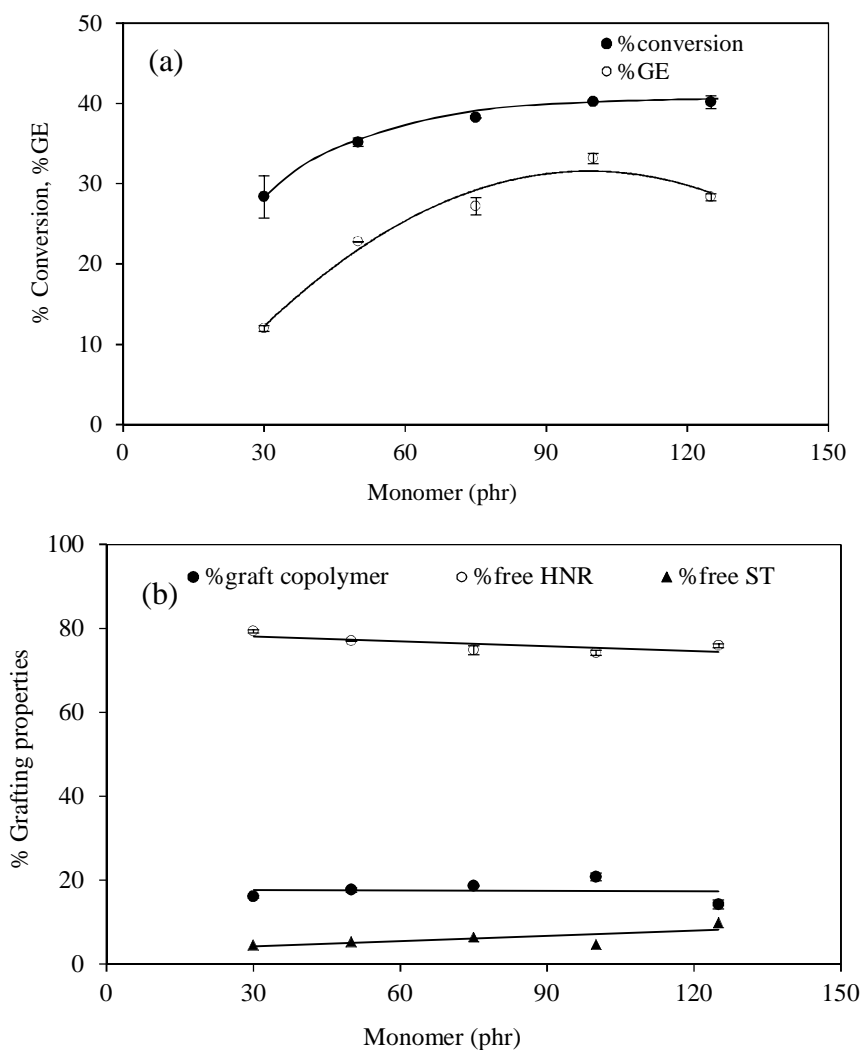
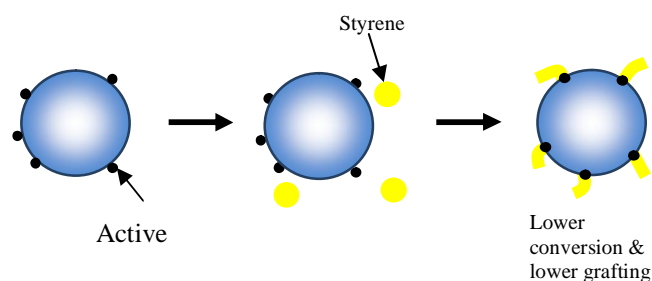


Figure 4.6 Effect of monomer concentration on grafting properties: (a) %conversion and %GE and (b) %graft HNR, %free HNR and %free ST. Condition: %hydrogenation = 54.3, [CHPO/TEPA] = 1/1 phr at 50 °C for 8 h.

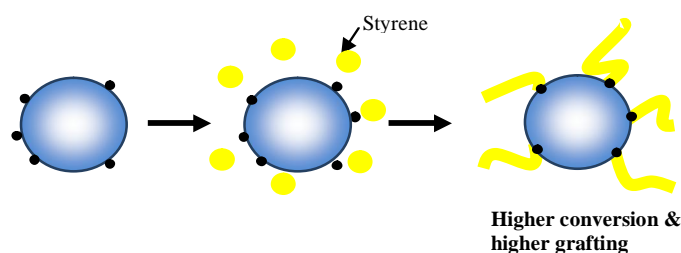
concentration (Figure 4.7a), the insufficient content of monomer for grafting sites led steric hindrance resulting from the growth polymeric chain to limit the newly arriving monomer molecules for grafting. The mechanism for the effect of monomer low %GE value. For appropriate monomer content (Figure 4.7b), all monomer was grafted and polymerized on the grafting sites to produce high %conversion and %GE. The rate of polymerization also increased with increasing of monomer concentration. However, high monomer concentration (Figure 4.7c) gave the long chains of grafting polymer (polystyrene) to promote the steric hindrance to inhibit the accessibility of the

monomer to grafting sites of polymer backbone resulting to low %conversion and %GE. Moreover, many reactions such as chain transfer and oligomer termination could compete with graft copolymerization at high monomer concentration. The homopolymerization was more polymerized than graft copolymerization (Kangwansupamonkon et al., 2005; Pukkate, Yamamoto and Kawahara, 2008; Thiraphattaraphum et al., 2001).

(a) At low monomer concentration



(b) At suitable monomer concentration



(c) At high monomer concentration

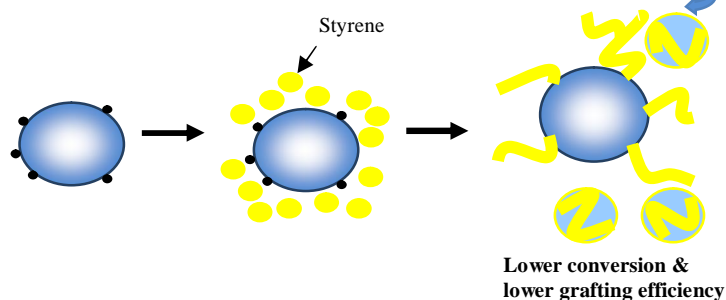


Figure 4.7 Schematic representation for mechanism of graft copolymerization (Pukkate et al., 2008).

4.4.3 Effect of initiator concentration

The effect of the initiator (CHPO/TEPA) concentration varied in the range of 1.0-2.5 phr on the graft copolymerization of ST onto HNR latex was investigated as shown in Figure 4.8. The reaction was performed by using 100 phr of monomer concentration at 50°C for 8 h.

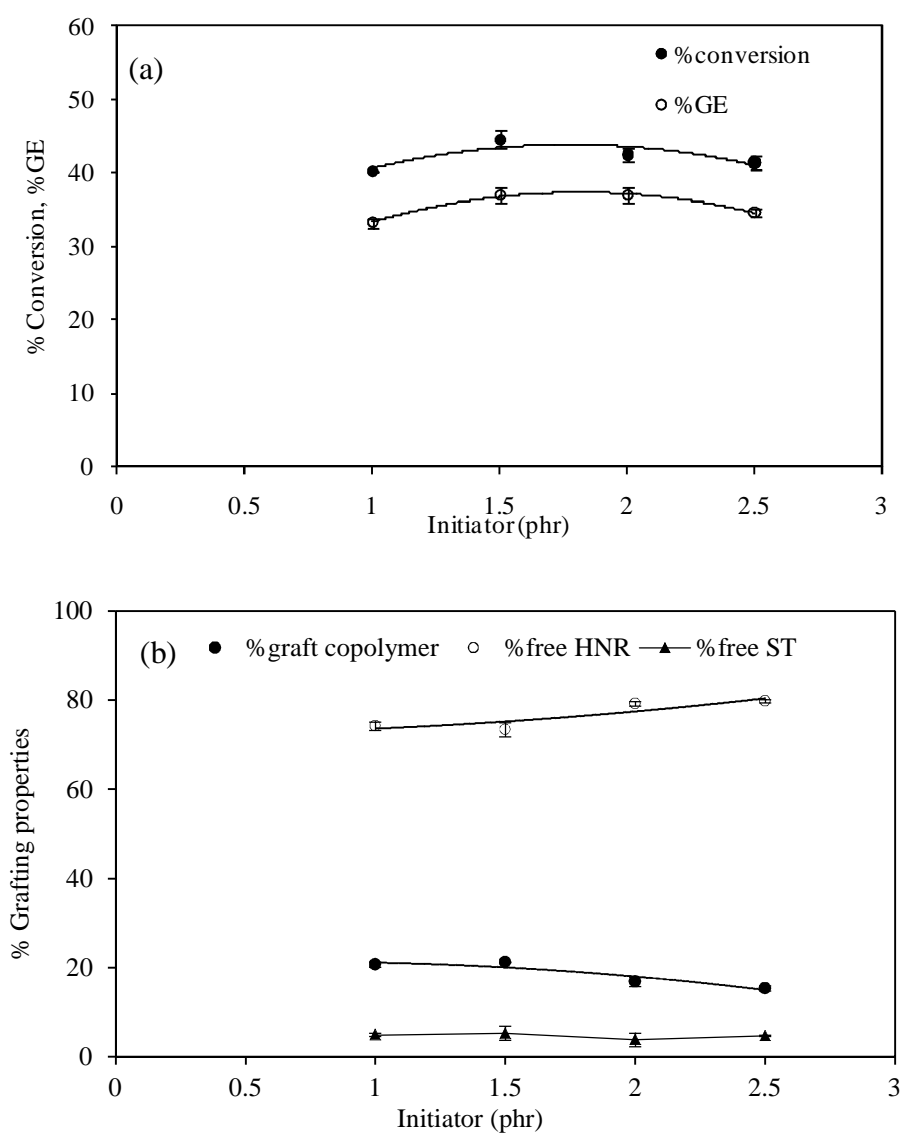


Figure 4.8 Effect of initiator on grafting properties: (a) %conversion and %GE and (b) % graft HNR, %free HNR and %free ST. Condition: %hydrogenation = 54.3, [ST] = 100 phr at 50°C for 8 h.

The results indicated that %conversion, %GE and %graft copolymer slightly increased with increasing the initiator concentration and reached to the maximum value at 44.6, 36.9 and 21.3%, respectively when CHPO/TEPA concentration was applied as 1.5 phr into the system. Thereafter, these grafting properties decreased with increasing the initiator content. This phenomena suggested that the high initiator content produced high loading of free radicals for increasing the number of grafting site. Moreover, the radicals transfer effect to either rubber or monomer also generate macroradicals providing the higher grafting efficiency. However, the overdose of initiator concentration gave excessive free radicals to decrease the rate of chain transfer to give the free polymeric radicals compared to the rate of termination of the free polymer radicals (Kangwansupamonkon et al., 2005). The high initiator loading could also promote the recombination of the initiator radicals (Nakason et al., 2004).

4.4.4 Effect of reaction time

The effect of the reaction time on the graft copolymerization of ST onto HNR latex was studied in range of 4 - 16 h by using 1 phr of [CHPO/TEPA] and 100 phr of [ST] at 50°C. The results shown in Figure 4.9 indicated that the the increase in the reaction time from 4-8 h enhance the %conversion, %GE and %graft copolymer from 23.9 to 40.2%, 23.2 to 33.2% and 14.3 to 20.8%, respectively. The longer reaction time than 8 h did not affect the grafting properties. It could be explained that the extent of initiation and propagation of grafting polymer increased with increasing the reaction time at the induction period (4-8 h) (Shukla, Rao and Athalye, 1991). Most of monomer was polymerized to form new polymeric radical until these monomers were completely consumed to reach the maximum conversion. However, these grafting properties leveled off when the reaction was leaved longer than 8 h due to the decrease in the monomer and initiator concentrations and retardation diffusion effect from the previous polymer produced on the surface of rubber particles (Lutfor, et al., 2000). This also decreased the formation of the active grafting sites on the HNR particles to increase the %free ST (Figure 4.5b) (Thiraphattaraphun et al., 2000; Arayapranee and Rempel, 2008).

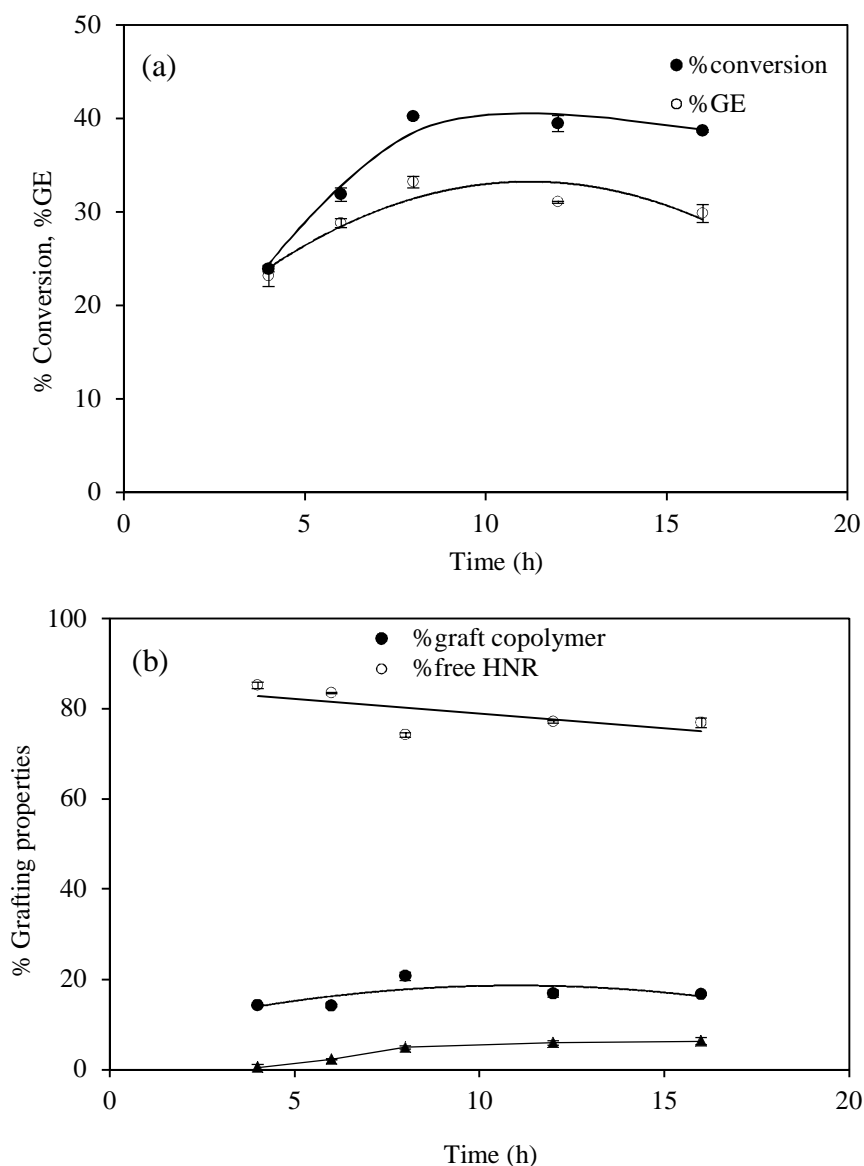


Figure 4.9 Effect of reaction time on grafting propertier: (a) %conversion and %GE and (b) %graft HNR, %free HNR and %free ST. Condition: %hydrogenation = 54.3, [CHPO/TEPA] = 1/1 phr, [ST] = 100 phr at 50°C.

4.4.5 Effect of reaction temperature

The effect of reaction temperature (30 - 80°C) on %conversion, %GE and %graft copolymer of graft copolymerization of ST onto HNR latex was

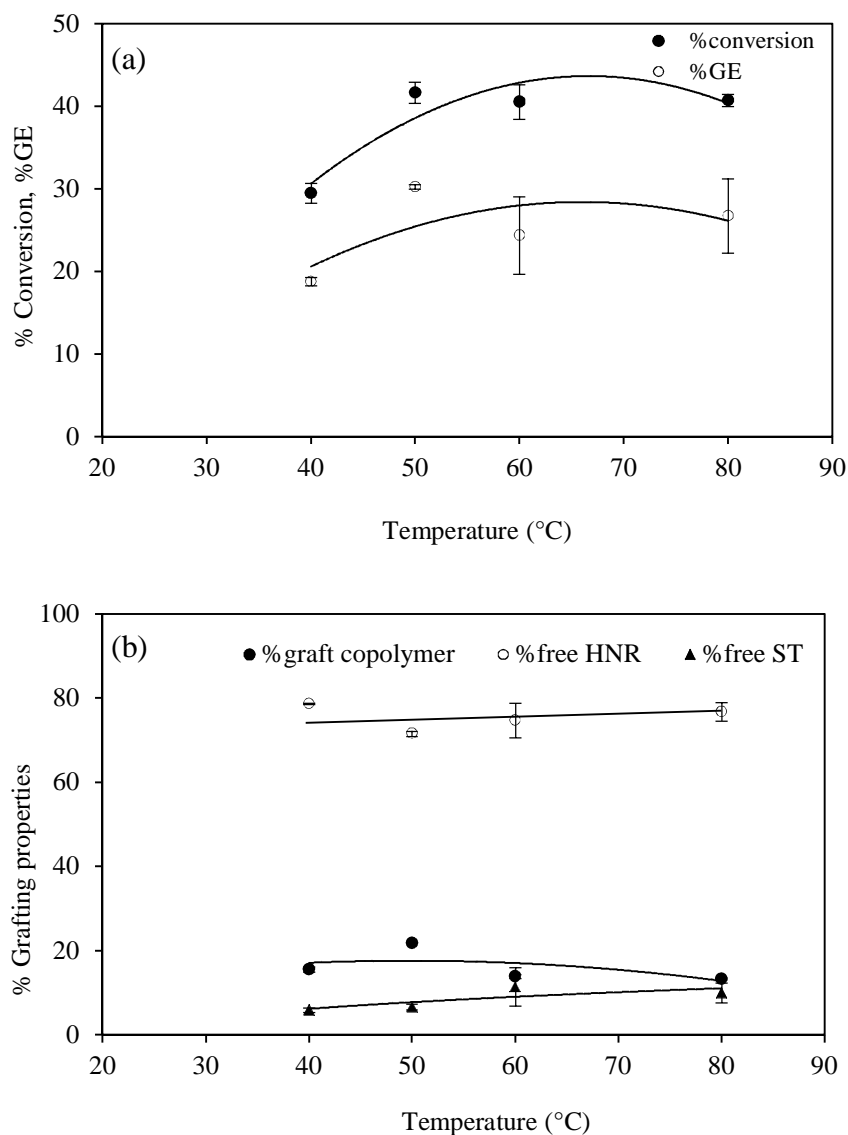


Figure 4.10 Effect of reaction temperature on grafting properties: (a) %conversion and %GE and (b) %graft HNR, %free HNR and %free ST. Condition: %hydrogenation = 54.3, [CHPO/TEPA] = 1 phr, [ST] = 100 phr for 8 h.

investigated when the reaction was performed at 100 phr of [ST] initiated by 1 phr of CHPO/TEPA for 8 h. The results shown in Figure 4.10 indicated that the %conversion, %GE and %graft copolymer increased with increasing the temperature. The reaction temperature at 50°C gave the highest %conversion, %GE and %free HNR (41.6, 30.2 and 21.8%, respectively). This could be explained that the higher rate of decomposition of the initiator induced the higher number of free radicals on the

backbone acted as grafting site. Moreover, the higher reaction temperature promoted the reduction in the viscosity of the system to enhance the mobility of the molecular chains to simplify for grafting. However, the increase in the reaction temperature above 50°C decreased the grafting properties and %GE due to the higher possibility to terminate the grafting polymeric chain resulting from the large amount of free radicals generated at high reduction temperature (Nakason, Kaesaman and Supasanthitikul, 2004).

4.5 Effect of MMA monomer for graft copolymerization of HNR latex

To improve the polarity of graft copolymer, the MMA monomer was selected as the co-monomer with ST. The effect of MMA on the graft copolymerization of ST onto HNR latex was also studied as shown in Table 4.2. The reaction was performed by using 100 phr of MMA/ST (25/75 % (w/w)) initiated by 1.5 phr of CHPO/TEPA (1/1 (w/w)) at 50°C for 8 h. The results showed that the addition of MMA did not affect the %conversion. Whereas, the %GE of graft copolymerization using ST/MMA decreased from 36.9% to 27.3% and the %graft copolymer also decreased from 21.3 to 17.7% . It could be theoretically explained that the binary monomer was more complex than one monomer due to the difference of the solubility of monomer to result the more complexed than one monomer and swelling ability of substrates in the grafting process. The reactivity ratio of ST ($r_{st} = 0.73 \pm 0.05$) was also higher than that of MMA ($r_{MMA} = 0.19 \pm 0.05$) (Annemieke et al., 1994). Thus, it was possible that ST could be grafted onto HNR particles than MMA (Kiatkamjornwong and Meechai, 1997).

Table 4.2 Effect of MMA on graft copolymerization of ST onto HNR latex.

Exp.	Grafting properties				
	%Conv.	%Graft HNR	%Free HNR	%Free ST	%GE
GHNR(ST)	44.6(1.20)	21.3(1.52)	67.7(0.05)	11.1(1.58)	36.9(1.06)
GHNR(ST/MMA)	44.3(2.67)	17.7(1.36)	67.4(1.29)	14.9(0.07)	27.3(2.42)

Condition: %Hydrogenation = 54.3, [CHPO/TEPA] = 1.5 phr, [ST/MMA] = 75:25 at 50°C for 8 h.

4.6 Morphology of HNR and GHNR latex

The latex morphologies of NR, HNR (54.3% hydrogenation), GHNR(ST) (54.3% hydrogenation; 19.2% GE) and GHNR(ST/MMA) (54.3% hydrogenation; 27.3% GE) by TEM are shown in Figure 4.11. The morphology of NR, HNR and both GHNR latexes were observed by OsO₄ staining of the carbon-carbon double bonds of NR to increase the contrast and gradation of the particles. From Figure 4.10a, the morphology of the NR particles shows the spherical shape having a smooth surface. After hydrogenation, the morphologies of HNR latex (54.3% hydrogenation) as shown in Figure 4.10b indicated the darker areas at core region representing the non-hydrogenated NR with high content of C=C bonds providing the OsO₄ absorption area. The lighter area at the shell covering the dark region was claimed as the hydrogenated NR due to the less C=C content resulting to the lower amount of OsO₄ absorption

After graft copolymerization of ST onto HNR latex, the TEM morphology of GHNR(ST) latex is shown in Figure 4.10c. It was observed that comb-like morphology which, the graft copolymer of ST attached at the outer surface of HNR particles. It was possible that some styryl radicals were firstly grafted with

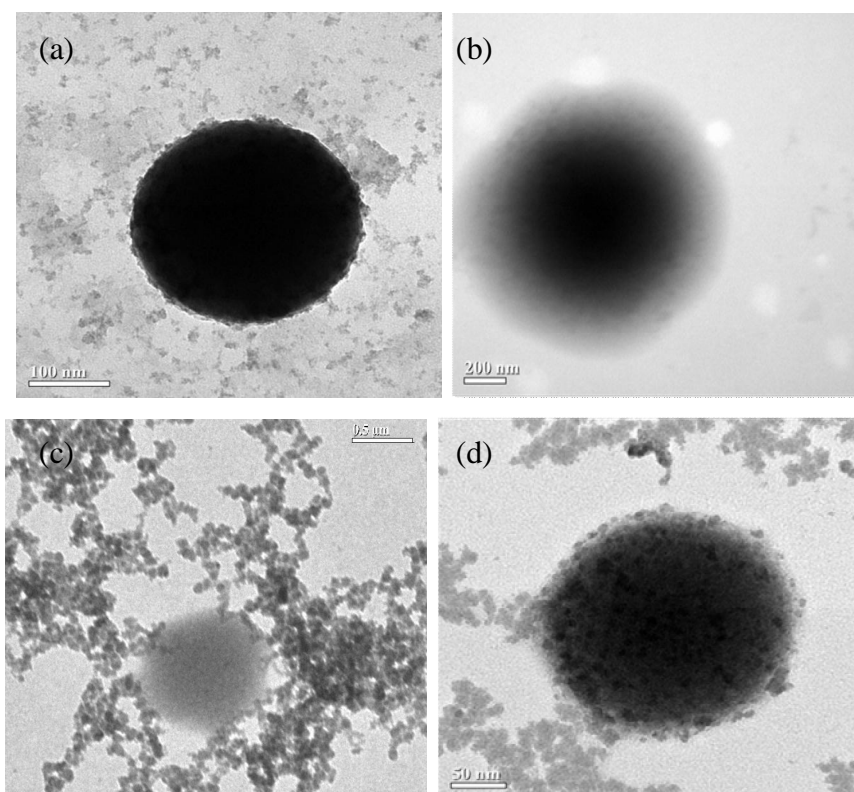


Figure 4.11 Morphologies (a) NR and modified NR; (b) HNR (54.3% hydrogenation), (c) GHNR(ST) (54.3% hydrogenation; 19.2% GE) and (d) GHNR(ST/MMA) (54.3% hydrogenation; 27.3% GE) (Magnification; 10,000x)

existing carbon-carbon double bond of HNR latex and then continuously propagated as long chain polystyrene. For grafting of ST/MMA onto HNR latex, the morphology of GHNR(ST/MMA) latex (Figure 4.10d) also showed the raspberry morphology which, the long chains of poly(ST-co-MMA) grafted at the outer surface of HNR particles. It could be postulated that the growing macroradical chains were grafted onto the surface of HNR particle through residue carbon-carbon bond and continued to propagate to form long grafting-polymeric chains (Arayapranee et al., 2004).

4.7 Flexural strength of modified NR/ABS before and after thermal aging and morphology

To apply the GHNR for ABS production for serving as the green-conceptual product, the GHNR was blended with ABS resin at a ratio of GHNR/ABS = 10/90 (w/w). The flexural strength of GHNR/ABS blends was examined and compared to the neat ABS, NR/ABS and HNR/ABS blends as shown in Figure 4.12 and 4.13. From the flexural stress-strain curve (Figure 4.12), all samples show the ductile failure characteristics. It was observed that the addition of NR with/without modification caused the reduction of flexural strength (Figure 4.13). Especially, the addition of HNR into the ABS resin showed the lowest flexural strength (78.5 ± 0.86 MPa) with lowest extension value. This might be due to the loss of elasticity of HNR compared to NR before hydrogenation (Hinchiranan et al., 2009). Moreover, the high difference in polarity also promoted incompatibility between HNR and ABS phase as shown in the SEM micrograph (Figure 4.14c) that exhibited the small holes dispersed throughout the surface of the HNR/ABS sample.

However, the graft copolymerization of ST and ST/MMA provided the functional groups that enhanced the polarity of HNR-backbone. This might increase the compatibility of the constituents in the specimens resulting the improvement of flexural strength of samples to 96.9 MPa and 99.8 MPa for the addition of GHNR(ST) and GHNR(ST/MMA), respectively. The higher homogeneity of the samples containing graft products was revealed by SEM micrographs as shown in Figure 4.14d and 4.14e. Although the addition of modified or unmodified NR gave the lower value of flexural strength of the specimens than that of ABS resin, this gave the advantage in a term of lower energy consumption applied for shaping the specimens in any desired forms.

The effect of thermal aging on the flexural strength of the specimen was also investigated at 165°C for 25 min in hot air oven for outdoor applications. The results shown in Figure 4.13 indicated that the flexural strength of ABS and rubber/ABS blends decreased.

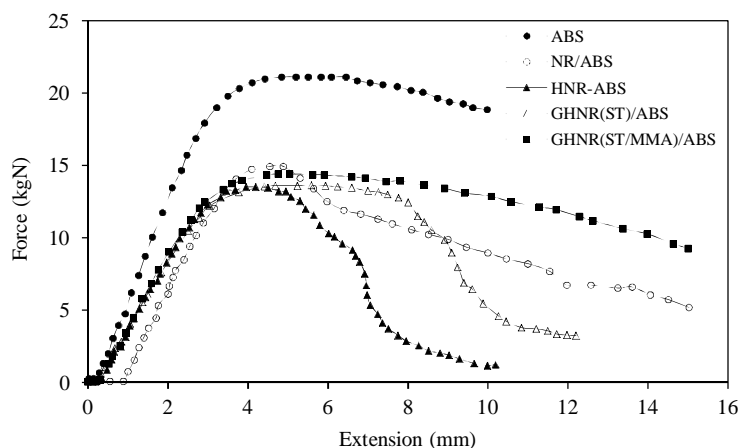


Figure 4.12 Stress-strain curve of modified rubber/ABS blend (ratio at 10/90 (w/w)).

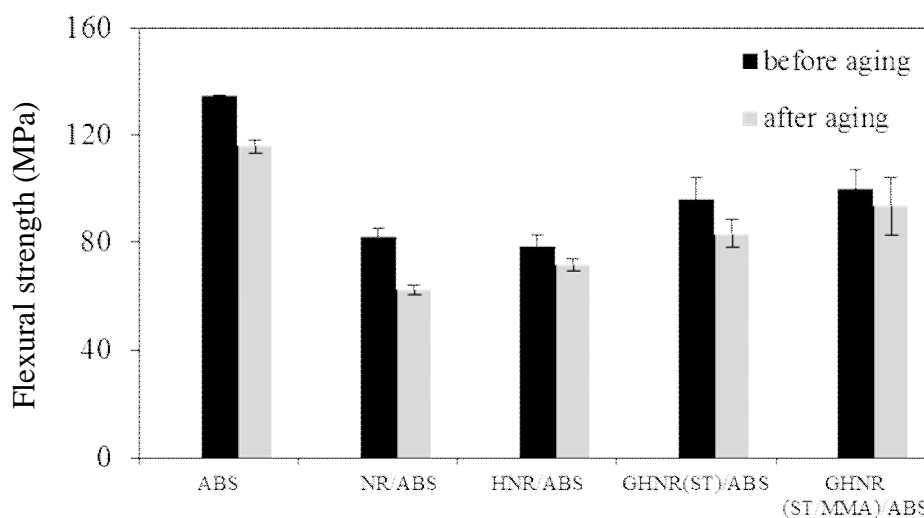


Figure 4.13 Flexural strength of modified rubber/ABS (10/90 w/w) before and after aging.

However, after addition of modified NR such as HNR, GHNR(ST) and GHNR(ST/MMA) in ABS, the flexural strength after thermal aging of modified NR/ABS blends decreased by 8.5, 13.0 and 6.0%, respectively. Thus, it implied that ABS containing GHNR(ST/MMA) could higher retain the flexural strength under long period in high temperature due to the HNR section with lower C=C bonds and styrenic group and methoxycarboxyl groups in PS and PMMA. However, ABS and

unmodified NR/ABS had lower resistance to the high temperature in long period due to the degradation of ABS occurred in the unsaturated PB phase via hydrogen abstraction from the the α -carbon to the *trans*-1,4 and 1,2 unsaturated PB leading to hydroperoxide radicals (Tiganis and Burn, 1999).

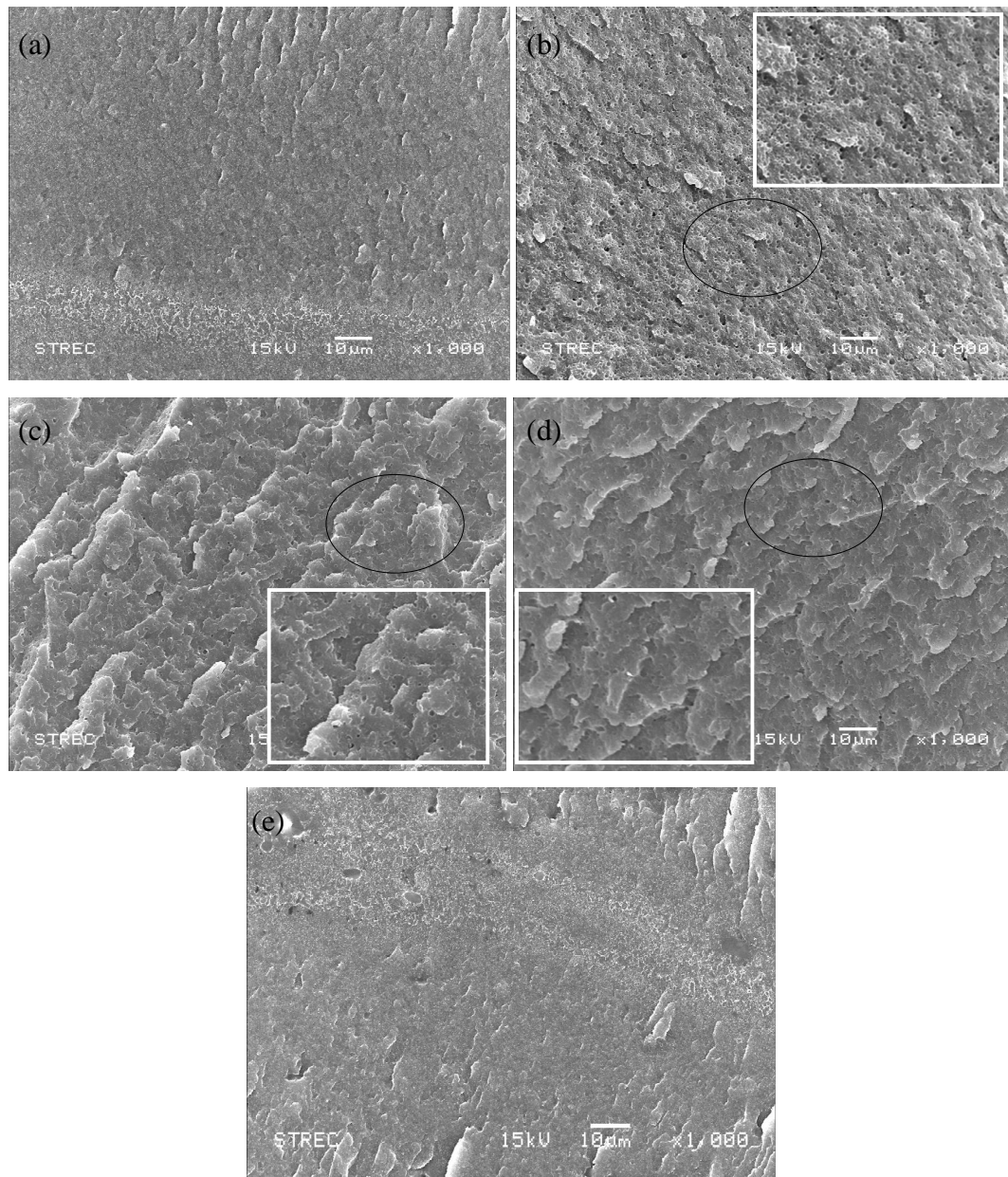


Figure 4.14 SEM morphology of modified rubber/ABS blends (10/90 w/w): (a) ABS, (b) NR/ABS, (c) HNR/ABS, (d) GHNR(S)/ABS and (e) GHNR(ST/MMA)/ABS (magnification: 1000x).

4.8 Thermal properties of modified NR and modified NR/ABS blends

The thermal analysis is used to study the thermal properties of the polymer as the function of temperature. The differential scanning calorimetry (DSC) and the thermal gravimetric analysis (TGA) were used to determine the glass transition temperature (T_g), initial decomposition temperature (T_{id}) and maximum decomposition temperature (T_{max}). The T_g value is the transition temperature related to the motion in the amorphous section of polymer. It could be obtained from the midpoint of based-line shift of the DSC thermogram. The T_{id} and T_{max} were analyzed from TGA thermogram. T_{id} was derived from the intersection of two tangents at the onset of the decomposition temperature and T_{max} was determined from the maximum peak of the derivative of the TGA curves. Moreover, TGA was also used to investigate the kinetics of the thermal decomposition of samples by varying the heating rates of 2.5, 5.0 and 10°C.

4.8.1 Glass transition temperature of samples analyzed by DSC

The DSC thermograms of NR, HNR, both GHNRs and their polymer blends were presented in Figures 4.15, 4.16 and Table 4.3. The DSC thermogram of NR (Figure 4.15a) exhibited the one step base-line shift at -64.3 °C. After hydrogenation, two step based-line shift was observed as shown in Figure 4.15b indicated the T_g values at -63.7 °C for non-hydrogenated NR and the T_g value at -42.6 °C for hydrogenated NR. This means that the T_g of HNR was increased due to the amorphous segments and partially replaced by crystalline units.

For the grafting HNR, DSC thermograms of GHNR(ST) (Figure 4.15c) and GHNR(ST/MMA) (Figure 4.15d) showed three and four based-line shift, respectively. It could be observed that the low T_g value was similar to that T_g HNR. Moreover, the higher T_g value at 62.1°C and 80.75°C were corresponded to the T_g value of polystyrene (PS) and poly(methyl methacrylate) (PMMA), respectively. Hence, it was confirmed that PS and PMMA were incorporated with HNR backbone.

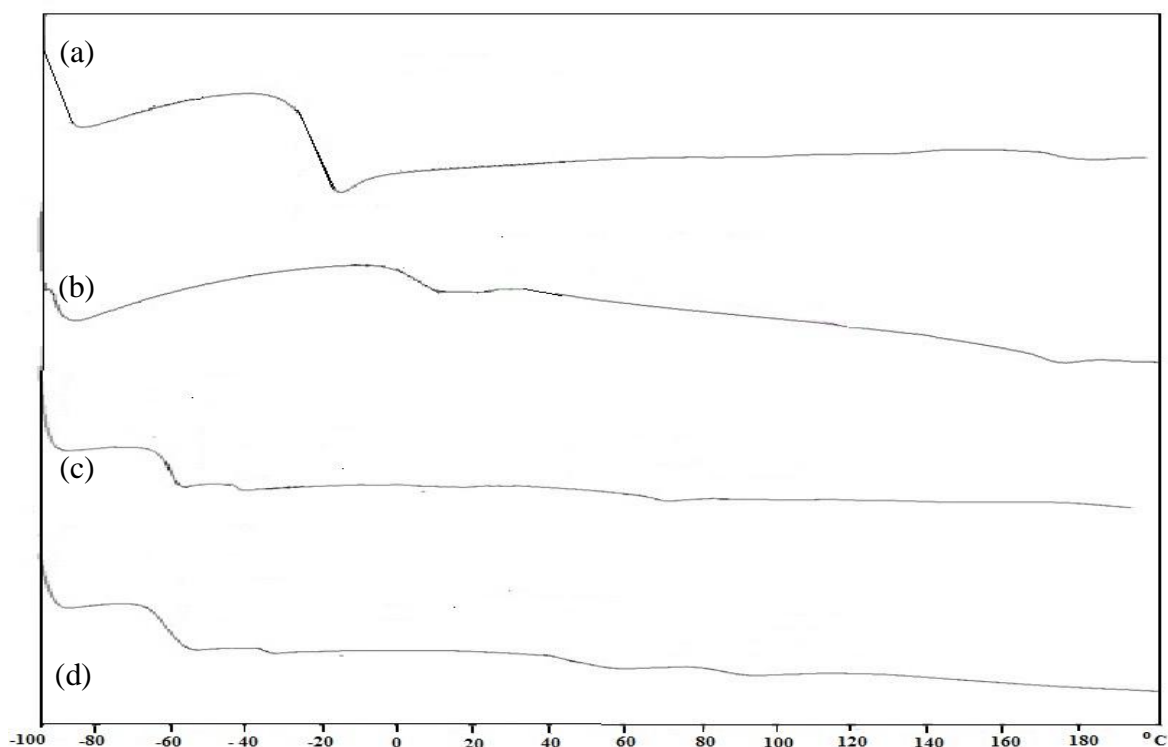


Figure 4.15 DSC thermograms of: (a) NR and modified NR; (b) HNR (%hydrogenation = 54.3), (c) GHNR(ST)(%hydrogenation = 54.3; %GE = 36.9) and (d) GHNR(ST/MMA) (%hydrogenation = 54.3; %GE = 27.3).

For the polymer blends, the T_g of the polymer blends plays an important role in differentiating the polymer blends as phase-separation or as a single-phase system. The one step based-line shift at 106.3°C was occurred in pure ABS as shown in Figure 4.16a (Lashgari et al., 2010), whereas, ABS containing NR or ABS containing modified NR showed the two step based-line shift. After addition of with/without modified NR, the T_g value of all samples containing NR or modified NR slightly decreased when compared with neat ABS due to the elasticity of rubber phase resulting to the increasing the mobility of the polymer chain. Moreover, the T_g of ABS containing GHNR(ST/MMA) (105.8°C) had higher than that ABS containing NR (103.2°C) because of the rigid structure of PS and PMMA providing the reduction of the mobility of polymer chain.

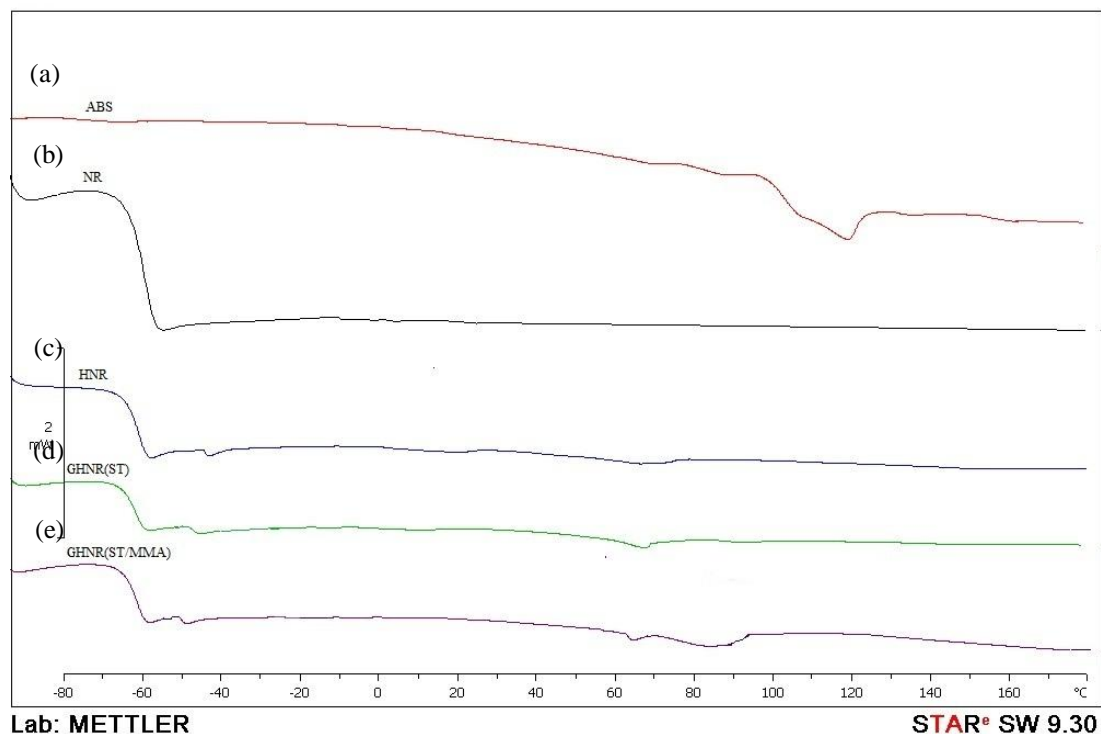


Figure 4.16 DSC thermogram (a) ABS, (b) NR/ABS, (c) HNR/ABS, (d) GHNR(ST)/ABS and (e) GHNR(ST/MMA)/ABS

4.8.2 Decomposition temperature and kinetics decomposition of samples analyzed by TGA

The TGA was used to analyse the initial decomposition temperature (T_{id}) and maximum decomposition temperature at the highest rate of decomposition (T_{max}) of polymer based on the simple principle to monitor the change in weight loss of a sample as the varying temperature. The experimentals were carried out under N_2 atmosphere to observe the weight change due to the degradation and to prevent other reaction caused by oxidation. The TG and DTG curves of ABS, NR, modified NR and their polymer blends were shown in Figures 4.17, 4.18 and Table 4.4. The results indicated that TG and DTG curves of ABS, NR, HNR, GHNR(ST) and GHNR(ST/MMA) (Entry 1-5) showed the single stage decomposition. The TG curve (Figure 4.17) showed that the T_{id} and T_{max} of HNR (54.3% hydrogenation) were

Table 4.3 Glass transition temperature (T_g) of samples

Sample	T _g (°C)	
	Rubber phase	Plastic phase
NR	-64.3	-
HNR (54.3% hydrogenation)	-63.7, -42.6	-
GHNR(ST) (54.3% hydrogenation; 36.9% GE)	-63.1, -42.7	62.1
GHNR(ST- <i>co</i> -MMA) (54.3% hydrogenation; 27.3% GE)	-63.7, -43.1	62.3, 80.75
ABS	-	106.3
NR/ABS	-64.1	103.2
HNR/ABS	-42.1	104.30
GHNR(ST)/ABS	-49.0	104.9
GHNR(ST/MMA)/ABS	-49.5	105.8

359.8°C and 394.6°C, respectively, which were higher than that NR due to the lower content of C=C bonds in HNR structure.

To consider the graft products, it was found that the T_{id} and T_{max} values of GHNR(ST) (54.3% hydrogenation, 36.9% GE) and GHNR(ST/MMA) (54.3% hydrogenation, 27.3% GE) were higher than that of HNR and NR. It might be explained that the graft copolymerization of ST or ST/MMA provided the functional groups (benzene ring and methoxycarbonyl groups) with higher thermal resistance. Moreover, the graft copolymerization via addition route (Eq. 4.4) might promote the

high saturated and also enhanced the thermal resistance. To evaluate the activation energy (E_a) of thermal decomposition, the T_{max} obtained from DTG curves was applied into Kissinger equation (Eq. 3.7). The E_a was calculated from the slope of the plot between $\ln(\beta/T_p^2)$ versus $1/T_p$ and summarized in Table 4.4. The results indicated that the E_a value of HNR (161.6 kJ/mol) which was higher than that of NR (139.2 kJ/mol) due to the higher content of saturated C-H bonds in HNR structure requiring the higher energy to break down. For the graft products, the E_a value of GHNR(ST) (178.4 kJ/mol) and GHNR(ST/MMA) (183.0 kJ/mol) were higher than that of HNR due to the effect of benzene ring in and methoxycarbonyl groups in polystyrene (PS) and poly(methyl methacrylate) (PMMA) segments grafted on HNR.

For the thermal decomposition of ABS and ABS containing NR and modified NR, the results in Figure 4.18 exhibited the slight change of decomposition profile of all samples due to a small amount of NR or modified NR added in the ABS. However, the E_a of ABS containing HNR (73.3 kJ/mol) had higher than ABS containing NR (66.6 kJ/mol) due to HNR induced to retarded thermal stability. The GHNR(ST/MMA) (96.1 kJ/mol) has highest the E_a value due to it has HNR in structure and also has functional groups (styrenic groups and methoxycarboxylic groups) which, are thermal resistance. Arayapranee et al. (2003) studied the GNR(ST/MMA)/PVC blends. It was found that the mechanical properties of GNR(ST/MMA)/PVC was improved because the PS and PMMA increased the compatibility. However, the thermal stability of GNR(ST/MMA) blends did not increase. In this research, the GHNR(ST/MMA)/ABS blends increased the mechanical properties and also increased the thermal stability due to higher saturated C=C bonds and functional group in structure. Thus, the GHNR(ST/MMA) was used as compatibilizer and also improve the thermal stability.

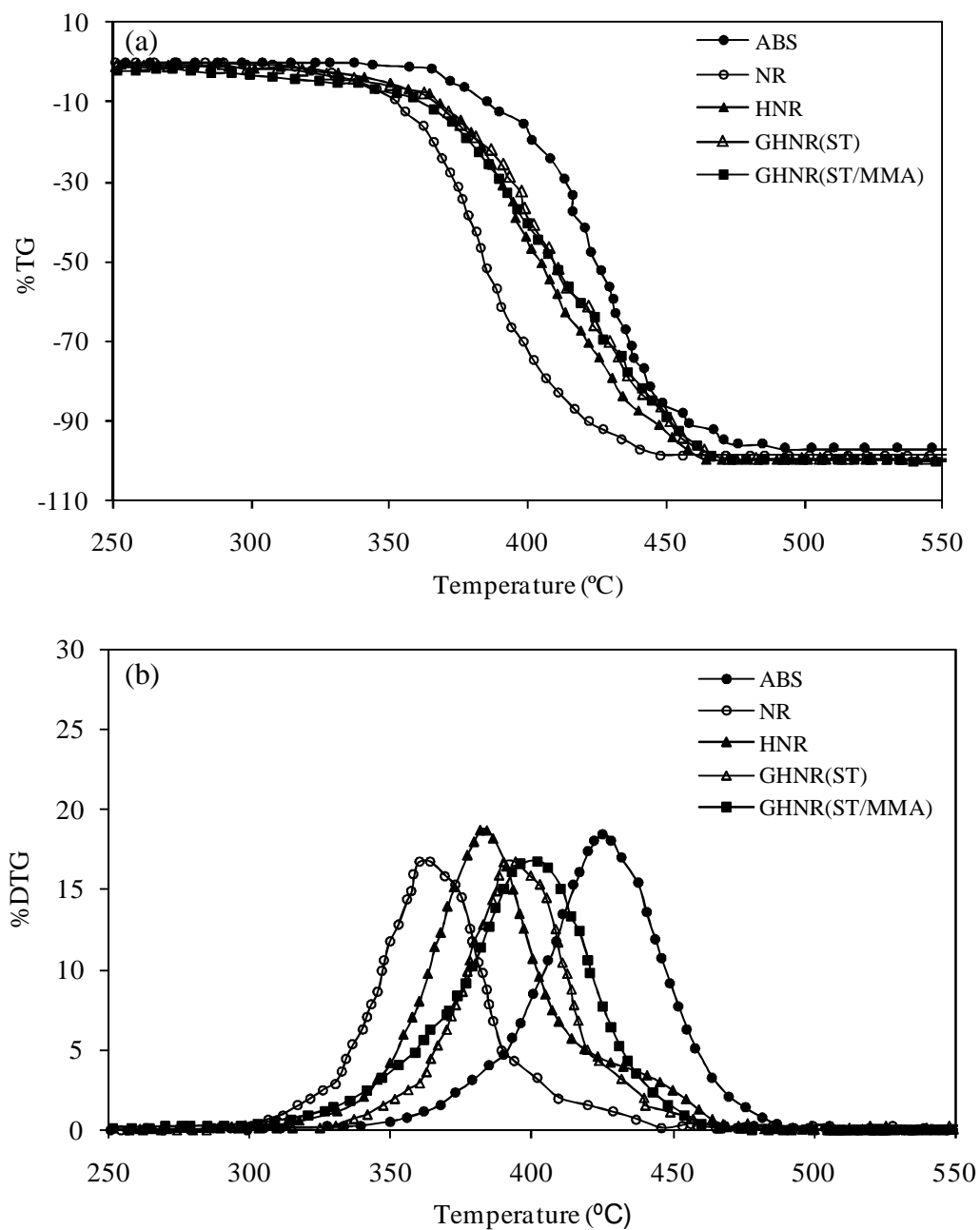


Figure 4.17 Thermal decomposition profiles of ABS, NR and modified NR: (a) TG and (b) DTG curves.

Table 4.4 Glass transition temperature (T_g) of rubber/ABS blends

Entry	Rubber	Decomposition temperature*		Activation energy (E_a) (kJ/mol)
		T_{id} (°C)	T_{max} (°C)	
1	NR	347.2	373.2	139.2
2	HNR (54.3% hydrogenation)	359.8	394.6	161.6
3	GHNR(ST) (54.3% hydrogenation; 36.9% GE)	362.4	399.6	178.4
4	GHNR (ST/MMA) (54.3% hydrogenation; 27.3% GE)	366.8	408.0	183.0
5	ABS	408.0	432.0	205.6
6	NR/ABS	396.0	410.0	66.6
7	HNR/ABS	399.1	421.5	73.3
8	GHNR(ST)/ABS	400.0	419.0	85.7
9	GHNR(ST/MMA)/ABS	402.7	426.0	96.1

* Recorded at 10°C/min of heating rate

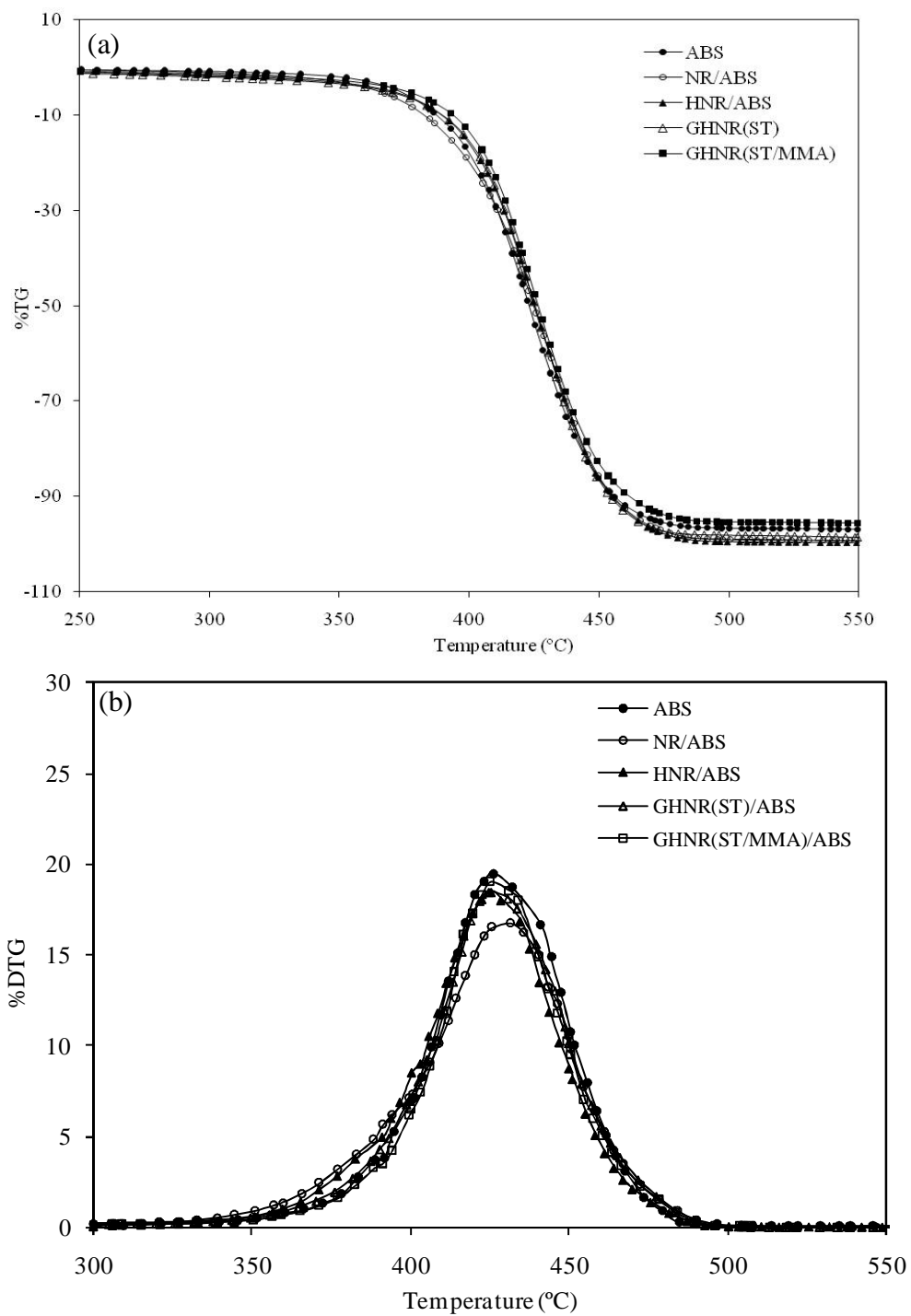


Figure 4.18 Thermal decomposition profiles of ABS, NR/ABS and modified NR/ABS: (a) TG and (b) DTG curves.

CHAPTER V

CONCLUSION AND RECOMMENDATION

In this research, the hydrogenated natural rubber (HNR) latex was prepared via diimide reduction to improve the thermal and oxidation stability. Then, the graft copolymerization of styrene (ST) or ST/ methyl methacrylate (MMA) onto HNR latex by emulsion polymerization initiated by using redox CHPO/TEPA initiator was investigated. Firstly the ST monomer was selected to investigate the effect of parameters on graft copolymerization onto HNR latex. The effects of %hydrogenation, monomer concentration, initiator content, reaction temperature and reaction time on grafting of ST onto HNRL were studied. The graft HNR (GHNR) was used to blend with acrylonitrile-butadiene-styrene (ABS). The flexural strength, and thermal properties of graft products and their blends were also investigated.

5.1 Graft copolymerization of ST or ST/MMA onto HNR latex

The NR latex was chemically modified via hydrogenation and graft copolymerization for extending its application. Firstly, the HNR latex was prepared for increasing the thermal and oxidative resistance. Then, the HNR latex with 54.3% hydrogenation was continuously grafted with ST or ST/MMA by using emulsion polymerization initiated by CHPO/TEPA redox initiator. The optimum condition for grafting ST onto HNR latex was 100 phr of monomer concentration, 1.5 phr of CHPO/TEPA (1/1 (w/w)) at 50°C for 8 h to obtain the 44.6% of conversion, 36.9% of %GE and 21.3% of graft HNR. For graft copolymerization of ST/MMA (75/25) onto HNR latex, the obtained optimum condition also induced 44.3% of conversion, 27.3% of GE and 17.7% of graft HNR. The morphology of both grafted HNR (GHNR) latexes from TEM micrograph indicated that grafted polystyrene (PS) attached at the outer surface of HNR particles and showed the long grafting chains. However, morphology of GHNR(ST/MMA) suggested that grafted ST/MMA attached at the outer later of and presence of nodules on the surfaces of the graft product particles

might be due to the growing macroradical chains, which were grafted onto the surface of NR particles and continued to propagate. The glass transition temperature (T_g) obtained from DSC thermogram indicated that GHNR(ST) had three T_g values at -63.1, -42.7 and 62.1 °C which corresponded with T_g of NR, HNR and PS, respectively. However, GHNR(ST/MMA) appeared four T_g at -63.7, -43.1, 62.3 and 80.7°C, which T_g at 80.7°C was related to T_g of PMMA. The initial decomposition temperature (T_{id}) and maximum decomposition temperature (T_{max}) of both GHNR(ST) (362.4°C and 399.6°C) and GHNR(ST/MMA) (364.8°C and 408.0°C) were higher than those of NR (347.2°C and 373.2°C). The activation energy of GHNR(ST) (178.4 kJ/mol) and GHNR(ST/MMA) (183.0 kJ/mol) was higher than that of NR (139.2 kJ/mol).

5.2 Flexural strength of modified NR/ABS blends and their thermal stability

The flexural strength of ABS containing NR and ABS containing modified NR was examined. The flexural strength of ABS containing GHNR(ST/MMA) was higher flexural strength (99.8 ± 7.33 MPa) than ABS containing NR (82.53 ± 2.78 MPa), but it did not reach to the flexural strength of the origin ABS (134 ± 0.02 MPa). After thermal aging, the retention in flexural strength of GHNR(ST/MMA) was higher than those of ABS and NR/ABS blends. This might be explained that GHNR(ST/MMA) had functional group to enhance the interfacial adhesion between two polymers. It was confirmed from SEM micrographs that the fractural surface of HNR/ABS blends showed the poor interfacial adhesive between ABS and HNR phase due to dissimilar polarity of two polymers. However, the GHNR(ST/MMA)/ABS appeared high homogeneity due to phenyl and methoxyl groups in ST and MMA. It was indicated that poor interfacial adhesion provided the poor mechanical properties. The DSC thermograms of ABS containing rubber were observed that the T_g decreased to 103.2 due to the increasing the mobility of polymer chains. The T_{id} and T_{max} of ABS containing modified rubber were higher than those of ABS containing NR (396.0°C, 410.0°C). Moreover, the E_a value of ABS containing of GHNR(ST/MMA) (96.1 kJ/mol) was higher than ABS containing NR (66.6 kJ/mol) due to lower unsaturated carbon-carbon double bonds. Moreover,

GHNR(ST/MMA)/ABS blends had PS and PMMA in structure to could enhance the interfacial adhesion between two phases leading to the higher energy in breaking bond.

5.3 Recommendations

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

1. Investigation of applying the GHNR for blending with other plastics such as PMMA because PMMA was applied in outdoor applications.
2. Investigation of the applying the EPDM in rubber/ABS blends because the EPDM are commercially saturated rubber.

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APPENDICES

APPENDIX A

Calculation of %conversion, %grafting properties and %GE

From graft copolymerization of ST onto HNR latex, all obtained data for GHNR was calculated as follow in below example:

Weight of NR latex (A)	= 10 g
NR content (from %DRC = 60.74) (B)	= 5.1145 g
Weight of ST charged (C)	= 1.5301 g
Weight of graft product (D)	= 5.6423g
Weight of sample (E)	= 3.1001 g
Weight of sample after extraction with PE (F)	= 0.6410 g
Weight of sample after extraction with acetone (G)	= 0.4911 g

1. %Conversion

$$\begin{aligned}
 \% \text{Conversion} &= (D - B)/C \times 100 \\
 &= (5.6423 - 5.1145)/1.5301 \times 100 \\
 &= 34.43
 \end{aligned}$$

2. %Graft hydrogenated natural rubber, GHNR

$$\begin{aligned}
 \% \text{GHNR} &= G/E \times 100 \\
 &= 0.4911/3.1001 \times 100 \\
 &= 15.84
 \end{aligned}$$

3. %Free HNR

$$\begin{aligned}
 \% \text{Free HNR} &= (E - F)/E \times 100 \\
 &= (3.1001 - 0.6410)/3.1001 \times 100 \\
 &= 79.32
 \end{aligned}$$

4. %Free polystyrene (PS)

$$\begin{aligned}\% \text{Free PS} &= (F - G)/E \times 100 \\ &= (0.6410 - 0.4911)/3.1001 \times 100 \\ &= 4.84\end{aligned}$$

5. Total ST

$$\begin{aligned}\text{Total ST} &= D - B \\ &= 5.6423 - 5.1145 \\ &= 0.53 \text{ g}\end{aligned}$$

6. Free PS

$$\begin{aligned}\text{Free PS} &= (\% \text{ free PS}/100) \times D \\ &= (4.84/100) \times 5.6423 \\ &= 0.27 \text{ g}\end{aligned}$$

7. Grafted PS

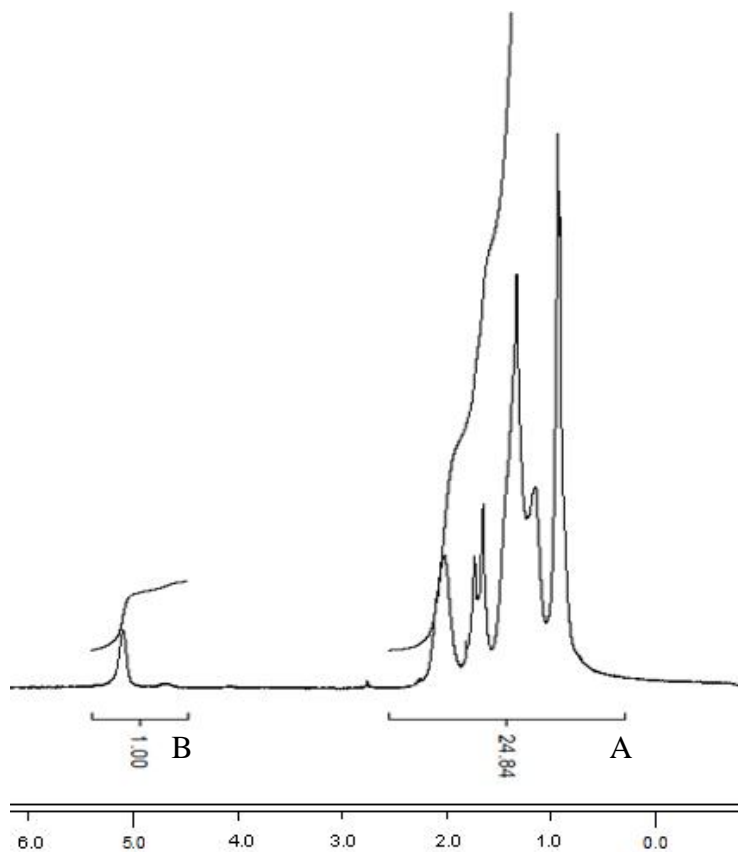
$$\begin{aligned}\text{Grafted PS} &= \text{Total ST} - \text{Free PS} \\ &= 0.53 - 0.27 \\ &= 0.26 \text{ g}\end{aligned}$$

8. %Grafting efficiency, GE

$$\begin{aligned}\% \text{GE} &= (\text{Grafted PS}/\text{Total monomer}) \times 100 \\ &= (0.26/1.5301) \times 100 \\ &= 16.9\end{aligned}$$

APPENDIX B

Calculation of %hydrogenation



Proton of repeating unit except =CH in species 1 = 7 protons

Proton of repeating unit in species 2 = 10 protons

A = Peak area except at 5.2 ppm

B = Peak area at 5.2 ppm

C = Peak area of saturated -CH₂- and -CH₃

$$A = 10C + 7B$$

$$C = \frac{A - 7B}{10}$$

Total Peak area = Peak area of saturated -CH₂- and -CH₃ + Peak are at 5.2 ppm

$$= \frac{A - 7B}{10} + B$$

$$\begin{aligned} &= \frac{A - 7B}{10} \\ \% \text{Hydrogenation} &= \left[\frac{\text{Peak area of sat. } -\text{CH}_2- \text{ and } -\text{CH}_3}{\text{Total peak area}} \right] \times 100 \end{aligned}$$

$$\begin{aligned} &= \frac{\left(\frac{A - 7B}{10} \right)}{\left(\frac{A + 3B}{10} \right)} \times 100 \\ &= \frac{A - 7B}{A + 3B} \times 100 \end{aligned}$$

For example: A = 24.84 and B = 1.00

$$\begin{aligned} \% \text{Hydrogenation} &= \frac{A - 7B}{A + 3B} \times 100 \\ &= \frac{24.84 - 7(1.00)}{24.84 + 3(1.00)} \times 100 \\ &= 64.08\% \end{aligned}$$

APPENDIX C

Data of graft copolymerization

Table D-1 Effect of hydrogenation level, monomer concentration, initiator content, reaction temperature and reaction time on the %conversion, %grafting efficiency (%GE),% free ST, % free HNR and %graft copolymrt obtained from emulsion graft copolymerization initiated by CHPO/TEPO

Exp.	%HD	[M] (phr)	[INT] (phr)	Temp (°C)	Time (h)	HNR Content (g)	ST (g)	Graft Product (g)	% Conv.	Sample (g)	Wt.A (g)	Wt.B (g)	% GHNR	%Free HNR	%Free PS	Total PS (g)	Free PS (g)	Grafted ST (g)	%GE
1	36.3	30	1	50	8	5.11	1.51	5.83	41.31	1.01	0.2993	0.2808	27.94	70.22	1.84	0.68	0.11	0.52	34.20
						5.09	1.52	5.79	38.25	1.01	0.2991	0.2748	27.26	70.33	2.41	0.58	0.14	0.44	29.06
2	44.1	30	1	50	8	5.11	1.51	5.75	35.69	1.03	0.2778	0.2561	24.77	73.13	2.10	0.54	0.12	0.42	27.70
						5.11	1.50	5.68	30.39	1.04	0.2630	0.2379	22.93	74.61	2.45	0.46	0.14	0.32	21.10
3	51.7	30	1	50	8	5.12	1.51	5.62	27.15	1.01	0.2255	0.1899	18.82	77.65	3.53	0.41	0.20	0.21	14.05
						5.11	1.51	5.60	25.57	1.01	0.2349	0.1874	18.55	76.74	4.70	0.39	0.26	0.12	8.150
4	54.3	30	1	50	8	5.10	1.61	5.63	25.75	1.02	0.2019	0.1609	15.81	80.17	4.03	0.41	0.23	0.19	11.67
						5.10	1.51	5.68	31.03	1.01	0.2166	0.1663	16.49	78.64	4.96	0.47	0.28	0.19	12.38
5	54.3	50	1	50	8	5.11	2.50	5.97	34.19	3.00	0.6998	0.5543	18.47	76.68	4.85	0.86	0.29	0.57	22.62
						5.13	2.51	6.02	35.66	3.00	0.6789	0.5198	17.32	77.38	5.38	0.90	0.32	0.58	22.94

Wt.A = Graft product was extracted by light petroleum ether for 24 h.

Wt.B = Graft product was extracted by light petroleum ether for 24 h. and then extracted by MEK for 24 h.

Exp.	%HD	[M]	[INT]	Temp	Time	HNR Content	ST	Graft Product	% Conv.	Sample	Wt.A	Wt.B	% GHNR	%Free HNR	%Free PS	Total PS	Free PS	Grafted ST	%GE
		(phr)	(phr)	(°C)	(h)	(g)	(g)	(g)		(g)	(g)	(g)				(g)	(g)	(g)	
6	54.3	75	1	50	8	5.12	3.75	6.55	38.15	3.01	0.7791	0.5727	18.92	74.08	6.99	1.49	0.47	1.02	26.13
						5.12	3.75	6.56	38.30	3.00	0.7667	0.5968	18.46	75.75	5.79	1.49	0.39	1.10	28.32
7	54.3	100	1	50	8	5.11	5.01	7.12	40.12	3.00	0.7511	0.5920	19.83	74.83	5.38	2.09	0.39	1.70	32.57
						5.11	5.01	7.14	40.29	3.00	0.7897	0.6539	21.71	73.70	4.60	2.10	0.34	1.76	33.84
8	54.3	125	1	50	8	5.22	7.25	8.08	39.67	3.00	0.7468	0.4665	15.28	75.12	9.60	2.56	0.75	1.81	27.89
						5.11	7.24	8.13	40.99	3.01	0.6957	0.3918	13.15	76.81	10.0	2.66	0.79	1.87	28.82
9	54.3	100	1.5	50	8	5.10	5.01	7.29	43.36	3.00	0.7944	0.6887	22.78	73.51	3.71	2.26	0.28	1.98	38.01
						5.12	5.01	7.41	45.76	3.02	0.8020	0.6014	19.73	73.40	6.89	2.39	0.52	1.87	35.88
10	54.3	100	2.0	50	8	5.11	5.10	7.22	41.44	3.00	0.5928	0.5206	17.36	80.25	2.39	2.16	0.18	1.98	38.03
						5.11	5.00	7.29	43.46	3.00	0.7950	0.6374	16.34	78.25	5.40	2.27	0.40	1.89	35.81
11	54.3	100	2.5	50	8	5.11	5.01	7.18	40.53	3.00	0.5890	0.4494	14.97	80.37	4.66	2.11	0.34	1.77	33.99
						5.22	5.10	7.39	42.21	3.00	0.6227	0.4586	15.79	79.24	4.97	2.20	0.37	1.83	35.14
12	54.3	100	1.0	40	8	5.12	5.01	6.64	28.24	3.00	0.6451	0.4865	16.13	78.50	5.37	1.44	0.36	1.08	21.23
						5.14	4.99	6.75	30.65	3.01	0.6378	0.4521	14.91	78.76	6.33	1.57	0.43	1.14	22.26
13	54.3	100	1.0	50	8	5.12	5.01	7.24	40.36	3.00	0.8343	0.6599	21.82	72.19	5.99	2.10	0.44	1.66	31.95
						5.12	5.00	7.37	42.90	3.00	0.8714	0.6601	21.79	70.96	7.25	2.24	0.54	1.69	32.52
14	54.3	100	1.0	60	8	5.11	5.01	7.25	42.60	3.00	0.8837	0.4078	13.38	70.57	16.1	2.21	1.19	1.02	19.67
						5.12	5.01	7.05	38.43	3.00	0.6361	0.4354	14.41	78.80	6.79	2.00	0.49	1.51	29.02

APPENDIX D
Data of flexural strength

Table D-2 Flexural strength before and after aging of modified NR/ABS blends

	ABS		NR/ABS		HNR/ABS		GHNR(ST)/ABS		GHNR(ST/MMA)/ABS	
	Before aging	After aging	Before aging	After aging	Before aging	After aging	Before aging	After aging	Before aging	After aging
Flexural strength (MPa)	134.7	114.3	85.92	60.59	75.29	73.25	90.03	87.37	94.65	101.52
	134.9	117.6	79.14	64.96	81.70	70.38	102.0	79.66	105.0	86.17
Mean	134.8	116.0	82.53	62.78	78.50	71.81	96.01	83.51	99.84	101.5
SD	0.166	2.346	2.772	1.780	4.523	2.029	8.450	5.458	7.335	93.85
%Retention	86.00		76.06		91.48		87.00		94.00	

VITA

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