ยางธรรมชาติกราฟต์สไตรีนและเมทิลเมทาคริเลตเพื่อเป็นสารเสริมการทนแรงกระแทกสำหรับพอลิไวนิลคลอไรด์

นางสาวกาญจนา เอี้ยวสุวรรณ

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NATURAL RUBBER GRAFTED STYRENE/METHYL METHACRYLATE AS IMPACT MODIFIER FOR POLY(VINYL CHLORIDE)

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กาญจนา เอี้ยวสุวรรณ : ยางธรรมชาติกราฟต์สไตรีนและเมทิลเมทาคริเลตเพื่อเป็นสารเสริมการทนแรงกระแทกสำหรับพอลิไวนิลคลอไรด์ (NATURAL RUBBER GRAFTED STYRENE/METHYL METHACRYLAT AS IMPACT MODIFIER FOR POLY(VINYL CHLORIDE). อาจารย์ที่ปรึกษา : ศ.ดร.ภัทรพรรณ ประศาสน์สารกิจ, 101 หน้า. ISBN 974-17-3432-8.

กราฟต์โคพอลิเมอร์ของสไตรีนและเมทิลเมทาคริเลตบนยางธรรมชาติสังเคราะห์ด้วยกระบวนการอิมัลชันพอลิเมอไรเซชัน โดยใช้คิวมีนไฮโดรเปอร์ออกไซด์และเททระเอทิลีนเพนทะเอมีนเป็นสารริเริ่มปฏิกิริยาแบบรีดอกซ์ การวิเคราะห์ทางสถิติโดยการออกแบบการทดลองเป็นแบบแฟกทอเรียลสองระดับ ตัวแปรที่ทำการศึกษา ได้แก่ ความเข้มข้นตัวริเริ่มปฏิกิริยา อุณหภูมิปฏิกิริยา อัตราส่วนสไตรีนต่อเมทิลเมทาคริเลต และอัตราส่วนมอนอเมอร์ต่อยางธรรมชาติ จากการศึกษาแบบแฟกทอเรียลสองระดับ พบว่า ความเข้มข้นตัวริเริ่มปฏิกิริยา อุณหภูมิปฏิกิริยา และอัตราส่วนมอนอเมอร์ต่อยางธรรมชาติมีผลต่อประสิทธิภาพการกราฟต์ และพบว่าอุณหภูมิปฏิกิริยา และอัตราส่วนมอนอเมอร์ต่อยางธรรมชาติมีผลต่อร้อยละยางธรรมชาติกราฟต์ หมู่ฟังก์ชันของยางธรรมชาติกราฟต์วิเคราะห์ด้วยอินฟราเรดสเปกโตรสโคปี สัณฐานวิทยาของยางธรรมชาติกราฟต์ศึกษาด้วยกล้องจุลทรรศน์อิเล็กตรอนแบบส่องผ่าน ยางธรรมชาติกราฟต์สามารถใช้เป็นสารเสริมการทนแรงกระแทกสำหรับพอลิไวนิลคลอไรด์ โดยการเตรียมพอลิเมอร์ผสมของยางธรรมชาติกราฟต์กับพอลิไวนิลคลอไรด์ สมบัติเชิงกล สมบัติเชิงความร้อน และสัณฐานวิทยาของพอลิเมอร์ผสมเป็นฟังก์ชันกับปริมาณยางธรรมชาติกราฟต์

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KANCHANA EAWSUWAN : NATURAL RUBBER GRAFTED STYRENE / METHYL METHACRYLATE AS IMPACT MODIFIER FOR POLY(VINYL CHLORIDE). THESIS ADVISOR: PROF. PATTARAPAN PRASASSARAKICH, Ph.D.; 101 pp. ISBN 974-17-3432-8.

Graft copolymer of styrene and methyl methacrylate onto natural rubber was synthesized by emulsion polymerization using cumene hydroperoxide and tetraethylene pentamine as a redox initiator. Statistical analysis, two-level factorial design, was used to study the influence of four process variables and the interaction of these process variables. The process variables were initiator concentration, reaction temperature, ratio of styrene to methyl methacrylate, and ratio of monomer to natural rubber. The two-level factorial experimental design showed that initiator concentration, reaction temperature, and ratio of monomer to natural rubber had a significant effect on grafting efficiency. Reaction temperature and ratio of monomer to natural rubber had a significant effect on percentage graft copolymer. The grafted natural rubber was characterized by FT-IR spectroscopy and the particle morphology was determined by transmission electron microscopy. The grafted natural rubber product could be used as an impact modifier for PVC, thus, blends of the grafted natural rubber products and PVC were prepared. The mechanical properties, thermal properties, and morphology of the grafted natural rubber modified PVC were investigated as a function of grafted natural rubber content.

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CONTENTS

PAGE

CONTENTS (CONTINUED)

PAGE

CONTENTS (CONTINUED)

PAGE

CONTENTS (CONTINUED)

LIST OF FIGURES

LIST OF FIGURES (CONTINUED)

LIST OF TABLES

LIST OF TABLES (CONTINUED)

TABLE **PAGE**

LIST OF ABBREVIATIONS

MBS	:	Methyl methacrylate-butadiene-styrene terpolymer
PVC	:	Poly(vinyl chloride)
HANR	:	High ammonia natural rubber
ST	:	Styrene
MMA	:	Methyl methacrylate
MEK	:	Methyl ethyl ketone
DRC	:	Dry rubber content
CHPO	:	Cumene hydroperoxide
TEPA	:	Tetraethylene pentamine
GNR	:	Grafted natural rubber
NR	:	Natural rubber
ASTM	:	The American Society for Testing and Material
INT	:	Initiator concentration
TEMP	:	Temperature
TEM	:	Transmission electron microscopy
SEM	:	Scanning electron microscopy
FT-IR	:	Fourier-transform infrared spectroscopy
phr	:	Part per hundred
Avg.	:	Average
GE	:	Grafting efficiency
T_g	:	Glass transition temperature
b.p.	:	Boiling point
°C	:	Degree Celsius
g	:	Gram (s)
hr	:	Hour (s)
Rp	:	Rate of propagation
c.m.c.	:	Critical micelle concentration

CHAPTER I

INTRODUCTION

1.1 The Purpose of the Investigation

Modifier has been introduced for high polymer additives for the selective improvement of the application properties of thermoplastic. Methyl methacrylate-Butadiene-Styrene (MBS) terpolymers have been incorporated into rigid PVC compounds for improving impact property. MBS-modified PVC compounds give better compatibility and transparency than unmodified PVC compounds and now account for in the area of building and construction: pipe, conduit window glazing, and profiles; packaging: film, sheet, and bottle; and other. Impact modifiers are usually particulate rubbery graft copolymers or blends of both hard and rubbery polymers.

Besides synthetic rubbers, natural rubber can be used as raw material of graft copolymers that are important technological materials in that they can greatly influence the interfacial region in polymer blends and composites. PVC is a brittle polymer and needs some sort of toughening of most application. The purpose of adding the rubber is to improve the brittle characteristics of the basic polymer and to improve the mechanical properties of the materials, in particular, impact resistance. Graft copolymerization is a selected method for a modification of the natural rubber. The grafted natural rubber can be used as an impact modifier in rigid PVC and to substitute the MBS. The graft copolymerization would effectively combine the desirable properties of natural rubber with vinyl monomer in order to produce tough, hard, and impact resistant materials with easy processibility.

Thailand is the world largest producers of natural rubber and the biggest exporter of natural rubber latex [1]. Therefore, the objective of this research is to prepare graft copolymer of styrene (ST) and methyl methacrylate (MMA) onto natural rubber by emulsion polymerization using redox initiator, cumene hydroperoxide (CHPO) and tetraethylene pentamine (TEPA). The blends of grafted natural rubber product and PVC were prepared and the mechanical properties of grafted natural rubber modifies PVC were investigated.

1.2 Objectives

The objectives of this research are as following:

1. To prepare the graft copolymers of styrene and methyl methacrylate onto natural rubber latex. Effects of initiator concentration, reaction temperature, styrene to methyl methacrylate ratio, and monomer to rubber ratio were studied by using two level factorial designs.
2. To prepare the PVC/grafted natural rubber blends and PVC/MBS blends and investigate the mechanical properties of the blends.

1.3 Scope of the Investigation

The graft copolymers of styrene and methyl methacrylate onto natural rubber latex using redox initiator were prepared. The suitable blend ratio of graft copolymers and PVC, which yielded the good mechanical properties was determined. The experimental procedures to carry out are as follows:

1. Literature survey and study the research work.
2. Prepare the graft copolymers of styrene and methyl methacrylate onto natural rubber latex using redox initiator system via emulsion polymerization.
3. Study the effect of parameters on grafting efficiency by using two level factorial design.
4. Characterize and study the morphology of the grafted natural rubber.
5. Prepare the polymer blends of grafted natural rubber product and PVC.
6. Investigate the mechanical properties of grafted natural rubber modified PVC such as tensile strength, impact strength, ultimate elongation, and hardness.
7. Study the thermal properties of grafted natural rubber modified PVC.
8. Summarize the results.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Natural Rubber

Natural rubber is a white milky fluid produced by specialised cells in a variety of plants, throughout the world, in totally unrelated families, including the *Compositae* and *Moraceae* as well as the *Euphorbiaceae* [2]. Although in the past many different species have been used for obtaining crops of latex the principal source of natural rubber, today, is *Hevea Brasiliensis*. *Hevea Brasiliensis* is a native of the tropical rain forest of the Amazon Basin in Brazil. Most of the world 's natural rubber comes today from South-East Asia, mainly Thailand, Malaysia, and Indonesia [3].

Hevea Brasiliensis, the commercial rubber tree, is a tall tree, growing naturally up to forty metres (130 feet) and living for one hundred years or more. *Hevea Brasiliensis* requires temperatures of 20-30°C, at least 2,000 mm of rainfall per year, and high atmospheric humidity. This naturally occurring polymer is known chemically as cis-1,4-polyisoprene.

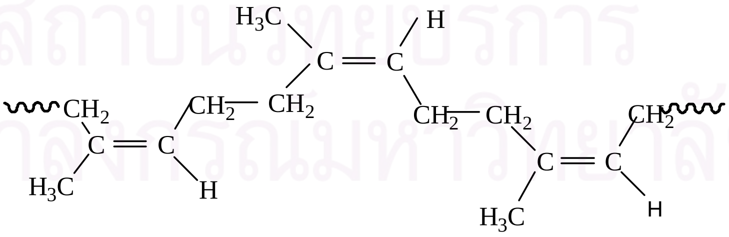


Figure 2.1 Cis-1,4-polyisoprene.

2.1.1 Natural Rubber Latex [2]

Natural rubber latex, a milk-like liquid, comes from a layer of tiny tubes spiralling up the tree beneath the outer bark. Like milk it is an emulsion particles suspended in water. Natural latex as it comes from the tree is known as field latex. Field latex is only about 36% rubber and 4% non-rubber substances. The non-rubber components include proteins, carbohydrates, liquids, and inorganic salts. Its composition varies according to the clones of rubber, age of rubber tree, and tapping method. The composition of typical field latex is presented in Table 2.1.

Table 2.1 Composition of latex [2]

Constituent	% Composition
Rubber particle	36.0
Proteinaceous substances	1.5
Sugar, Lipids, Resinnous substances	2.5
Water	60.0

About 10% of natural rubber is not processed into dry rubber but sold as latex. Latex concentrate is usually made by centrifugation-spinning at high speed to separate off a cream of about 60% rubber from a liquid of about 5% rubber, from which dry skim rubber is made. A little ammonia is added to the latex, both on collection and before centrifugation, to stop it coagulating and turning into dry rubber. Another concentrate, made by evaporation, evaporated latex concentrate, has a higher rubber content and so slightly different properties. Finally, there is creamed latex concentrate: the field latex is mixed with a chemical, such as ammonium alginate, which makes the rubber particles rise to the top of the liquid, like cream, when left to stand for several weeks. All latex concentrates are chemically treated to prevent coagulation.

2.1.2 Properties of Raw Natural Rubber

Natural rubber latex consists of hydrogen and carbon in the ratio expressed by C_5H_8. It has a chemical structure of almost 100% cis-1,4-polyisoprene units. Physical properties of natural rubber may very slightly due to the non-rubber constituents present and to the degree of crystallinity. When natural rubber is held below 100°C, crystallization occurs, resulting in a change of density from 0.92 to about 0.95. Listed in Table 2.2 are some average physical properties.

Table 2.2 Physical properties of natural rubber [4]

Physical property	Value
Density	0.92
Refractive index (20°C)	1.52
Coefficient of cubical expansion	0.00062/°C
Cohesive energy density	63.7 cal./c.c.
Heat of combustion	10,700 cal./g
Thermal conductivity	0.00032 cal./sec/cm^2/°C
Dielectric constant	2.37
Power factor (1,000 cycles)	0.15-0.2

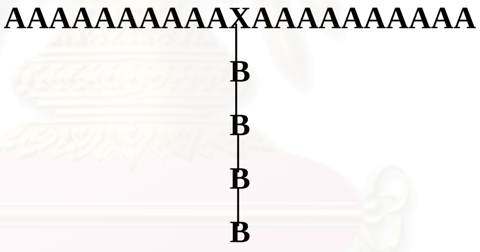
Natural rubber exhibits two phases, sol and gel. The differences are exhibited in degree of solubility in certain organic solvents due to different amounts of highly branched and lightly crosslinked components intertwined in the rubber. Mechanical shear, as in milling, or oxidative breakdown with heat and oxygen tends to disaggregate the gel phase, thereby increasing solubility. Effective solvents for masticated natural rubber include aliphatic and aromatic hydrocarbons, chlorinated hydrocarbons, ethers, and carbon disulfide. Nonsolvents include the lower ketones, alcohols, and lower esters.

2.1.3 Modification of Natural Rubber

Natural rubber has been modified in many ways since the establishment of a continuous supply of plantation rubber. Modification highly affects its physical properties. Even thermoplastic or resinous material can be obtained by a modification of rubber. The most well known types of modification are oxidation, hydrogenation, halogenation, hydrochlorination, chlorosulphonation, and free radical addition or grafting [5].

2.2 Graft Copolymers

In graft copolymerizations polymer side chains are formed attached to preformed macromolecules of different chemical composition [6]. The simplest case of graft copolymer can be represented by the following structure.



AAAAAAAAAAXAAAAAAAAAA
B
B
B
B

Where a sequence of A monomer units is referred to as the main chain or backbone, the sequence of B units is the side chain of graft, and X is the backbone to which the graft is attached.

Graft copolymers produced by causing a post polymerization of vinyl monomers such as styrene, acrylonitrile, methyl methacrylate either independently or as a mixture of a plurality thereof to a rubber-like polymer latex have been well known.

Although graft copolymerizations are widely practiced with vinyl monomers and polymers, especially for improving compatibility, impact, and low temperature properties of thermoplastics, the technology has been based more upon art than upon science. Often small proportions of actual grafting have been sufficient to give worthwhile modification of properties. If grafting does not give directly the properties desired, it may improve morphology or compatibility with specific added polymers or plasticizers that impart the desired effect. In addition, these graft copolymers have been mixed with other resins such as poly(vinyl chloride) to improve compatibility, impact, and low temperature properties of thermoplastic.

2.2.1 Graft Copolymers from Natural Rubber [7]

Useful rubbery behavior in polymers which could be processed as thermoplastic was reported as early as 1958. There was increasing interest in the blending of rubbery and hard polymers to generate materials which had greater flexibility than many of the conventional plastics and rubber like elasticity approaching that of vulcanized rubber. In 1965, the styrene-diene block copolymers were introduced by commercial announcement. Soon after their commercial announcement, the materials of many different types are now used in thermoplastic rubber technology.

The Natural Rubber Research Organizations had investigated processes for grafting polymers to natural rubber using free radical chemistry. Materials were obtained which contained both plastic and rubber constituents and Heveaplus-MG, a graft copolymer of natural rubber and poly(methyl methacrylate), become commercially available. The material still has its uses, but it did not behave as a thermoplastic rubber in the currently used sense of the worlds.

2.2.2 Graft Copolymers as Thermoplastic Rubbers [7]

Graft copolymers differ in many ways from block copolymers but the two types of material possess the common structural feature of having two or more disparate polymer species chemically bound to each other. The thermodynamic constraints which cause phase separation on a molecular scale should apply to both types of copolymer and properly constructed graft copolymers should be capable of forming an elastic network anchored by dispersed hard microphases.

The thermodynamic incompatibility between pairs of polymers finds semiquantitative expression in the difference between their Hildebrand solubility parameter. A low driving force for chain segregation will result in poor phase integrity under physical stress. Conversely, if the driving force for phase separation is large, the material may show excellent phase integrity and strength but fail to allow the large scale chain mobility at higher temperatures which is necessary for technological processing. The phase separation must also result in trapping of entanglements along the rubbery chain. This can only happen in graft copolymers if the rubbery component constitutes the backbone and if there are at least two graft sites on each chain.

2.2.3 Graft Copolymers Synthesis [8]

The synthesis of graft copolymers is much more diverse, but can nevertheless be divided into groups of related processes;

a) Chain Transfer

In a free radical polymerization, chain transfer, is an important reaction. Chain transfer to a monomer, solvent, mercaptan, or other growing chain can take place. When a chain transfer reaction to another chain takes place, it creates a radical which acts as a site for further chain growth and grafting. The simplest technique is to dissolve the polymer in the appropriate solvent; add the peroxide initiator, which abstracts a hydrogen radical and generates a radical on the polymer chain; and then add fresh monomer for grafting onto this site. In many cases when latex grafting has been used, the product has usually been targeted toward thermoplastic applications.

b) Copolymerization via Unsaturated Groups

In natural rubber, a few such groups per molecule are always present and these undoubtedly participate during normal grafting. By carrying out the reaction to about 4% of the available double bonds in a solvent such as toluene at low temperature followed by a nitrogen purge, grafting can be effected by addition under nitrogen monomer and formation of two monomer chains attached to the oxygens of the opend -O-O- bridge. This technique should be applicable to isoprene and butadiene copolymers.

c) <u>Redox Polymerization</u>

Redox polymerizations are among the most popular techniques for grafting reactions. In a redox polymerization, a hydroperoxide or similar group is reduced to a free radical plus an anion, while the metal ion is oxidized to a higher valency state, and at the same time a monomer is added. When the reducible group is attached to a polymeric chain, the free radical grafting sites thus formed on the macromolecular backbone act as initiators for graft copolymerization.

Hydroxy polymers can be grafted by redox polymerization by using a water-insoluble peroxide, such as hydrogen peroxide in conjuction with ferrous ions. The hydroxy radicals thus produced abstract hydrogen atoms from the hydroxy groups in the polymer, giving free radical grafting sites on the backbone. The advantage of this reaction lies in the fact that only hydroxyls on the polymer are converted into R–O free radicals, so that no homopolymer can be produced and pure graft is obtained.

d) <u>High-Energy Reaction Techniques</u>

During high-energy irradiation in vacuo, e.g., from a ^{60}Co source, some main chain degradation of natural rubber and other polyisoprenes occurs. The irradiation of natural rubber in the presence of a vinyl monomer thus leads primarily to a synthesis of graft copolymers, but some block copolymer is certainly always present. Irradiation syntheses may be carried out in solution, either in contact with liquid monomer (with or without a diluent) or in contact with monomer in the vapor phase, or in emulsion or suspension. The rubber may be preirradiated in the absence of air to produce free radicals for later monomer addition, but the life of these radicals is short as a result of mobility within the rubber matrix. Irradiation at very low temperature makes it possible to use the trapped radicals technique for a variety of natural and synthetic rubbers. Latex phase grafting is generally favored for its simplicity; natural rubber grafts with methyl methacrylate, styrene, acrylonitrile, and vinyl chloride have been made in this way.

e) Photochemical Synthesis

Macromolecules containing photosensitive groups which absorb energy from ultraviolet frequencies often degrade by free radical processes. The degradative process as a rule is fairly slow, but by the addition of photosensitizer, such as xanthone, benzyl, benzoin, and 1-chloroanthraquinone, the rate can be speeded up to enable graft copolymerization to take place in the presence of monomers. This can be done in the case of natural rubber in the latex phase with reasonably high yields of graft copolymer.

f) Metallation Using Activated Organolithium with Chelating Diamines

Unsaturated elastomers can be readily metallated with activated organolithium compounds in the presence of chelating diamines or alkoxides of potassium or sodium. They can also be grafted with ionically polymerizable monomers to produce comblike materials.

2.3 Emulsion Polymerization [9]

The emulsion polymerization method employs various possibilities to prepare particles with controlled morphologies and surface properties. The core-shell arrangements provided by the emulsion polymerization technique. The production of two phase latex particles with defined morphology is of great technical interest. A two step procedure has emerged in which an outer layer of polymer is polymerized onto an inner core of a different polymer. According to the polymer particle morphology, there are two main kinds of core-shell copolymers: soft core-hard shell and hard core-soft shell. The core shell latex with a glassy core and rubbery shell can be used in coating and adhesive formulation; on the contrary, the latex particles with rubbery cores and glassy shells are used as impact modifiers in plastics. The rubbery particle structure could be easily made in the synthesis of core-shell particle via emulsion polymerization. The rubbery core latex particles are produced in the first stage of the polymerization. These particles are then used as a seed in a second stage emulsion polymerization, for coating with a glassy shell by grafting. By stepwise growth from a seed, the core-shell rubber particles having wide ranging sizes, composition and layer thickness could be synthesized for used as model systems in the improvement of impact modification.

2.3.1 Ingredients and Processes

An overview of the major ingredients and processes in emulsion polymerization is now presented: monomer, initiator, surfactant, and other ingredients.

a) Monomers

The major polymerizable component of an emulsion polymerization is a monomer that is of limited solubility in water, and that swells its polymer. The monomers used in emulsion polymerization are thus often of the vinyl type, $CH_2=CHX$. X may be C_6H_5, CN, O_2CCH_3, Cl, and CO_2R. Some monomers that used in commonly by commercial emulsion polymerization are shown in Table 2.3.

b) Initiators

A source of free radicals is needed for water-borne emulsion polymerization. The free radicals can be produced by thermal decomposition of peroxy compounds like persulfate [10, 11], or by redox reactions like the cumene hydroperoxide/sodium formaldehyde sulfoxylate [12, 13], or by γ-radiation [14, 15]. The free radical initiators can be either water or oil soluble, determining the preferred phase in which the free radicals will be produced. For redox initiators, the combination of certain oxidizing and reducing agents will produce free radicals even at low temperatures. This can be particularly useful when high molecular weight polymers are sought with low levels of branching.

Table 2.3 Types of monomer [16]

Monomer	Examples of common usage
styrene	ingredient in artificial rubber (SBR-also used in paper coating.)
butadiene	1) ingredient in artificial rubber (SBR-also used in paper coating.) 2) impact modifier (toughening of plastic), e.g. HIPS, ABS
tetrafluoroethylene	1) polytetrafluoroethylene, e.g. Teflon 2) ingredient in fluoropolymers, e.g. Viton
vinyl acetate	1) polyvinyl acetate (PVA) adhesive 2) ingredient in paint
methyl methacrylate	ingredient in surface coatings
acrylic acid	minor ingredient in paint formulation
itaconic acid	minor ingredient in paint formulation
2-chloro-1,3-butadiene (chloroprene)	neoprene rubber (which has sulfur as co-monomer)
butyl acrylate	rubber ingredient in surface coatings
butyl methacrylate	rubber ingredient in surface coatings
methyl acrylate	co-monomer in surface coatings, adhesives
vinyl chloride	PVC (usually produced by suspension method, sometimes by emulsion)

c) Surfactants and Stabilizer

Surfactants are a key formulation variable in emulsion polymerizations. They are generally categorized into four major classes: anionic, cationic, nonionic, and zwitterionic (amphoteric). The anionic and nonionic surfactants are the most widely used because of enhanced compatibility with negatively charged latex particles as compared to the cationic or zwitterionic surfactants. In addition, in many latex formulations, mixtures of surfactants are often used together in a synergistic manner to control the particle size and to impart enhanced colloidal stability to the latex with regard to mechanical shear, electrolyte, and extremes in temperatures. The most widely used anionic surfactants are sodium dodecyl sulfate, sodium dodecylbenzene sulfonate, and sodium or potassium salts of fatty acids.

The dispersion stabilizers used are not confined to anionic and nonionic surfactants. Sometimes it is beneficial to add so-called protective colloids such as hydroxyethyl cellulose, polyvinyl alcohol, and rosin derivatives. In emulsion polymerization, a protective colloid, which is a water soluble polymer, is usually used to increase the particle stability against coagulation.

d) Other Ingredients

It is often to add a modifier in commercial emulsion polymerization such as chain transfer agents to control molecular weight, buffer to control pH without hydrolysis of surfactant, and electrolytes.

2.4 Poly(vinyl chloride) (PVC)

PVC is one of the largest volume thermoplastics in the world. It is chemically inert and versatile, ranging from soft to rigid products that are available at economic costs.

PVC is partially syndiotactic; it has a low degree of crystallinity due to the presence of structural irregularities. PVC is relatively unstable to heat and light. So, in practice, a number of ingredients must be added to PVC to enhance thermal stability and hence improve processing, toughness, and product performance. The toughness of PVC can also be improved by blending with high-impact resin like ABS or MBS.

The largest single use of PVC is for piping systems. The major area of use and typical applications of PVC are listed in Table 2.4.

Table 2.4 Typical applications of poly(vinyl chloride) [17]

Area	Typical application
Piping systems	Pressure pipes: water supply and distribution, agricultural irrigation, chemical processing Non-pressure pipes: drain, waste and vent pipes, sever systems, conduits for electrical and telephone cables
Building construction	Siding, window frames, gutters, interior molding and trim, flooring, wire and cable insulation, wall coverings, upholstery, shower curtains, refrigerator gaskets
Transportation	Upholstery, floor mats, auto tops, automotive wire, interior and Exterior trim
Consumer products	Footwear, outerwear, phonograph records, sporting goods, toys

2.5 Impact Modifiers for PVC [18]

2.5.1 Theory of Impact Strength Improvement

The term modifier has been introduced for high polymeric additives for the selective improvement of the application properties of thermoplastic. For example, impact modifier mean those additives which convert an intrinsically brittle plastic to one with high toughness.

The structure of polymer mixture, polyblend, is based on the simple idea of combining polymers having a wider spectrum of applications result from them. In this case, improvement is sought principally of the impact strength of a thermoplastic by the addition of high polymeric additive. When final articles made from impact-modified polymers are subjected to shock and impact stress the mechanical energy imparted is initially absorbed by the coherent matrix, the hard phase. If the brittle fracture is to be prevented, the energy must be transferred, being diverted to the build up of stress peak at unfavorable locations, which initiate fracture.

Investigation of the structure of impact resistant polyblends formed in different ways have revealed two types of blends which differ fundamentally from each other in their structures and accordingly in their fracture mechanisms.

a) Systems with an elastomeric phase distributed as a honeycombed network such as PVC/EVA and PVC/PE-C.

b) Systems with spherical elastomeric particles, which are dispersed in a hard polymer matrix such as PVC/ABS and PVC/MBS.

In these systems good adhesion must exist at the phase boundary, since this is subjected to stresses of various origin. Since the matrix, the hard phase, and the elastomeric phase have unequal thermal coefficients of expansion, shrinkage stresses occur in the rubber particles on cooling after processing (so-call internal stresses). Above the glass transition temperature (T_g) of the matrix the coefficients of expansion of both phases are approximately equal, while below T_g the coefficient of expansion of the matrix becomes smaller and that of the elastomer remains essentially unchanged. Therefore, on cooling the rubber has more pronounced shrinkage than the matrix, whereby tensile stresses are generated between the matrix and the elastomeric particles. To ensure a large excess stress, the matrix must have low elasticity, i.e. a high modulus of elasticity, which harmonizes with the requirement for a large difference in modulus between the elastomeric phase and the matrix.

For polymers, the following molecular processes are taken as the basis for the dissipation of energy under the influence of shock and impact effects.

a) Craze formation (fibrillated deformation zones): dissipation of energy by the formation of microscopic voids by stretching processes resulting in increased volume.

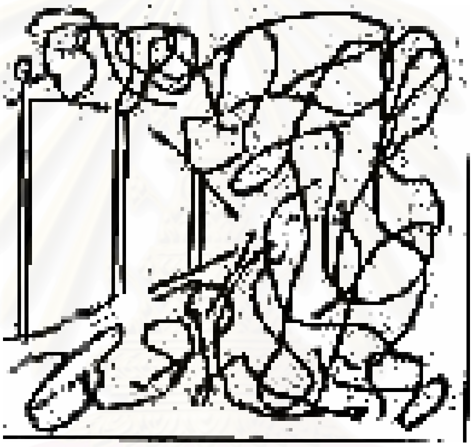


Figure 2.2 Craze formation (volume increase) [18].

b) Shear deformation (shear yielding): dissipation of energy by slip processes of the polymer chains of the matrix without significant change in volume.

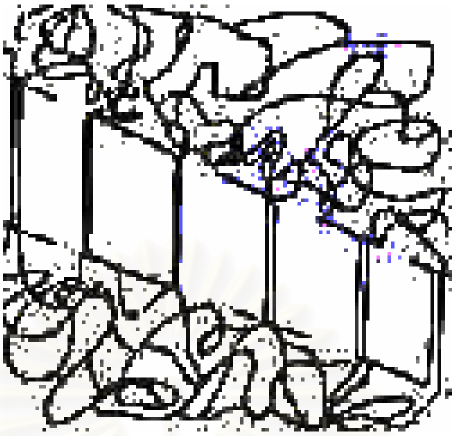


Figure 2.3 Shear deformation (volume unchanged) [18].

2.5.2 Impact-Modified PVC [19]

Impact modifiers are generally compounded into rigid PVC to improve the impact behavior of the PVC while retaining other critical performance properties necessary to achieve the demanding application requirements for clear and opaque rigid PVC.

The impact resistance of rigid PVC compounds is the key factor allowing their use in application such as shatterproof clear bottles, crease-resistant clear packaging film, opaque pipe or house siding, and opaque flame-resistant injection molded housings. Even though rigid PVC has inherent toughness due to its polarity and low temperature molecular relaxation and is ductile over a range of use conditions, it would be brittle and have inadequate toughness under conditions of high deformation rate and concentrated stress without the incorporation of impact modifiers.

2.5.2.1 Performance Requirements for Impact-Modified PVC

Incorporating rubbery particulate impact modifiers into rigid PVC by the process of powder blending followed by melt mixing enhances the toughness of PVC. Impact modifiers raise the ductile-brittle strain rate and lower the PVC brittleness temperature.

Impact modification reduces the notch sensitivity of PVC in that it can remain ductile under the severe geometrics and stress conditions of the notched Izod impact test.

2.5.2.2 Effects of Modifier Structure on Modified PVC Properties

Impact modifiers are usually particulate rubbery graft polymers or blends of both hard and rubbery polymers. The rubber component of the modifier is usually insoluble and incompatible with PVC and forms a distinct disperse phase with a low glass transition temperature, T_g. The rubbery particulate usually has a grafted outer glassy shell to achieve the desired controlled compatibility or wetting with the PVC matrix and good dispersion.

Typically, the rubber component will have a T_g lower than the -40°C β- relaxation of PVC to confer toughness at lower use temperatures. The brittleness temperature of PVC is lowered progressively by addition of impact modifier. The rubber content and particle size distribution of the impact modifier as well as the composition and molecular structure of the graft polymer influence the effectiveness of the impact modifier in lowering the brittleness temperature of the PVC. The number and size distribution of rubber particles per unit volume of glassy PVC and the adhesion of the grafted rubber particles with the PVC rigid continuum are the major factors affecting the efficiency of the impact modifier in reducing the brittleness temperature or increasing the strain rate for embrittlement of the PVC resin.

Grafting of each rubber particle is essential for attaching the rubber particles to the surrounding glassy matrix. This allows the transfer of strain and energy necessary for the rubber particles to dissipate impact energy. The degree of grafting controls the amount of free or ungrafted rigid copolymer which can be mixed or solubilized into the PVC. The melt flow of the PVC can be improved in this manner, but careful control of molecular weight of the ungrafted polymer must be maintained to control PVC processing and impact resistance.

2.5.2.3 Types of Impact Modifier for PVC

a) Methyl Methacrylate-Butadiene-Styrene Polymers (MBS)

MBS modifiers are graft polymers prepared by polymerizing methyl methacrylate or mixtures of methyl methacrylate with other monomers in the presence of polybutadiene or polybutadiene-styrene rubber. MBS have been incorporated at 5-10 % into PVC for improving impact [20].

Whilst modifiers of this class can be used in opaque formulation, they are of particular interest for clear compositions (e.g. bottle, film, and sheeting compounds), as many have refractive indices in the right range to promote good clarity: with several MBS modifiers this may be combined with good colour and surface gloss as well as resistance to stress whitening, good heat stability and low degree of odour and taste transfer in containers [21].

It is generally true that PVC grades which are impact modified with MBS is unsuitable for outdoor use. This is because of the fact that these plastics contain polybutadiene which is highly susceptible to photodegradation.

b) Acrylonitrile-Butadiene-Styrene Polymers (ABS)

ABS graft copolymers were introduced on the European market more than 20 years ago. Depending on their particular composition they are used for a large variety of applications, and they are suitable for both opaque and transparent formulations of rigid and semirigid PVC. The latter application is of importance in particular of dashboards (crashpads) in the automotive industry. Products which have a lesser impact modifying effect are more suitable for transparent articles, while highly effective ABS types are primarily intended for opaque PVC articles.

ABS graft copolymers are prepared by chemically grafting styrene and acrylonitrile monomers onto polybutadiene or styrene-butadiene rubber substrates in emulsion. The diene emulsion is prepared as a precursor to the grafting polymerization. The grafting has the purpose of improving the coupling (bonding) of the dispersed elastomeric phase with the hard PVC phase. ABS type impact modifiers confer high impact strength to PVC because of their good compatibility. Styrene facilitates processing by improvement of flow, acrylonitrile improves heat and chemical resistance, and moreover, increases the hardness of the material; and finally, butadiene increases impact strength.

c) Acrylic Impact Modifiers

All-acrylic and modified acrylic impact modifiers are used primarily for opaque outdoor or PVC applications requiring good retention of toughness, color, and appearance. They have been the principal impact modifiers used in high molecular weight PVC for weatherable applications such as window profile, house siding, gutters, downspouts, and other related PVC items.

Most acrylic modifiers are grafts of methyl methacrylate onto poly(alkyl acrylate) substrates such as poly(butyl- or 2-ethylhexyl acrylate). Core-shell acrylic modifiers have been described. Also, acrylic impact modifiers combining impact with processing and functionality are now available.

2.6 Literature Reviews

Zhao et al. [22] studied the graft copolymerization of styrene and methyl methacrylate on SBR latex particles in the core-shell emulsion process. It was conducted in a 600 ml glass stirred vessel with the BPO-Fe^{2+} redox initiator. The influences of the principal factors on the grafting degree and the grafting efficiency were initiator content, reaction temperature, mercaptan content, emulsifier content, monomer-to-rubber ratio, the frequency of monomer addition, and conversion. The local viscosity at the surface of the latex particles is quite large and the graft polymerization is a surface-controlled process.

Aerdts et al. [11] studied the emulsifier free grafting of styrene (ST) and methyl methacrylate (MMA) onto polybutadiene (PB) and determined the copolymer microstructure. ST/MMA (75/25) monomer mixtures were copolymerized at 323 K in the presence of a polybutadiene seed latex using either a water soluble (potassium persulfate) or an oil soluble (cumene hydroperoxide) initiator. The grafting of ST and MMA onto PB seed particles, stabilized by sulfate end groups, gives stable composite particles. By using emulsifier free grafting process, high degree of grafting value was achieved, while neither coagulation formation of a new crop of particles occurred. The intramolecular microstructure of ST/MMA grafted copolymer shifted more strongly to higher MMA contents than that of free ST/MMA. The chemical composition distributions (CCDs) of ST-g-MMA was broad but not bimodal. Moreover, the lower fraction of S in the grafted copolymer were believed to be caused by the dominant grafting on the PB backbone of polymeric free radicals originating from the aqueous phase or by particle precursor coagulation. The initiator type had no influenced on the copolymer microstructure but affected the latex stability and through its intrinsic radical activity the degree of grafting.

Aerdts et al. [23] studied the grafting of styrene (ST) and methyl methacrylate (MMA) onto polybutadiene (PB) in semi-continuous emulsion processes and determined the copolymer microstructure. ST and MMA were copolymerized at 323 K in the presence of a PB seed latex in emulsifier-free semi-continuous and, for comparison, batch processes using cumene hydroperoxide as initiator. The semi-continuous experiments gave much higher grafting efficiency values and also larger degree of grafting values than the batch processes. Other important differences were observed in the particle morphology, the number of grafting sites, the average molecular weight, and the microstructure of the copolymers. The chemical composition distributions (CCDs) of the semi-continuous graft copolymer was even broader than that of the batch graft copolymer.

Lenka et al. [24] studied the graft copolymerization of methyl methacrylate (MMA) onto rubber using potassium peroxydisulfate catalyzed by silver ion. The percentage of grafting was maximum at 5 hr. It was observed that, with increase of monomer concentration up to 1.4082 mol/L, the graft yield increases and, with further increase of monomer concentration, the graft yield decreases. The graft yield increases with increasing the peroxydisulfate concentration up to 2.5 x 10^{-2} mol/L and with further increase of the initiator concentration, the graft yield decreases. By increasing temperature, high percentage of grafting value was achieved, which might be due to swellability of rubber, solubility of monomer and its high diffusion rate.

Merkel et al. [25] studied the grafting of methyl methacrylate (MMA) onto polybutadiene (PB) via seeded emulsion polymerization at 50°C. Grafting MMA onto PB increased with increasing specific surface area of the seed latex while the molecular weight of the acetone-soluble graft copolymer decreased, indicating that the grafting reaction is a surface-controlled process. Increasing the monomer-to-polymer ratio decreased the proportion of grafted copolymer, supporting the theory that the periphery of the latex particle is the site of the grafting reaction. The influence of the initiator flux reflected the dependence of the concentration of free radicals on the grafting reaction (first order) and on the termination reaction (second order).

Brydon et al. [26] studied the grafting styrene (ST) monomer onto polybutadiene (PB) in benzene solution at 60°C with benzoyl peroxide (BPO) as initiator. They found that the proportion of polystyrene grafted onto PB was governed by the ratio of PB to ST in the reaction mixture. An increase in this ratio, either by an increase in PB relative to ST or by a decrease in ST relative to PB, resulted in an increase in grafting efficiency. Allied to this behavior was the observation that the rate of consumption of PB decreases as the relative ST concentration increases. On the other hand, the grafting efficiency was little affected by changes in the BPO concentration. They propose the cis and trans isomers have equal reactivity. In addition, the polymerization of the ST appears to follow normal kinetics, Rate of propagation (R_p) showing a first order dependence on monomer concentration and a square root dependence on initiator concentration. Furthermore, R_p was independent of PB concentration up to about 1.0 monomer mole/L. This classical kinetic behavior was also reflected in the molecular weight dependence of the free polystyrene on monomer and initiator concentrations.

Gasperowicz et al. [10] studied the grafting of styrene (St) onto poly(butyl acrylate) in emulsion with potassium persulfate as initiator. They found that the changes in the monomer conversion proceeded in the opposite direction to the changes in the grafting efficiency resulting from the variation of reaction parameters. Such relationships could be expected in the case of two competitive reactions in which the monomer is consumed, i.e., homopolymerization and graft copolymerization. The particles of a support polymer were the sites where both these reaction take place. Together with a higher extent of reaction, the availability of the support polymer in relation to the monomer probably decreases, manifested by a decrease in the grafting efficiency. At emulsifier concentrations higher than the critical micelle concentration (c.m.c.), the grafting efficiency rapidly decreases, suggesting that under such conditions the probability of the monomer homopolymerization was greater according to the micellar mechanism.

Dompas et al. [27] studied the toughening behavior of rubber-modified thermoplastic polymers involving very small rubber particles: impact mechanical behaviour of poly(vinyl chloride) (PVC)/methyl methacrylate-butadiene-styrene graft copolymer (MBS) blends. The resistance of MBS particles against cavitation increased with decreasing particle size, and there existed a critical particle size below which the MBS particles were unable to cavitate. The inability of small particles to cavitate was the reason for the decrease of the impact properties of PVC/MBS blends with very small MBS particles ($d_0 < 150$ nm). A toughening mechanism was proposed for the PVC/MBS blends in which the particle size of the rubber particles and the interparticles distance played equally crucial roles.

Prasassarakich et al. [28] studied the enhanced graft copolymerization of styrene and acrylonitrile onto natural rubber. Grafted natural rubber was prepared by an emulsion polymerization process using potassium persulfate as initiator. The rubber macroradical interacted with styrene and acrylonitrile monomers to form graft copolymer. The monomer conversion and grafting efficiency increased as reaction temperature and pressure increased. Grafted natural rubber could be used as impact modifier in SAN. Good mechanical properties of blends were obtained at grafted natural rubber to SAN ratio of 20 : 80.

Charmondusit et al. [29] studied the grafting of methyl methacrylate and styrene onto natural rubber in emulsion process. The rubber macroradicals reacted with methyl methacrylate and styrene monomers to form graft copolymers. The particle structure of grafted natural rubber was the core-shell type. The grafted natural rubber properties were strongly influenced by the reaction temperature. The grafted natural rubber prepared using 100 parts by weight of monomer per 100 parts by weight of natural rubber, 1.5 parts by weight of emulsifier, and 1.5 parts by weight of initiator at 70°C showed a high grafting efficiency and graft ratio. The grafted natural rubber product could be used as an impact modifier for PVC resin to form PVC/grafted natural rubber product blends by mechanical blending and compression molding. The good mechanical properties of blends were obtained at 10 and 15 phr of the grafted natural rubber.

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

	Chemical	Supplier
1.	Natural rubber latex, high ammonia	Thai Rubber Latex Corporation (Thailand) Public Co., Ltd.
2.	Styrene monomer, commercial grade	Eternal Resin Co., Ltd.
3.	Methyl methacrylate monomer, commercial grade	Siam Chemical Industry Co., Ltd.
4.	Potassium hydroxide, AR grade	BDH
5.	Sodium dodecyl sulfate, AR grade	APS Ajax Finechem.
6.	Oleic acid, AR grade	Fluka
7.	Cumene hydroperoxide	Fluka
8.	Tetraethylene pentamine	Fluka
9.	Light petroleum ether, AR grade	Lab Scan Analytical Sciences
10.	Acetone, commercial grade	Arsom Co., Ltd.
11.	Sodium hydroxide	Akzo Nobel
12.	Sodium sulfate anhydrous, AR grade	Riedel-de Haen
13.	Methyl ethyl ketone, AR grade	Lab Scan Analytical Sciences
14.	Poly(vinyl chloride) compound	Thai Plastic and Chemicals Public Co., Ltd.
15.	Methyl methacrylate butadiene styrene terpolymer	Thai Plastic and Chemicals Public Co., Ltd.
16.	Formic acid, commercial grade	Arsom Co., Ltd.
17.	Toluene, AR grade	Fisher Scientific
18.	Aluminum oxide	Fluka

3.2 Equipments

1. 4-Necked round bottom reactor, 500 ml capacity with condenser
2. Soxhlet extraction apparatus
3. Fourier-Transform Infrared Spectrometer : Nicolet (Impact 410), England
4. Transmission Electron Microscope : TEM-200 CX, Japan
5. Two-roll mills : Lab Tech Engineering, Thailand
6. Compression molding machine : Lab Tech Engineering, Thailand
7. Dynamic Machanical Analyzer : Perkin Elmer DMA 7e
8. Universal testing machine : LLOYD LR 5K
9. Hardness testing machine : INDENTECH 4150 AK
10. Impact testing machine : GOTECH GT-7045
11. Scanning Electron Microscope : JEOL, Model JSM-6400, Japan
12. Differential Scanning Calorimeter : Mettler Toledo DSC 522

3.3 Procedure

3.3.1 Purification of Monomer

The styrene monomer (b.p. 145.2°C/760 mmHg), contained a trace amount of hydroquinone as inhibitor. The inhibitor was removed by washing with 10% NaOH solution. The styrene monomer was washed with distilled water until neutral, and then dried with anhydrous Na_2SO_4, and passed through an activated aluminum oxide column to remove the residual inhibitor. The purified styrene was stored in the refrigerator.

The methyl methacrylate monomer (b.p. 98°C/760 mmHg), contained a trace amount of hydroquinone as inhibitor was purified by following the above procedure as for styrene monomer purification. The purified methyl methacrylate was stored in the refrigerator.

3.3.2 Preparation of Grafted Natural Rubber

The graft copolymer of styrene (ST) and methyl methacrylate (MMA) onto natural rubber (NR) was prepared by emulsion polymerization. The equipment setup is shown in Figure 3.1.

The high ammonia natural rubber latex (50 g, DRC 60%) was placed in a round bottom reactor along with 100 ml of distilled water. Potassium hydroxide, 1 wt% of the dry rubber content (phr) was added as a buffer, and sodium dodecyl sulfate (1 phr) as an emulsifier was then added while stirring. The mixture was deoxygenated by bubbling the nitrogen gas for approximately 15 mins at room temperature. The stabilizer, oleic acid (10 phr) was added, after 15 mins of stirring, the mixture of styrene and methyl methacrylate was then added, continually while stirring for 30 mins to allow the latex particles to attain swelling. The mixture was warmed up to reaction temperature, the initiator (CHPO) was then added. After 15 mins of mixing, the amine activator (10% aqueous solution of TEPA) was added. The bipolar redox initiating system was employed at a ratio 1 : 1 (CHPO : TERA). The reaction was then allowed to proceed for 8 hrs under continuous stirring to complete the polymerization and then the reaction was stopped. The product latex was discharged into boiling water containing 5% formic acid and the polymer product precipitated. The gross polymer was recovered and dried to a constant weight in vacuum pump. The complete experimental procedure is summarized in Figure 3.2. The standard recipe used for graft copolymerization is shown in Table 3.1.

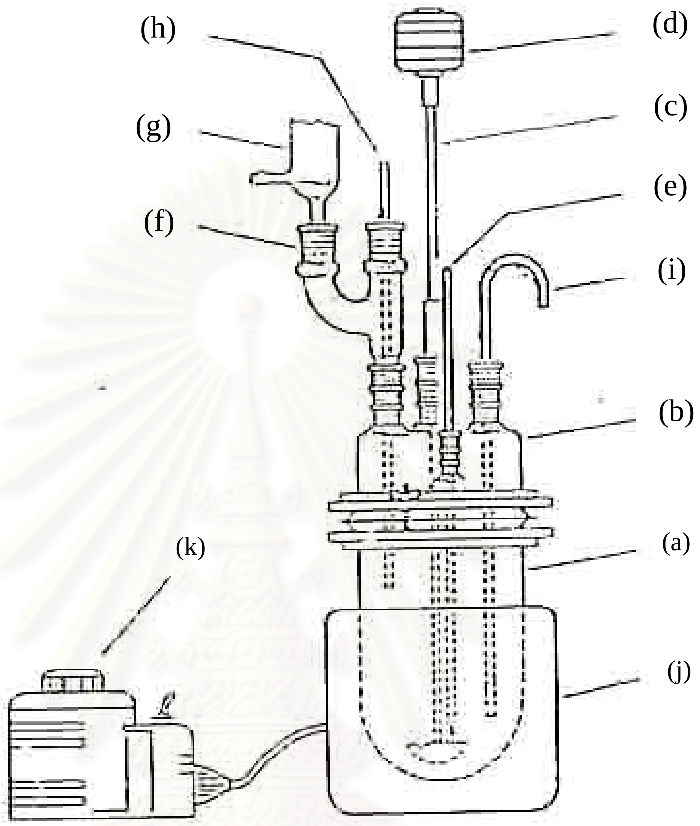


Figure 3.1 Apparatus for emulsion graft copolymerization of monomer styrene and methyl methacrylate onto natural rubber latex.

(a) reaction kettle bottom
(b) reaction kettle top
(c) stainless steel stirrer
(d) air motor
(e) thermometer
(f) adapter

(g) condenser
(h) nitrogen-inlet tube
(i) sampling tube
(j) water bath
(k) variable transformer

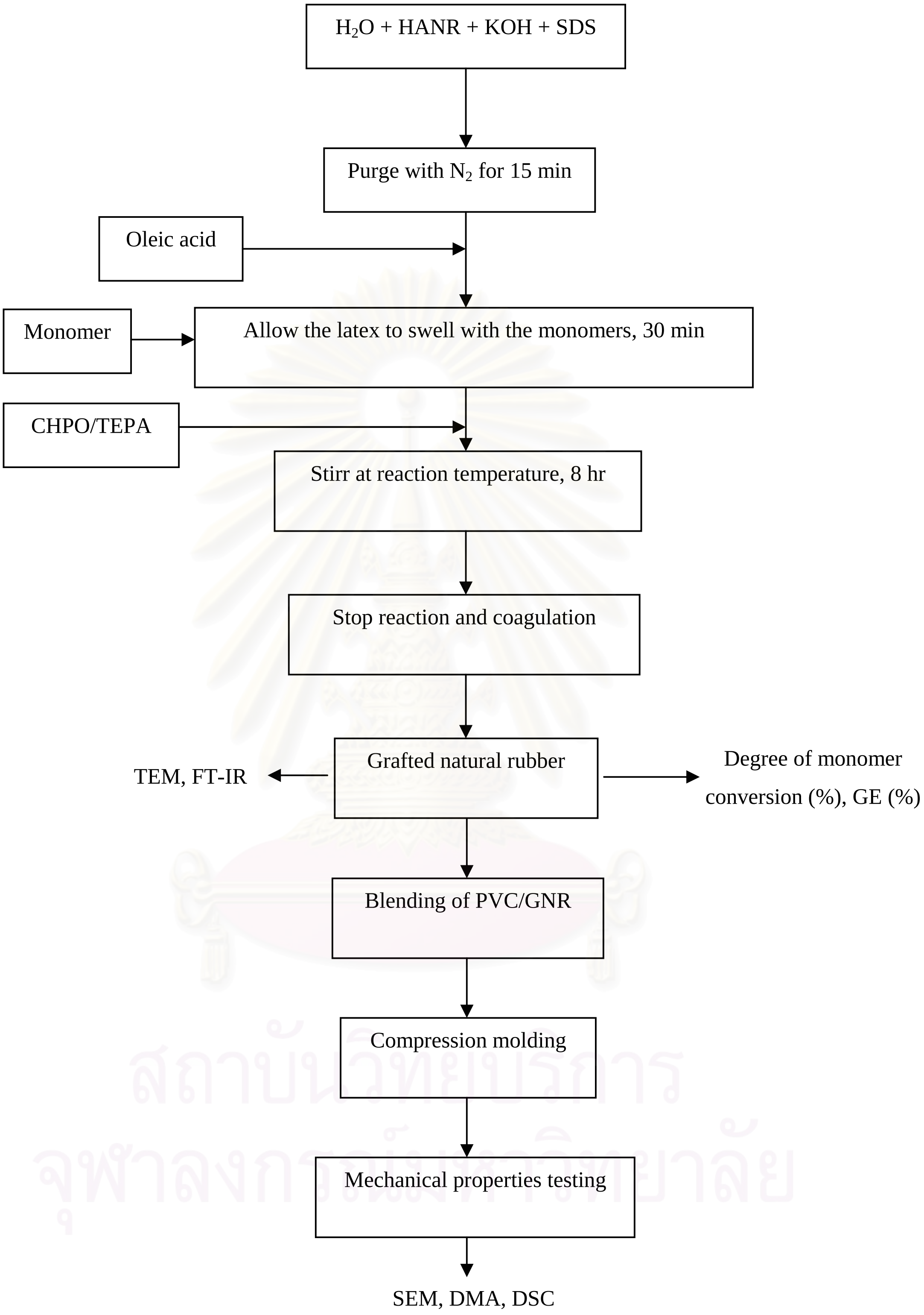


Figure 3.2 The overall schematic experimental process.

Table 3.1 Standard recipe used for graft copolymerization.

Ingredients	Quantities
Natural rubber (60% DRC)	50 g
Water	100 g
Stabilizer (oleic acid) amount	3 g
Buffer (potassium hydroxide) amount	0.3 g
Surfactant (sodium dodecyl sulfate) amount	0.3 g
Redox initiator (CHPO : TEPA = 1 : 1) amount	Variable
Styrene amount	Variable
Methyl methacrylate amount	Variable
Reaction temperature	Variable

3.3.3 Experimental Designs

Factorial designs require 2^k experiments if k factors have to be investigated. In this research work, a 2^4 design had 16 experiments. Process variables were varied according a 2^4 design. For each process variable “low level” and “high level” were chosen in the range to be studied. The low level is coded as –1 while the high level of each design factor is coded as +1. The independent variables listed in Table 3.2 are initiator concentration (INT), reaction temperature (TEMP), styrene to methyl methacrylate ratio (ST/MMA), and monomer to rubber ratio (M/R).

Table 3.2 Graft copolymerization run : low and high level of design factors

Ingredient	Name	Amount (Low = -1)	Amount (High = +1)
[INT]	cumene hydroperoxide	1 phr	2 phr
TEMP	reaction temperature	50°C	70°C
ST/MMA	styrene/methyl methacrylate ratio	1.0	1.25
M/R	monomer/rubber ratio	0.75	1.0

3.4 Determination of the Grafted Natural Rubber

3.4.1 Determination of the Conversion of Graft Copolymerization

The conversion of graft copolymerization was determined by the percentage increase of rubber weight. The calculations are as following equation.

$$\text{Total Conversion (\%)} = \frac{\text{Total weight of polymer formed}}{\text{Weight of monomer charged}} \times 100 \qquad (3.1)$$

3.4.2 Determination of the Percentage Grafted Natural Rubber and Grafting Efficiency

The amount of grafted natural rubber, free natural rubber, free homopolymer, and free copolymer in the product could be determined by soxhlet extraction. The free natural rubber was extracted by light petroleum ether (60-80°C) for 24 hrs. The residue was dried to constant weight in an oven at 40°C under vacuum for 24 hrs. To remove free copolymer and free homopolymer, the residue was extracted in a methyl ethyl ketone (MEK)/acetone (50 : 50 (v/v)) mixture just as described when petroleum ether was used [13]. The weight difference between the initial sample and extracted samples is the measure of free natural rubber, free copolymers, grafted natural rubber, and grafting efficiency. All of calculations are as following equations.

$$\text{Free Natural Rubber (\%)} = \frac{\text{Total weight of free natural rubber}}{\text{Total weight of the gross polymers}} \times 100 \qquad (3.2)$$

$$\text{Free Copolymers (\%)} = \frac{\text{Total weight of free copolymers}}{\text{Total weight of the gross polymers}} \times 100 \qquad (3.3)$$

$$\text{Grafted Natural Rubber (\%)} = \frac{\text{Total weight of graft copolymers}}{\text{Total weight of the gross polymers}} \times 100 \qquad (3.4)$$

$$\text{Grafting Efficiency (\%)} = \frac{\text{Total weight of monomers grafted}}{\text{Total weight of monomers polymerized}} \times 100 \qquad (3.5)$$

3.4.3 Characterization of Grafted Natural Rubber Product

After the soxhlet extraction of grafted natural rubber product, the grafted natural rubber (NR-g-ST/MMA) was characterized. The solution after the extraction by a MEK/acetone (50 : 50 (v/v)) mixture was analyzed by fourier-transform infrared spectroscopy (FT-IR).

Sample after the soxhlet extraction of grafted natural rubber product was dissolved in toluene and casted on the NaCl cell for IR investigation.

3.4.4 Determination of the Morphology of Grafted Natural Rubber

The grafted natural rubber latex was diluted 400 times with distilled water. To this solution 3 drops of a 2% aqueous OsO_4 solution was added, and allowed to stain the natural rubber in the grafted natural rubber for overnight. A drop of each diluted latex was placed on a grid and dried in the dessicator. The morphology of the natural rubber latex and grafted natural rubber latex were examined by a transmission electron microscopy technique (TEM model JEM-200 CX) at 100 kV.

3.5 Preparation of PVC/Grafted Natural Rubber Blends

The mixing roll temperature of two roll-mills was kept constant at 180°C. The PVC (100 phr) were fed to the two-roll mills for 3 mins and then blended with grafted natural rubber (0, 5, 10 ,and 15 phr) for 7 mins until the surface of blend was smooth.

The sheets were pressed into a preheated mold of compression molding at 190°C and pressure of 150 kg/cm^2 for 5 mins. After pressing, the mold was transferred to a water cooled press for 5 mins. The sheet thickness was 3 mm. The sheet was cut into the standard specimens according to the ASTM test method. The compositions of grafted natural rubber and PVC blends are shown in Table 3.3.

Table 3.3 Grafted natural rubber (GNR) and PVC composition

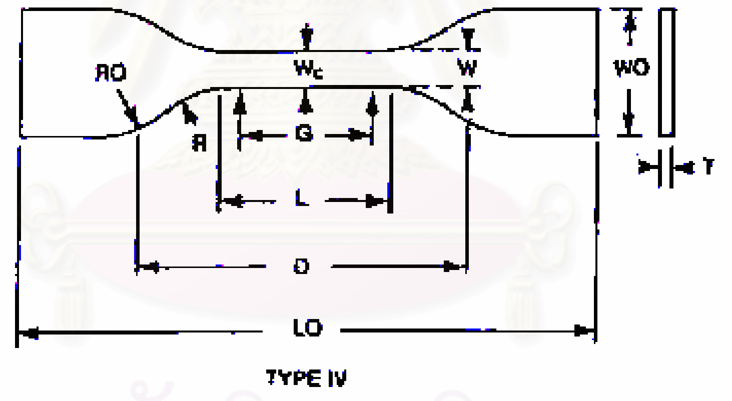
Material	Unmodified PVC (phr)	Impact modified PVC (phr)
PVC compound	100	100
Graft copolymer impact modified		
MBS	-	5, 10, and 15
GNR	-	5, 10, and 15
NR	-	5 and 10

3.6 Mechanical Testing

The mechanical properties of the grafted natural rubber modified PVC, MBS modified PVC, and NR modified PVC were measured by following the ASTM test methods.

3.6.1 Tensile Properties (ASTM D 638)

Tensile properties of the samples were measured at 25°C and humidity of 60% using dumbbell-shaped test pieces (Type IV) as illustrated in Figure 3.3. The specimens were cut from a 3.0 mm thick sheet. The testing were performed on a Universal testing machine (LLOYD LR 5K) with a crosshead speed of 500 mm/min.

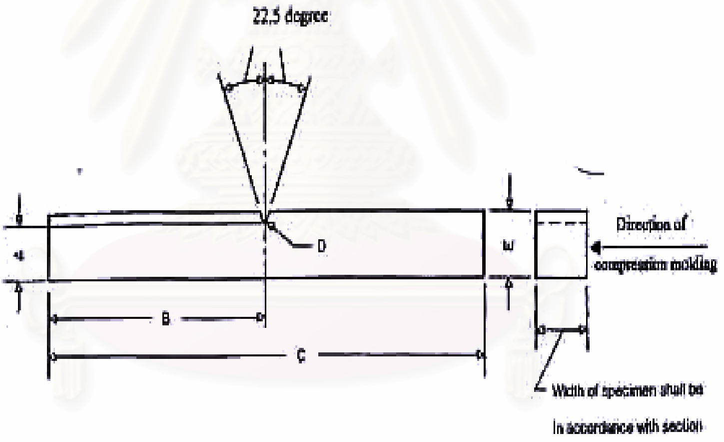


W : 6 mm   WO : 19 mm   G : 25 mm   R : 14 mm   T : 4 mm or under
L : 33 mm   LO : 115 mm   D : 65 mm   RO : 25 mm

Figure 3.3 Schematic diagram of tensile test specimen (type IV) [17].

3.6.2 Impact Strength (ASTM D 256)

The test specimen should conform to the dimensions and geometry of Figure 3.4. The machine used in the present investigation was Izod-Charpy Impact Tester. The width of each specimen was measured in the region of the notch with a micrometer caliper and recorded its average width along with its identifying markings. The test specimen was put in a horizontal position so that it will be impacted edgewise at its center on the face opposite the notch for notched specimens. The breaking energy of the specimen was estimated and a pendulum of suitable energy was selected. The pendulum was released and the excess energy remaining in the pendulum was recorded after breaking the specimen, together with a description of the appearance of a broken specimen. The average impact energy was calculated in the group of specimens.



Unit : mm

A : 10.16 ± 0.05

B : 32.00 max., 31.50 min.

C : 63.50 max., 63.30 min.

D : 0.25 ± 0.05

E : 12.70 ± 0.05

Figure 3.4 Dimensions of simple beam, charpy type, impact test specimen [17].

3.6.3 Hardness

The test specimen shall be at least 3 mm in thickness. The lateral dimensions of the specimen shall be sufficient to permit measurements at least 12 mm from any edge. The specimen shall be flat and parallel over a sufficient area to permit the presser foot to contact the specimen.

The specimen was placed on a hard and horizontal surface. The presser was held on a vertical position with the point of the indentor at least 12 mm from any edge of the specimen. The presser was applied to the specimen. After the presser foot was in firm contact with the specimen, the scale reading was taken within 30 s. One measurement was made at five different points distributed over the specimen and the median of these measurements was used as the hardness value.

3.7 Scanning Electron Microscopy (SEM)

The scanning electron microscopy (SEM) was used to investigate the fracture surface of the grafted natural rubber modified PVC, MBS modified PVC, and NR modified PVC from the tensile properties test. Samples for SEM were mounted on a SEM stub using a double-side tape and the fracture specimens were coated with gold. The SEM (JEOL model JSM-6400) was operated at 15 kV.

3.8 Dynamic Mechanical Properties

The dynamic mechanical properties of grafted natural rubber were measured on a dynamic mechanical analyzer (Perkin-Elmer DMA 7e) with a liquid nitrogen cooling system. The parallel plate mode was used to characterize the grafted natural rubber in a temperature range of –90 to 50°C at a heating rate of 5°C min^{-1} and at a frequency of 1 Hz. The dual cantilever mode of deformation geometry, known as three-point bending was used to characterize the grafted natural rubber modified PVC in temperature range of –90 to +90°C at a heating rate of 5°C min^{-1} and at a frequency of 1 Hz. Test specimen dimension was 15 mm length, 3 mm width and 2 mm thickness.

3.9 Differential Scanning Calorimeter (DSC)

The differential scanning calorimeter (DSC) used to evaluate the thermal properties of the grafted natural rubber modified PVC was a Mettler Toledo DSC 822. The sample of 10 mg was placed in an aluminum pan. The differential scanning calorimetry of the grafted natural rubber modified PVC was carried out under N_2 atmosphere at heating rate of 20°C/min from -100°C to 120°C.

CHAPTER IV

RESULTS AND DISCUSSION

The graft copolymers of styrene and methyl methacrylate onto natural rubber were prepared by emulsion polymerization with redox system of cumene hydroperoxide (CHPO)/tetraethylene pentamine (TEPA) as initiator. Most of the free radicals are produced at the monomer swollen particle/water interface, taking into account the fact that the peroxide is soluble in the organic phase, whereas the activator tetraethylene pentamine is water-soluble [13]. The four process variables, which were expected to have an effect on grafting efficiency, percentage graft copolymer, and percentage free copolymer were initiator concentration, reaction temperature, styrene to methyl methacrylate ratio, and monomer to rubber ratio. Statistical analysis, factorial design, was used to study the influence of each process variable irrespective of and in combination with the other process variables on the grafting efficiency, percentage graft copolymer, and percentage free copolymer. The grafted natural rubber was used as an impact modifiers for PVC. The grafted natural rubber was blended with PVC at various percentage of the grafted natural rubber contents using a two roll-mills and a compression molding. The mechanical properties of the grafted natural rubber modified PVC were investigated.

4.1 Properties of Natural Rubber Latex

The high ammonia natural rubber latex (HANR) obtained from Thai Rubber Latex Corporation (Thailand) Public Co., Ltd. has the properties as shown in Table 4.1.

Table 4.1 The properties of high ammonia natural rubber latex

Properties	Test Results
Total Solids Content, %	61.73
Dry Rubber Content, %	60.14
Non Rubber Solids, %	1.59
Ammonia Content (on Total Weight), %	0.70
Ammonia Content (on Total Phase), %	1.83
pH Value	10.45
KOH Number	0.5660
Volatile Fatty Acid Number (V.F.A.)	0.0165
Mechanical Stability Time @ 55 % TS (secs.)	710 on 5/1/03
Specific Gravity at 25°C	0.9420
Magnesium Content (on Solids), ppm.	33
Viscosity on 60 % TS (Spindle # 1 Speed 60 rpm)	87.4

4.2 Characterization of Grafted Natural Rubber

4.2.1 Functional Groups in the Grafted Natural Rubber

The grafted natural rubber product consisting of free copolymers and grafted copolymers. Ungrafted poly(methyl methacrylate) (PMMA), polystyrene (PST), and poly(styrene-*co*-methyl methacrylate) (P(ST/MMA)) are referred to as free copolymers. Grafted copolymers are referred to as NR-g-PMMA, NR-g-PST, and NR-g-PST/MMA.

The function groups in the natural rubber, the grafted natural rubber, and the solution after the extraction by a MEK/acetone (50:50 (v/v)) mixture were analyzed by IR spectroscopy. Figures 4.1, 4.2, and 4.3 show the infrared spectra in the region of 4000-400 cm^{-1} for natural rubber, grafted natural rubber, and solution after the extraction by MEK/acetone (50:50 (v/v)) mixture, respectively. The IR spectra of natural rubber exhibited the characteristic absorption bands of C=C stretching vibration at 1680 cm^{-1}, the C-H vibration at 2997, 1473, and 1376 cm^{-1}, and the C=C bending vibration at 853 cm^{-1}. The new peaks in IR spectrum of the grafted natural rubber show absorption bands of C=O stretching vibration at 1736 cm^{-1}, the C-O-C stretching vibration at 1131 cm^{-1}, the C=C stretching of aromatic ring at 1510 cm^{-1}, and the C=C-H bending of aromatic ring at 787 and 695 cm^{-1}. This confirms the occurance of grafting of styrene and methyl methacrylate onto natural rubber. The IR spectrum of mixture of MEK/acetone extract exhibited the characteristic absorption band of C=O stretching vibration at 1736 cm^{-1}, the C-O-C stretching vibration at 1131 cm^{-1}, and the C=C-H bending of aromatic ring at 787 and 695 cm^{-1}. This confirms that mixture of MEK/acetone could extract removed free copolymer (ST/MMA) from grafted natural rubber product.

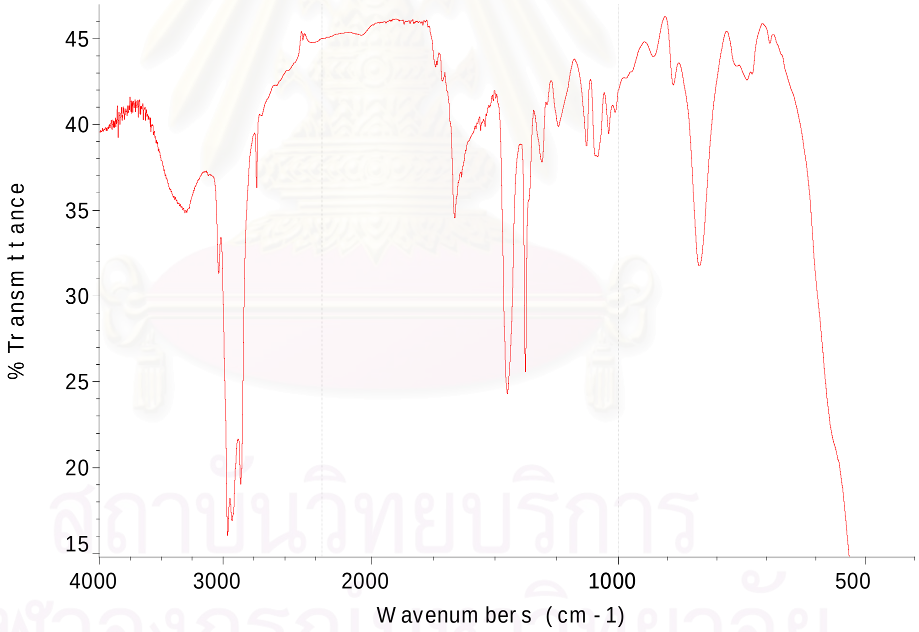


Figure 4.1 IR spectrum of natural rubber.

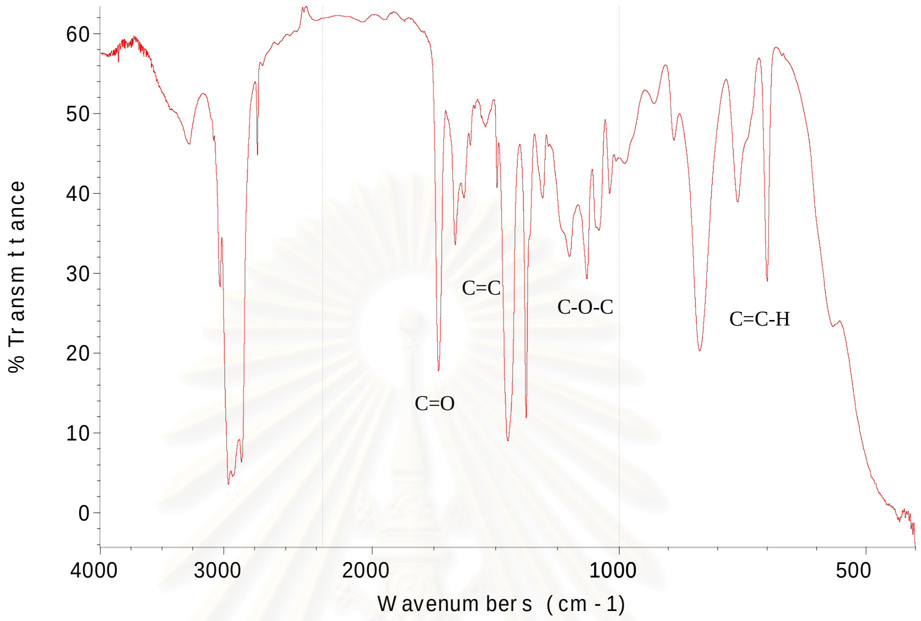


Figure 4.2 IR spectrum of grafted natural rubber.

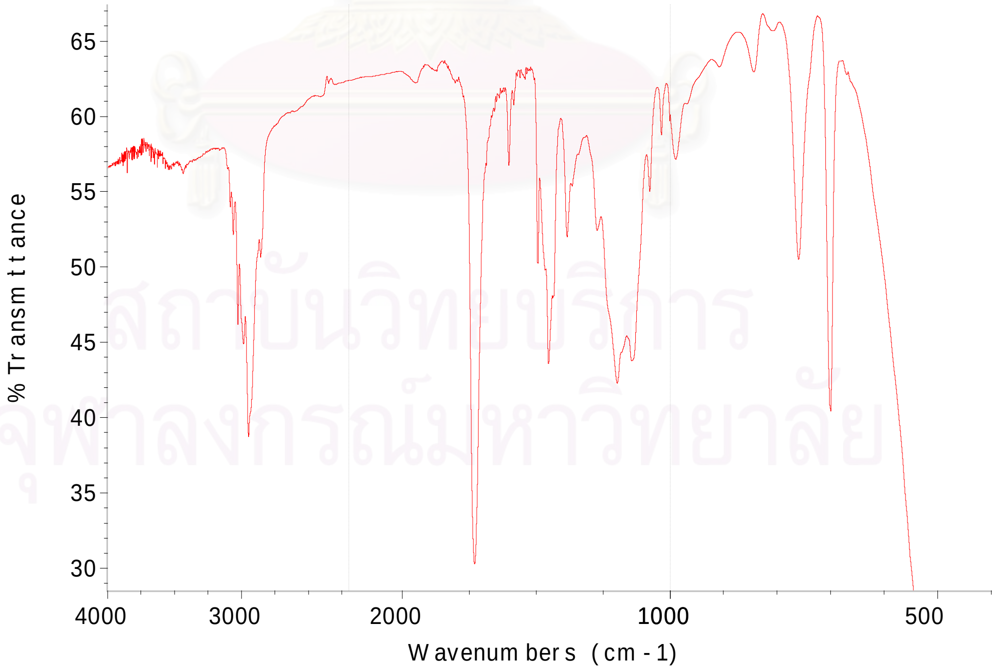


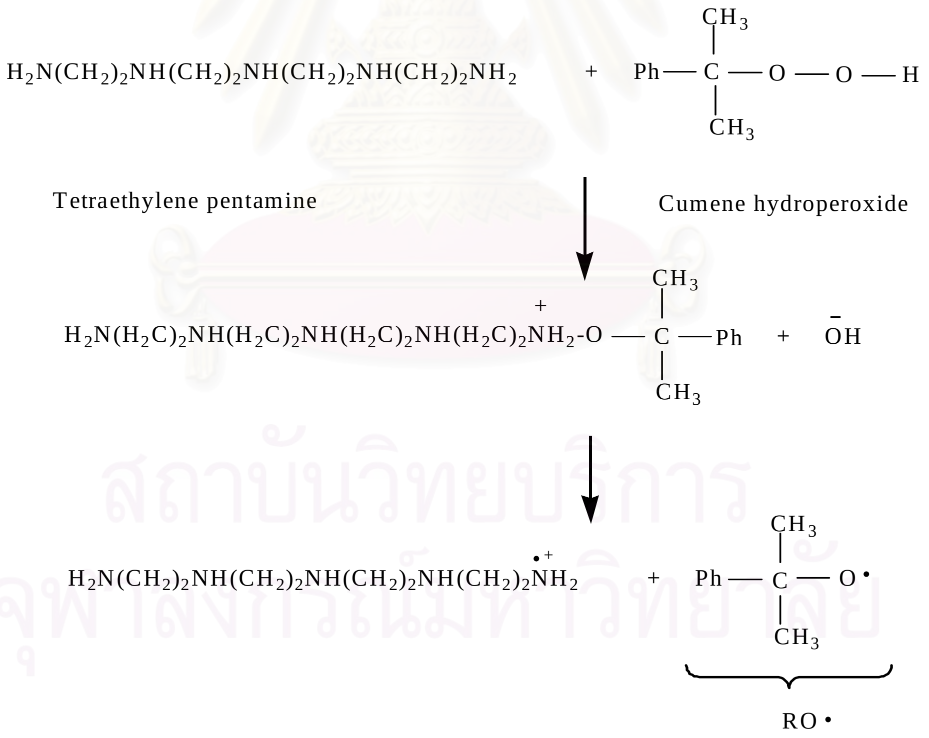
Figure 4.3 IR spectrum of mixture of MEK/acetone extract.

4.3 Mechanism of Grafting

The following reaction scheme is proposed for the graft copolymerization of vinyl monomers onto natural rubber by the free radical method :

a) Initiation

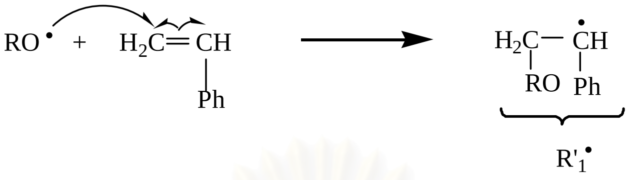
Initiating radicals are then produced by the resulting redox catalyst system, i.e. by one electron oxidation-reduction reactions. The cumene hydroperoxides (CHPO) in the dilute aqueous solution induced by tetraethylene pentamine (TEPA) decompose to yield alkoxy radicals (RO•). The alkoxy radical might interact with the monomer or the rubber molecule leading to the formation of the actual active sites for polymerization.



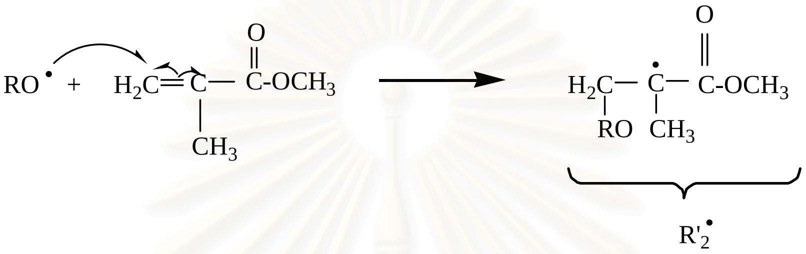
(4.1)

(4.2)

i) Attacking Monomer :

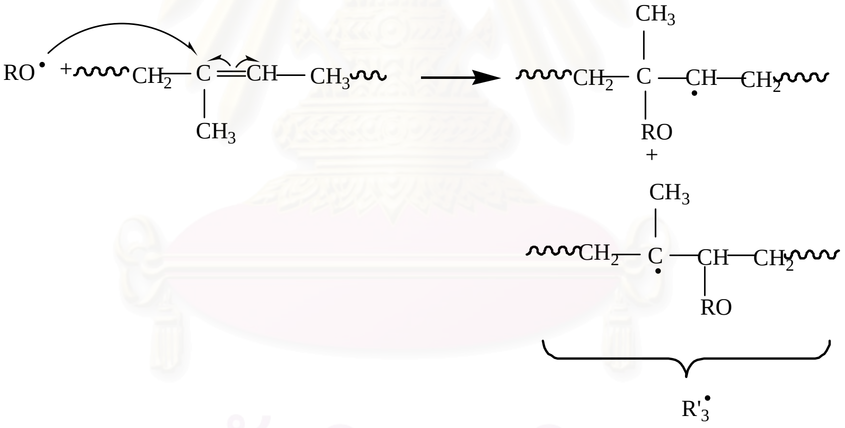


(4.3a)



(4.3b)

ii) Attacking Rubber :



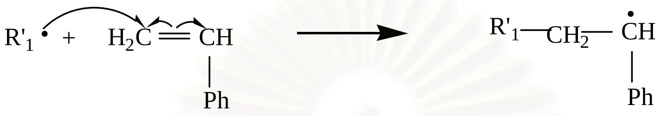
(4.4)

b) Propagation

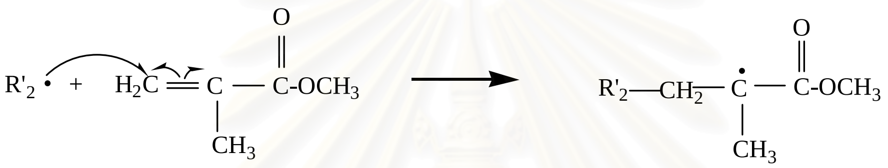
Both free and grafted chains are in the same environment and are presumed to grow at equivalent rates as described by :

i) Propagation of Free Copolymerization :

Polymerization of monomer itself, both styrene and methyl methacrylate can be occurred. It is proposed that the alkoxy radical initiate double bond of the monomer to give the radical (styryl or MMA radical) which then react with other styrene or methyl methacrylate monomers.



(4.5a)

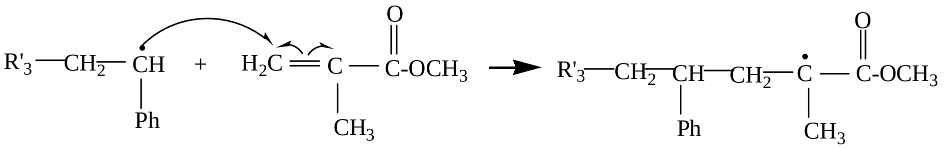


(4.5b)

ii) Propagation of Graft Copolymerization :

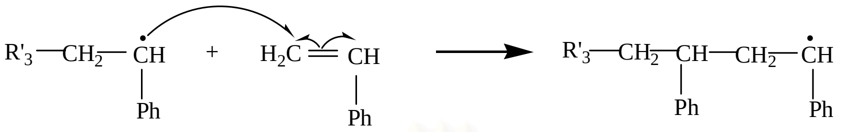
In the styrene polymerization, the polyisoprenyl radical could be completed for styrene monomer and formed graft copolymers because the reactivity of the polystyryl radical as same as the polyisoprenyl radical. Styrene is quite an active monomer compared to methyl methacrylate. Aerdts et al. [11] reported a large difference in reactivity ratio, namely $r_{MMA} = 0.19 \pm 0.05$ and $r_{ST} = 0.73 \pm 0.05$. So, styrene reacts first with natural rubber macroradicals and the resulting styryl radicals then copolymerize readily with methyl methacrylate or styrene.

(4.6a)



$$R'_3-CH_2-\dot{C}H(Ph) + H_2C=C(CH_3)-C(=O)-OCH_3 \rightarrow R'_3-CH_2-CH(Ph)-CH_2-\dot{C}(CH_3)-C(=O)-OCH_3$$

(4.6b)



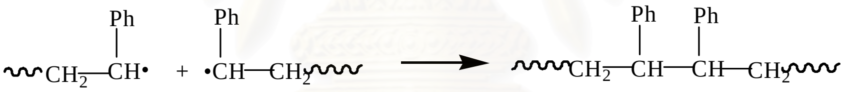
$$R'_3-CH_2-\dot{C}H(Ph) + H_2C=CH(Ph) \longrightarrow R'_3-CH_2-CH(Ph)-CH_2-\dot{C}H(Ph)$$

(4.6c)

b) Termination

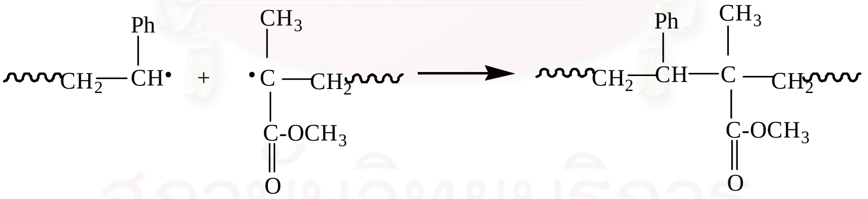
A termination reaction always involves two radicals reacting by recombination. In the former case, a bond is formed between two growing radicals, whereby the polymer molecule is the summation of the sizes of the radicals upon termination.

i) Termination of Free Copolymerization :



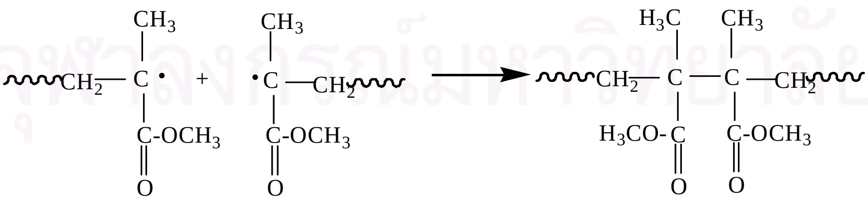
$$\sim CH_2-CH(Ph)\cdot + \cdot CH(Ph)-CH_2\sim \longrightarrow \sim CH_2-CH(Ph)-CH(Ph)-CH_2\sim$$

(4.7a)



$$\sim CH_2-CH(Ph)\cdot + \cdot C(CH_3)(C(=O)-OCH_3)-CH_2\sim \longrightarrow \sim CH_2-CH(Ph)-C(CH_3)(C(=O)-OCH_3)-CH_2\sim$$

(4.7b)

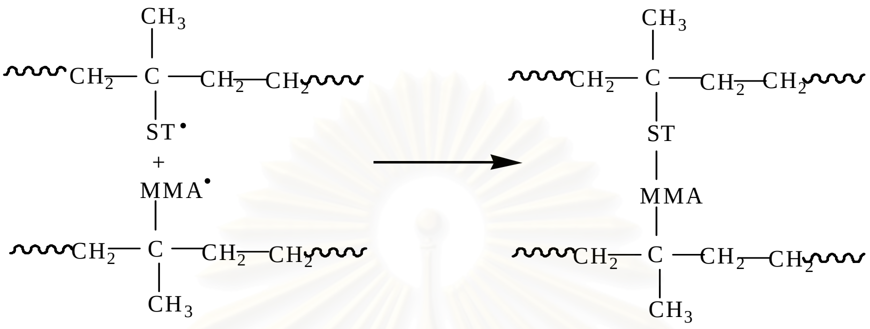


$$\sim CH_2-C(CH_3)(C(=O)-OCH_3)\cdot + \cdot C(CH_3)(C(=O)-OCH_3)-CH_2\sim \longrightarrow \sim CH_2-C(CH_3)(C(=O)-OCH_3)-C(CH_3)(C(=O)-OCH_3)-CH_2\sim$$

(4.7c)

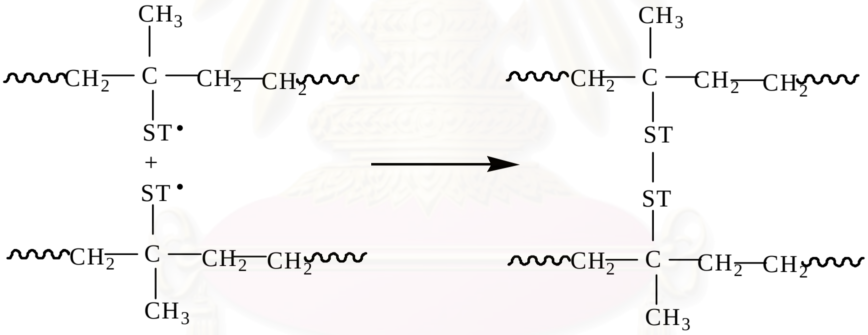
ii) Termination of Graft Copolymerization :

iia) Recombination between Styryl and MMA macroradicals



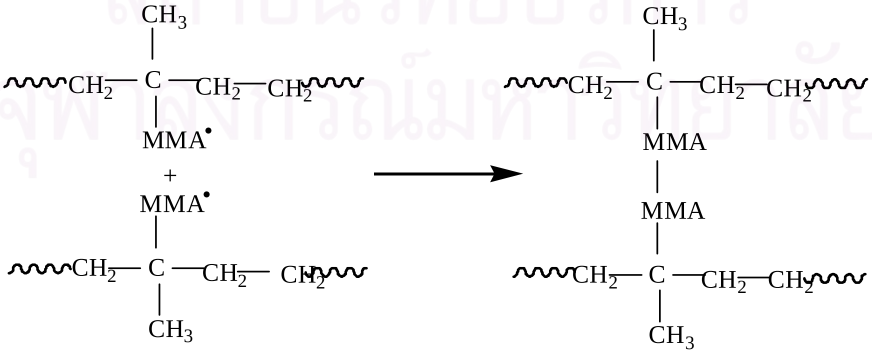
(4.8a)

iib) Recombination between Styryl macroradicals



(4.8b)

iic) Recombination between MMA macroradicals



(4.8c)

4.4 Experimental Designs

4.4.1 The Influence of Process Variables

Factorial experiments were carried out in this research work to study the factors thought to influence the grafting efficiency, percentage graft copolymer, and percentage free copolymer. The four process variables were initiator concentration (A), reaction temperature (B), styrene to methyl methacrylate ratio (C), and monomer to rubber ratio (D). To ensure that the assumptions of normality and constant variance were met, the response variable, grafting efficiency and percentage graft copolymer, were calculated. The response variables were analyzed by constructing a normal probability plot of the effect estimates. The table of plus and minus signs for the 2^4 factorial design are shown in Table 4.2.

From Table 4.2, the calculation of contrasts, estimate effects, and summation of squares are shown in Appendix B. Results for the mean grafting efficiency, percentage graft copolymer, and percentage free copolymer are shown in Table 4.3. The normal probability plots of effect estimate on grafting efficiency, percentage graft copolymer, and percentage free copolymer are shown in Figure 4.4.

All of the effects that lie along the line are negligible, whereas the large effects are far from the line. For grafting efficiency, the important effects that emerged from this analysis were A, B, and D and the BD interaction (Figure 4.4a). For percentage graft copolymer, the factors B and D along with the BC interaction are significant (Figure 4.4b). For percentage free copolymer, the main effects are A, B, and D (Figure 4.4c). The analysis of variance (ANOVA) of grafting efficiency, percentage graft copolymer, and percentage free copolymer display for this model are shown in Table 4.4. Table 4.4 shows the F test of effects of the process variables. The effects of the variables and any interactions, which are significant with respect to grafting efficiency, percentage graft copolymer, and percentage free copolymer, can be identified. An “ effect ” is defined as the change in the response on changing the variable from the “ - ” level to the “ + ” level.

Table 4.2 Design factor levels for factorial designed experiments

Experiment	Design factor				Total	Free	Free	Graft	GE
	INT	TEMP	ST/MMA	M/R	conversion	rubber	copolymer	copolymer	
	A	B	C	D	(%)	(%)	(%)	(%)	(%)
GNR 01	-	-	-	-	85.9	26.8	29.5	43.7	24.3
GNR 02	+	-	-	-	97.4	24.3	34.7	41.0	17.6
GNR 03	-	+	-	-	65.8	23.6	14.1	62.3	57.0
GNR 04	+	+	-	-	66.0	20.7	17.7	61.6	46.6
GNR 05	-	-	+	-	87.7	19.9	28.3	51.8	28.5
GNR 06	+	-	+	-	97.8	20.7	34.0	45.3	19.7
GNR 07	-	+	+	-	64.4	19.8	14.1	66.1	56.7
GNR 08	+	+	+	-	67.9	21.3	18.5	60.2	45.2
GNR 09	-	-	-	+	82.6	30.5	35.0	34.5	22.6
GNR 10	+	-	-	+	96.9	26.4	39.8	33.8	18.9
GNR 11	-	+	-	+	62.2	24.4	20.9	54.7	45.4
GNR 12	+	+	-	+	63.5	16.1	24.7	59.2	36.1
GNR 13	-	-	+	+	81.1	18.0	35.1	46.9	21.1
GNR 14	+	-	+	+	90.4	23.9	39.5	36.6	16.5
GNR 15	-	+	+	+	64.4	26.0	22.6	51.4	42.2
GNR 16	+	+	+	+	65.1	19.9	24.1	56.0	38.7

INT : + (2 phr), - (1 phr)
TEMP : + (70°C), - (50°C)
ST/MMA : + (1.25), - (1.0)
M/R : + (1.0), - (0.75)

Table 4.3 The effect of process variables for grafted natural rubber

Statistical experimental design	Means grafting efficiency	Means graft copolymer	Means free copolymer
INT			
-1	37.2	50.4	25.0
+1	29.9	49.2	29.1
TEMP			
-1	21.1	41.7	34.5
+1	46.0	58.9	15.6
ST/MMA			
-1	33.6	48.8	27.0
+1	33.6	51.8	27.0
M/R			
-1	37.1	54.0	23.9
+1	30.2	46.6	30.2

INT : + (2 phr), - (1 phr)
TEMP : + (70°C), - (50°C)
ST/MMA : + (1.25), - (1.0)
M/R : + (1.0), - (0.75)

Regarding the decision about which terms were significant, for the purpose of this research work, the 95 % confidence interval was used. Based on the analysis of variance, factors A, B, and D along with the BD interaction were significant effects ($F_{0.05,1,11} > 4.84$) on grafting efficiency [30]. In this analysis of variance, factors B and D were significant effects ($F_{0.05,1,12} > 4.75$) on percentage graft copolymer [30]. In addition, the factors A, B, and D were significant effects ($F_{0.05,1,12} > 4.75$) on percentage free copolymer [30]. To assist in the practical interpretation of this research work, Figure 4.5 presents plots of the four main effects on grafting efficiency and percentage graft copolymer. The main effect plots are just graphs of the response averages, mean grafting efficiency and mean percentage graft copolymer, at the levels of the four factors. The main effect plots on percentage free copolymer are shown in Figure 4.6. The interaction on grafting efficiency is presented in Figure 4.7.

INT was the negative effect since the grafting efficiency and percentage graft copolymer decreased with increasing amount of initiator (Figure 4.5a). The mean grafting efficiency decreased from 37.2 to 29.9 and mean percentage graft copolymer decreased from 50.4 to 49.2 when the amount of initiator was increased from 1.0 to 2.0 phr, respectively. The increase in the initiator concentration caused the increase initiator radical and the increase in radical chains to graft but the recombination of two radical chains can occur. So, grafting efficiency and percentage graft copolymer were decreased at high initiator concentration.

The positive effect, TEMP, was the result of an increase in reaction temperature (Figure 4.5b). The mean grafting efficiency increased from 21.1 to 46.0 and mean percentage graft copolymer increased from 41.7 to 58.9 when the reaction temperature was increased from 50° C to 70°C, respectively. It is well known that grafts were produced by transfer of radical to the rubber chain. As reaction temperature increased, the activation energy of the transfer reaction was greater than that of the propagation reaction, so grafting efficiency and percentage graft copolymer increased when the reaction temperature was increased [10].

No effect of ST/MMA ratio is shown in Figure 4.5c. The constant mean grafting efficiency and means percentage graft copolymer were presented when the styrene to methyl methacrylate ratio was increased from 1.0 to 1.25, respectively.

The grafting efficiency and percentage graft copolymer decreased with increasing monomer to rubber ratio (M/R) (Figure 4.5d). The mean grafting efficiency decreased from 37.1 to 30.2 and mean graft copolymer decreased from 54.0 to 46.6 when the monomer to rubber ratio was increased from 0.75 to 1.0, respectively. This result may be explained by a mechanism involving a surface-controlled process, which has previously been reported [13, 25]. This suggests that the graft reactions occur mainly on the surface of the latex particles so the polymerization occurs mainly in the shell of the particles. As grafting proceeds and a certain shell thickness of the second stage polymer is reached, the contact area between monomer and rubber decreases. Therefore, it is more difficult for graft copolymerization to occur though diffusion of the monomer to the rubber chain, compared to the copolymerization of monomers. As a result, the grafting efficiency and graft copolymer decreases with increasing monomer to rubber ratio.

Figure 4.6 shows the effect plots on percentage free copolymer. It was found that A and D were positive effects, whereas B was negative effect. The increase in the initiator concentration caused the increase in initiator radical leading to the production of free copolymer radicals. The excessive free copolymer radicals react with each other to form free copolymer more than to graft on the natural rubber. As reaction temperature increased, the activation energy of the transfer reaction was greater than that of the propagation reaction, so percentage free copolymer decreased with increasing reaction temperature. And the percentage free copolymer increased with increasing M/R ratio. It can be explained that there was most monomers on the outerface of the natural rubber core at the high M/R ratio, so it was easier for the monomer to propagate with free copolymer radicals and percentage free copolymer was higher. This research work aims to reduce the percentage free copolymer, so the optimum condition for grafting was at the low level of D and the high level of B.

The BD interaction is plotted in Figure 4.7. This interaction is the key to solve the problem. The optimum grafting efficiency would appear to be obtained when B was at the high level, whereas D was at the low level.

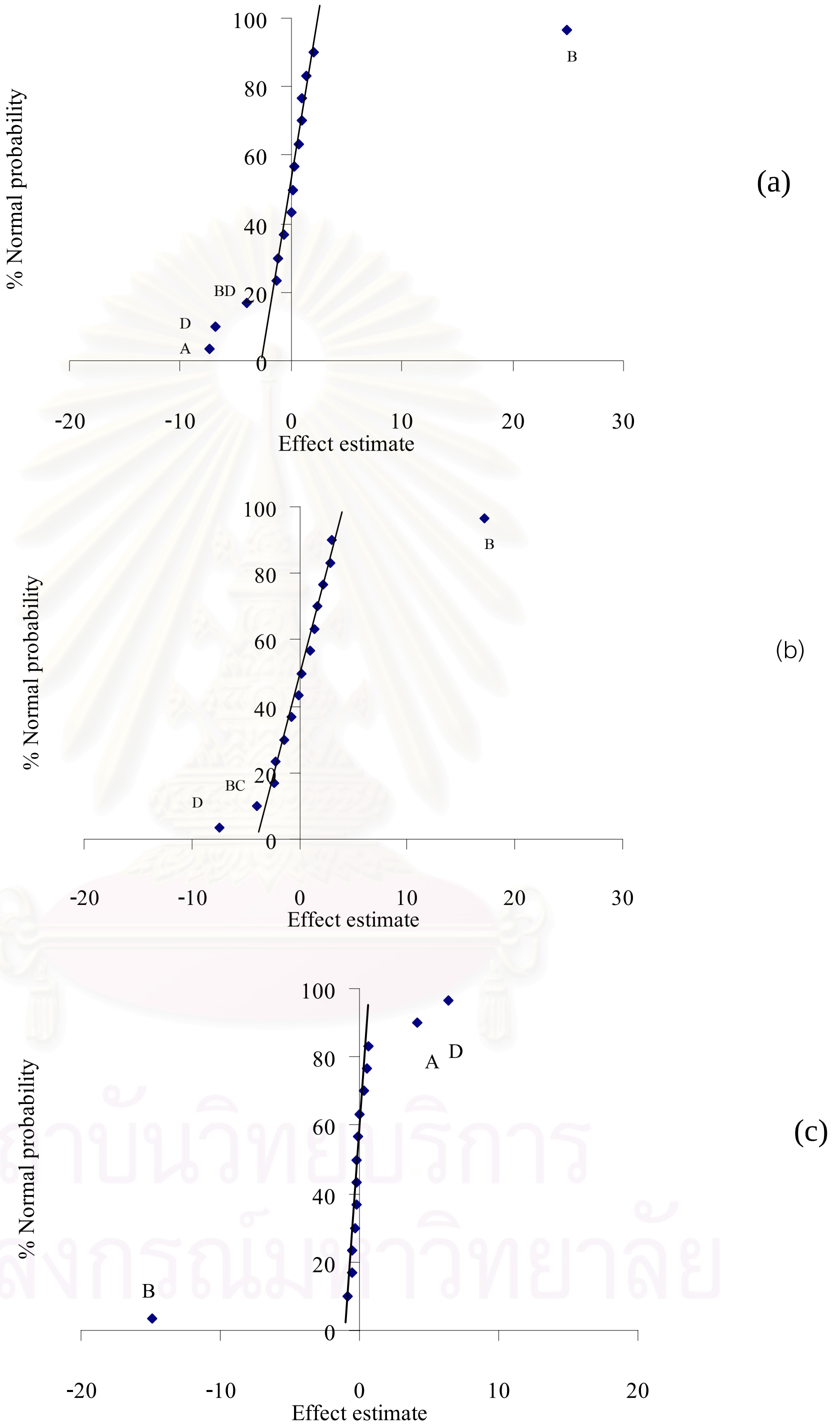


Figure 4.4 The normal probability plots of effect estimate on (a) grafting efficiency, (b) percentage graft copolymer, and (c) percentage free copolymer.

Table 4.4 The analysis of variance

Effect Name	Estimate Effect	Sum of Square	Degree of Freedom	Mean Square	F_0
Grafting efficiency					
A	-7.32	214.33	1	214.33	48.73
B	24.84	2467.61	1	2467.61	561.02
D	-6.77	183.33	1	183.33	41.68
BD	-4.02	64.56	1	64.56	14.68
Error		48.38	11	4.40	
Total		2978.21	15		
Percentage graft copolymer					
B	17.23	1187.66	1	1187.66	88.44
D	-7.37	217.19	1	217.19	16.17
BC	-3.96	62.69	1	62.69	4.67
Error		161.14	12	13.43	
Total		1628.68	15		
Percentage free copolymer					
A	4.17	69.47	1	69.47	94.88
B	-14.90	887.44	1	887.44	1211.99
D	6.37	162.43	1	162.43	221.84
Error		8.79	12	0.732	
Total		1128.14	15		

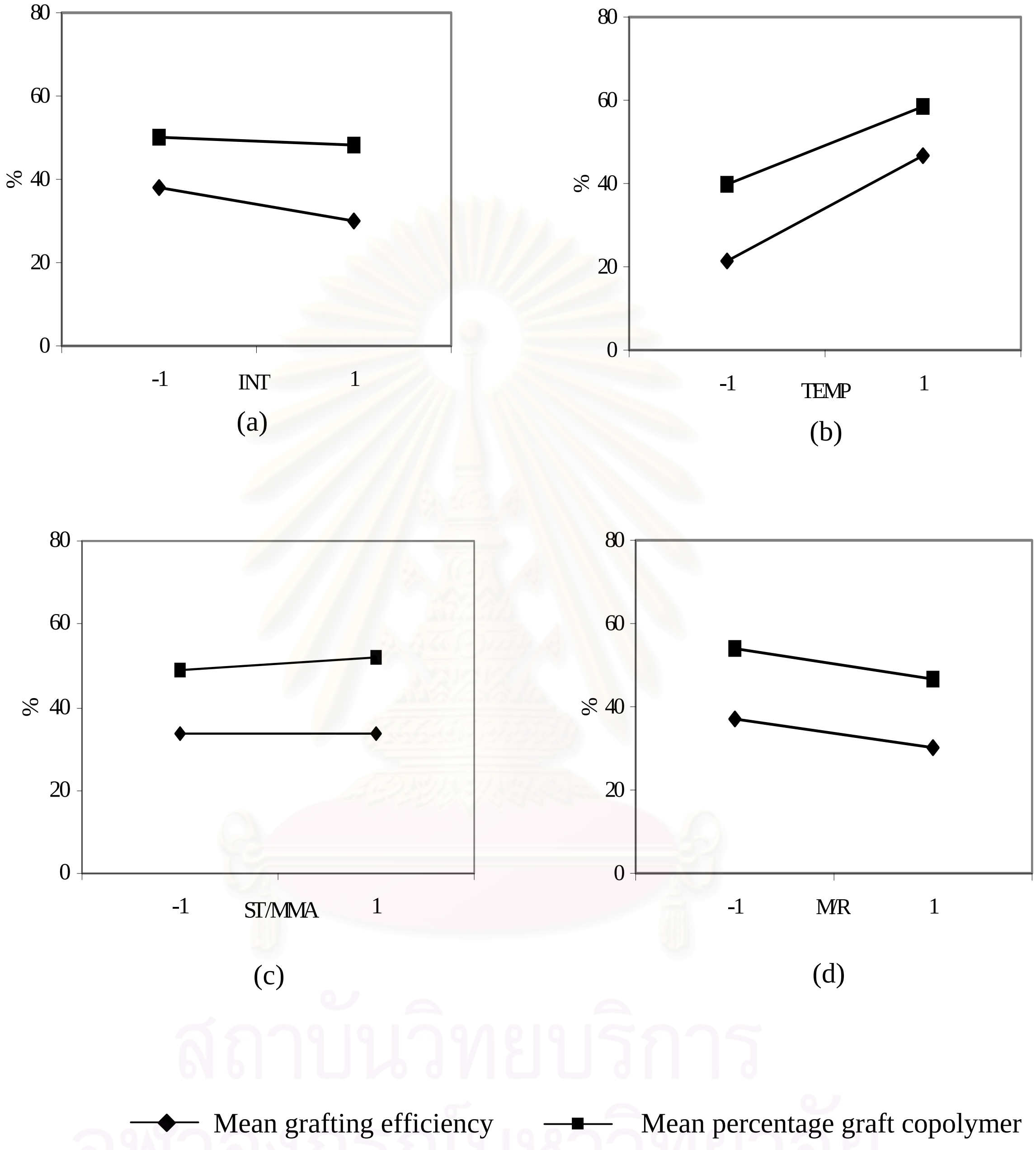


Figure 4.5 Effect of (a) INT, (b) TEMP, (c) ST/MMA, and (d) M/R on grafting efficiency and percentage graft copolymer.

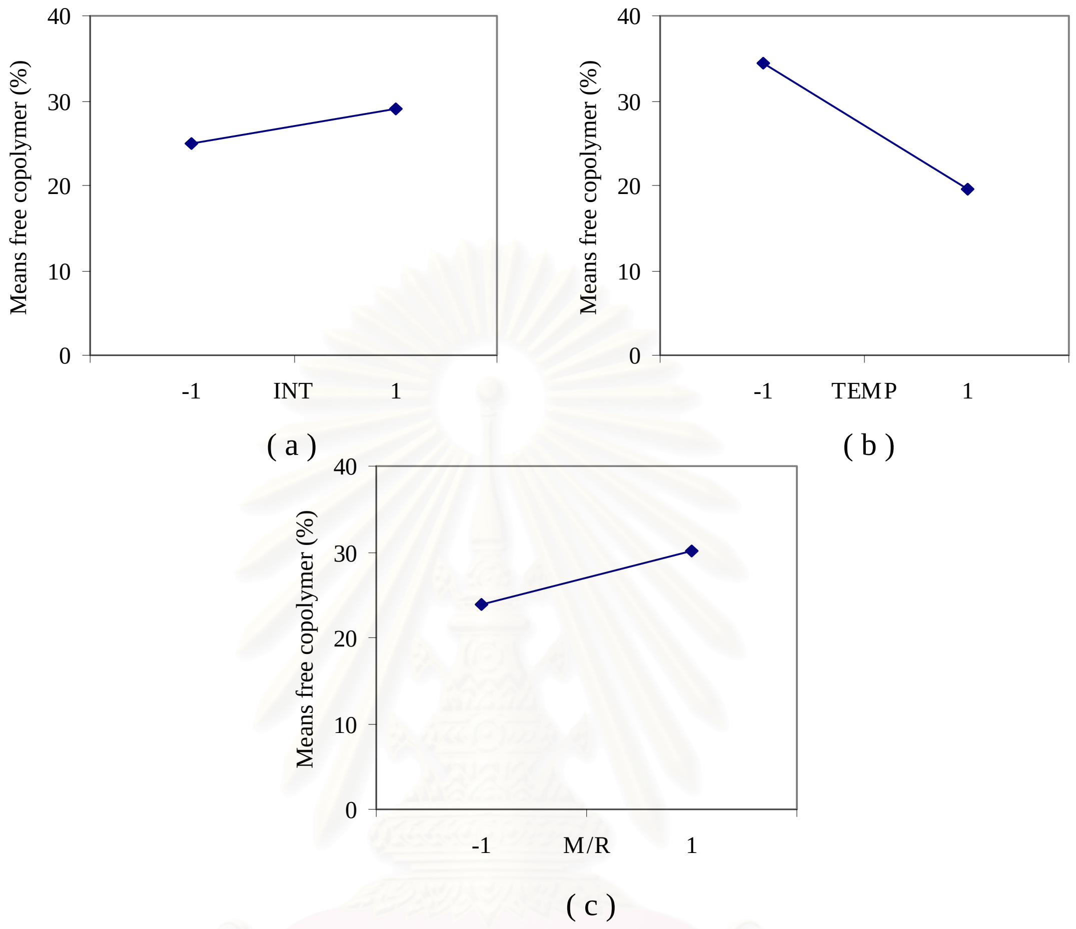


Figure 4.6 Effect of (a) INT, (b) TEMP, and (c) M/R on percentage free copolymer.

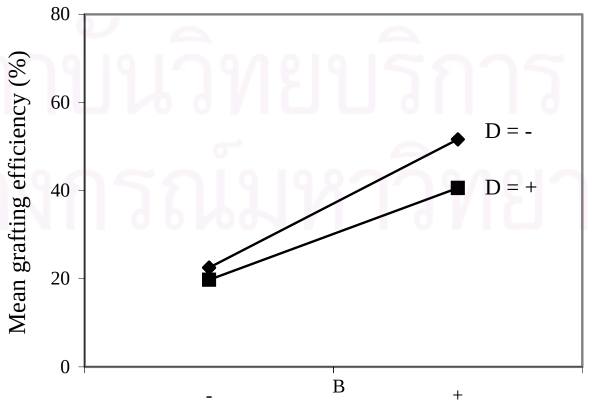


Figure 4.7 Effect of BD interaction on grafting efficiency.

4.4.2 The Regression Model

In a 2^4 factorial design, it is easy to express the results of the experiment in terms of a regression model. A factorial design could also use either an effects or a means model. In this work, for predicting grafting efficiency, the regression model is

$$\hat{\mathbf{Y}} = \boldsymbol{\beta}_0 + \boldsymbol{\beta}_1\mathbf{X}_1 + \boldsymbol{\beta}_2\mathbf{X}_2 + \boldsymbol{\beta}_4\mathbf{X}_4 + \boldsymbol{\beta}_{24}\mathbf{X}_2\mathbf{X}_4 \qquad (4.9)$$

The regression model for predicting percentage graft copolymer is

$$\hat{\mathbf{Y}}^* = \boldsymbol{\beta}^*_0 + \boldsymbol{\beta}^*_2\mathbf{X}_2 + \boldsymbol{\beta}^*_4\mathbf{X}_4 \qquad (4.10)$$

where $\hat{\mathbf{Y}}$ and $\hat{\mathbf{Y}}^*$ are a fitted values of grafting efficiency and percentage graft copolymer.

$\mathbf{X}_1$ is a coded variable that represents the initiator concentration.

$\mathbf{X}_2$ is a coded variable that represents the reaction temperature.

$\mathbf{X}_4$ is a coded variable that represents the ratio of monomer to rubber.

$\boldsymbol{\beta}_0$ and $\boldsymbol{\beta}^*_0$ are the average response of all sixteen observations.

$\boldsymbol{\beta}$ and $\boldsymbol{\beta}^*$ are regression coefficients.

The regression model can be used to obtain the predicted or fitted value of Y at the sixteen points in a 2^4 factorial design. According to the definition, the residuals are the differences between the observed and fitted values. Results for the observed, fitted and residuals values of grafting efficiency and percentage graft copolymer are shown in Table 4.5.

From the regression model (Equations 4.9-4.10), the normal probability plots of the residuals on grafting efficiency and percentage graft copolymer are shown in Figure 4.8. The points on plots in Figure 4.8a and Figure 4.8b lie reasonably close to a straight line. This supported the conclusion that A, B, D, and BD were the only significant effects on grafting efficiency and B and D were the only significant effects on percentage

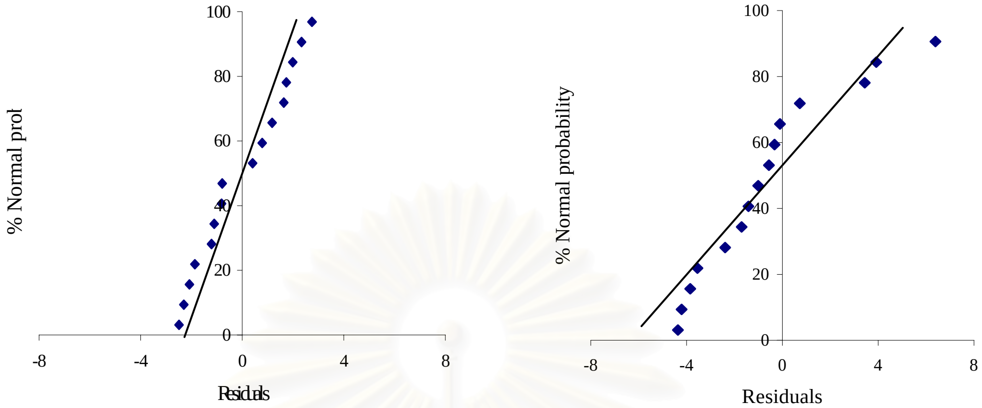
Table 4.5 The values of observed, fitted, and residuals of grafting efficiency and percentage graft copolymer

Run Label	Grafting Efficiency			Percentage Graft Copolymer		
	Y	$\hat{Y}$	ε	Y^*	$\hat{Y}^*$	ε^*
(1)	24.32	26.18	-1.86	43.69	45.39	-1.70
a	17.65	18.86	-1.21	41.03	45.39	-4.36
b	57.04	55.04	1.99	62.29	62.62	-0.33
ab	46.62	47.72	-1.10	61.61	62.62	-1.01
c	28.53	26.18	2.34	51.78	45.39	6.39
ac	19.66	18.86	0.79	45.29	45.39	-0.10
bc	56.69	55.04	1.64	66.06	62.62	3.44
abc	45.23	47.72	-2.49	60.23	62.62	-2.39
d	22.62	23.43	-0.81	34.47	38.02	-3.55
ad	18.87	16.11	2.75	33.81	38.02	-4.21
bd	45.44	44.25	1.18	54.69	55.25	-0.56
abd	36.14	36.93	-0.79	59.17	55.25	3.92
cd	21.13	23.43	-2.30	46.91	38.02	8.89
acd	16.53	16.11	0.41	36.60	38.02	-1.42
bcd	42.17	44.25	-2.08	51.40	55.25	-3.85
abcd	38.68	36.93	1.74	55.98	55.25	0.73
Mean	33.57			50.32		

* = Percentage graft copolymer ε = Residual β_0 = 33.57 β^*_0 = 50.32

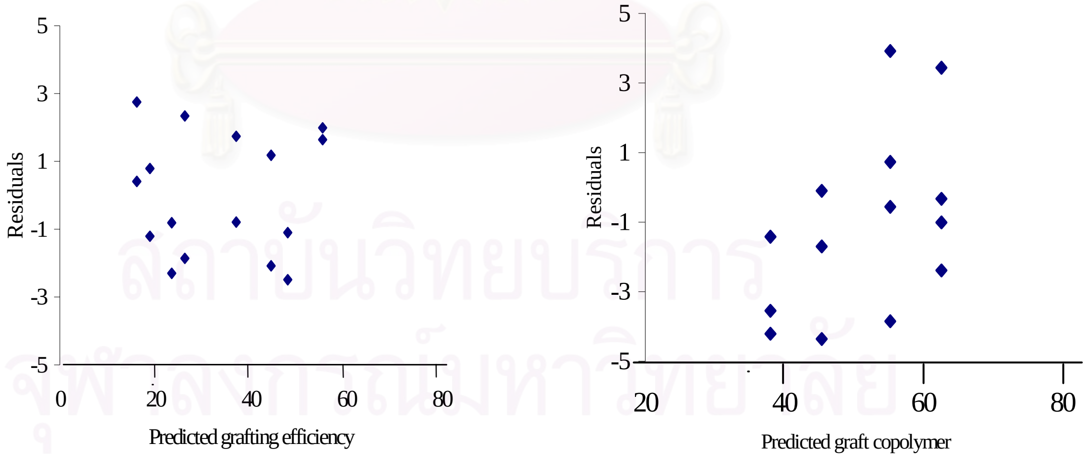
graft copolymer. Therefore, the underlying assumptions of these analysis were satisfied. The details of all calculations are shown in the Appendix C.

Figure 4.9 is the plots of the residuals versus the predicted grafting efficiency and the residuals versus the predicted percentage graft copolymer from the model containing the identified factors. There is no relationship between the size of the residuals and the fitted values (predicted grafting efficiency and predicted percentage graft copolymer). These plot revealed nothing of unusual interest.



(a) (b)

Figure 4.8 The normal probability plots of residuals; (a) grafting efficiency and (b) percentage graft copolymer.



(a) (b)

Figure 4.9 The plots of the residuals versus the predicted values; (a) grafting efficiency and (b) percentage graft copolymer.

4.5 Rate of Polymerization

For graft copolymerization of styrene and methyl methacrylate onto natural rubber, monomer conversion as a function of reaction time was investigated. Figure 4.10 shows the conversion profiles of GNR 03. From the shape of conversion versus reaction time curve, the polymerization rate was extreamly high at initial period (< 60 min.) before reaching a plateau level. At one hour, conversion of vinyl monomers was about 60% and then slightly increased at above 1 hour.

Figure 4.11 shows the plot of grafting efficiency versus conversion. As the polymerization proceeds, the grafting efficiency increased gradually in the range of conversion 0 to 60% and then steeply increased at conversion above 60%. The results can be explained by encapsulation process [13]. At the beginning, the conversion increased rapidly since the occurrence of most of styrene and methyl methacrylate may be polymerized in the aqueous phase to form new particles which bound to the swollen particle surface and then encapsulated the seed.

A sudden increase in grafting efficiency (from 25% to 50%) with conversion (at 60%) can be explained by the growth of seed particles that take place by encapsulation of the copolymer chain initiated in the aqueous phase at the surface of seed particles. In this study, the hydroperoxide-polyamine initiator, which is partially water soluble, is believed to produce initiating radicals at or near the particle interface and thus causes preferential polymerization of the monomer in the region of the particle surface. At the beginning, most monomers may be polymerized to form new particles of copolymers related to increasing conversion. The growing polymeric radicals, preferentially concentrated at the surface of the particles, will be combined with polyisoprenyl radicals to terminate or transfer to natural rubber to form graft copolymers, thus resulting in an increase in grafting efficiency at good conversion. The extent of graft copolymers formation depends upon the time.

The grafted natural rubber particles consisting of natural rubber core and compatibilizing styrene and methyl methacrylate shell were prepared by emulsion polymerization. The key process lies in the grafting of a significant portion of the growing styrene-methyl methacrylate onto the double bonds of the existing elastomeric

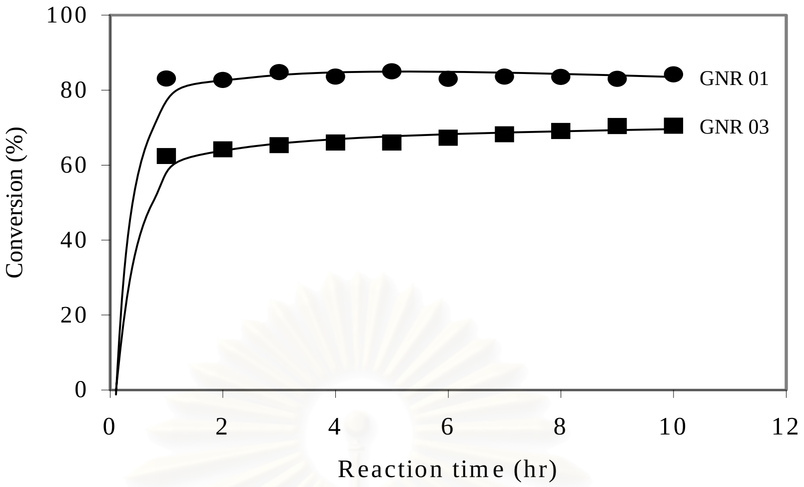


Figure 4.10 Conversion (%) versus reaction time (hr).

GNR 01 : INT = 1 phr, TEMP = 50°C, ST/MMA = 1.0, M/R = 0.75.
GNR 03 : INT = 1 phr, TEMP = 70°C, ST/MMA = 1.0, M/R = 0.75.

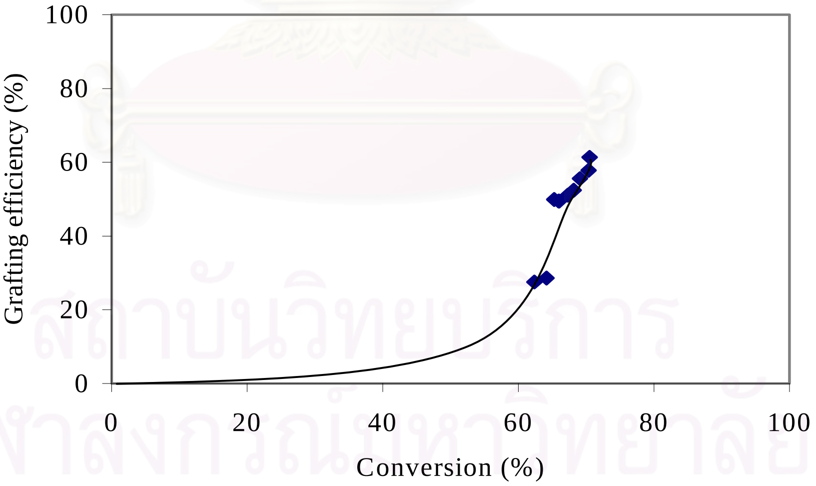


Figure 4.11 Grafting efficiency (%) versus conversion (%) for GNR 03.

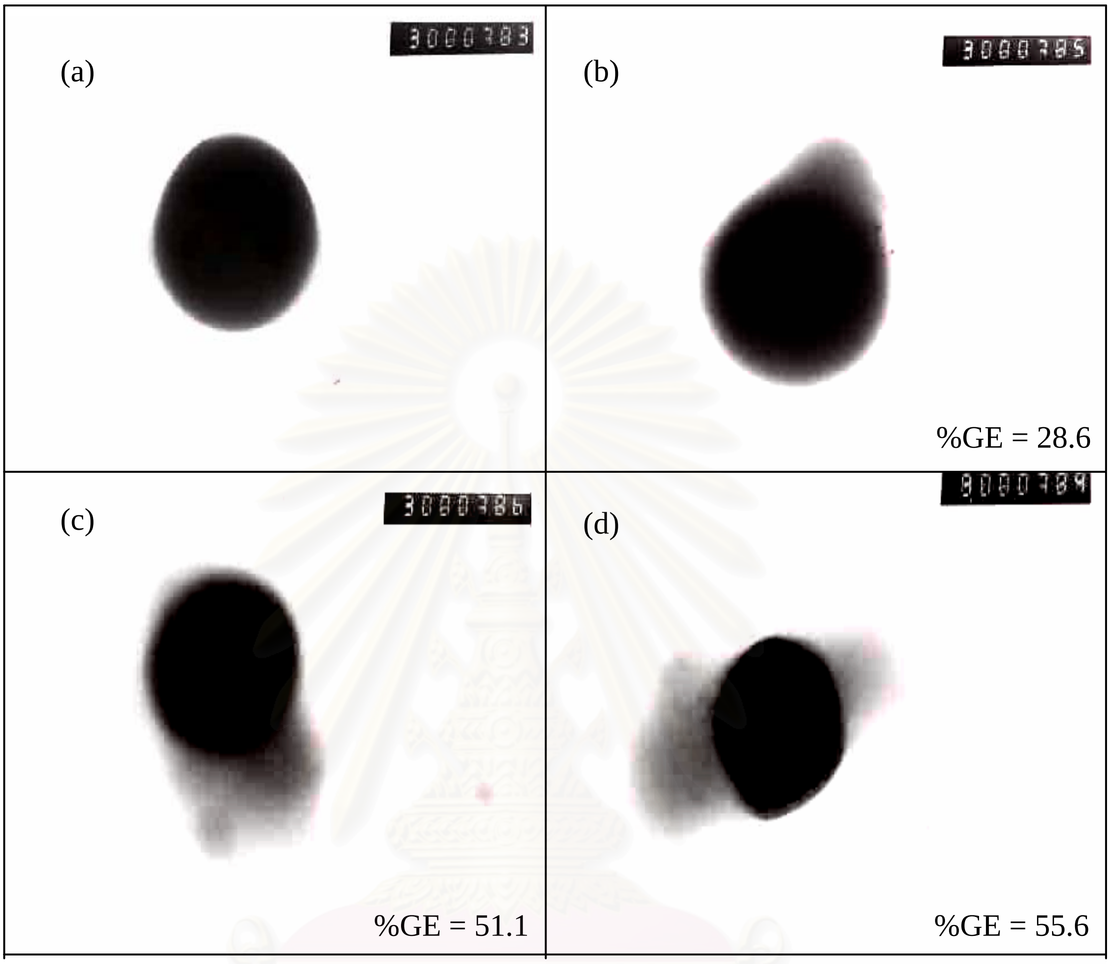


Figure 4.12 Transmission electron micrographs of polymer (GNR 03); (a) natural rubber, (b) 2 h, (c) 6 h, and (d) 8 h (x 45000).

components. The morphology of natural rubber and the core-shell formation of grafted natural rubber latex at various reaction time and grafting efficiency are shown in Figure 4.12. The surface morphology of the grafted natural rubber was studied by OsO_4 staining. The dark area represents the natural rubber core regions, while the lighter area is PST/MMA film as shell. The presence of nodules on the surface of the graft copolymers (see Figures 4.12b-4.12d) may be due to the growing macroradical chains, which were grafted onto the surface of the natural rubber particle and continue to propagate to form the shell layer as the grafting efficiency increased.

4.6 Mechanical Properties of the PVC Blended with Grafted Natural Rubber, MBS, and Natural Rubber.

A suspension-type homopolymer of PVC having an intermediate average molecular weight or a K-value of 64 was used. Three graft copolymers with different grafting efficiency and grafting properties (GNR 01, GNR 03, and GNR 04) were prepared from natural rubber. The graft properties of graft copolymers are presented in Table 4.6. The grafted natural rubber modified PVC were prepared and the mechanical properties were investigated. The properties of MBS modified PVC and NR modified PVC were compared. The value of tensile properties, impact strength, and hardness of PVC blends are shown in Table 4.7 and Figures 4.13-4.14.

Table 4.6 Properties of graft copolymers

	GNR 03	GNR 04	GNR 01
Total conversion (%)	65.8	66.0	85.9
Grafting efficiency (%)	57.0	46.6	24.3
Graft properties			
Grafted natural rubber (%)	62.3	61.6	43.7
Free natural rubber (%)	23.6	20.7	26.8
Free copolymer (%)	14.1	17.7	29.5

GNR 03 : INT = 1 phr, TEMP = 70°C, ST/MMA = 1.0, M/R = 0.75
GNR 04 : INT = 2 phr, TEMP = 70°C, ST/MMA = 1.0, M/R = 0.75
GNR 01 : INT = 1 phr, TEMP = 50°C, ST/MMA = 1.0, M/R = 0.75

a) <u>Tensile Properties</u>

From Figure 4.13a, the tensile strength of PVC blends decreased with increasing the grafted natural rubber, MBS, and NR contents. For grafted natural rubber modified PVC, the tensile strength decreased to 40.5 MPa (20%) when the grafted natural rubber was increased up to 10 phr. The tensile strength of MBS modified PVC decreased to

41.2 MPa (19%) when MBS was increased up to 10 phr. This can be explained that the toughness was obtained by the addition of an amorphous rubbery phase, whereas the stiffness and strength of the PVC were degraded [29]. For NR modified PVC, tensile strength decreased rapidly with increasing natural rubber content. The tensile strength of NR modified PVC decreased to 34.4 MPa (32%) when natural rubber was added up to 10 phr. This result may be explained that the natural rubber was insoluble and incompatible with PVC and formed a distinct dispersed phase. The grafted natural rubber which formed the outer glassy shell of rubbery particulate was compatible with PVC and formed continuous phase. Consequently, the decrease in tensile strength of NR modified PVC were greater than that of graft copolymers modified PVC.

For PVC modified with grafted natural rubber at different percentage grafted natural rubber (GNR 01, GNR 03, and GNR 04) (Figure 4.14a), the tensile strength of grafted natural rubber modified PVC decreased with increasing grafted natural rubber content. Comparison between GNR 03 and GNR 04 modified PVC, the higher percentage grafted natural rubber of GNR 03 exhibited the better tensile strength due to the better adhesion between the components in the compatibilized system. However, GNR 01 modified PVC which grafted natural rubber had a high content of free copolymer which have similar property to continuous phase (PVC), therefore, it exhibited higher tensile strength than that of GNR 03 and GNR 04 modified PVC.

Ultimate elongation is another mechanical property that is important for determining the application of the blends. Figures 4.13b-7.14b show that ultimate elongation of grafted natural rubber modified PVC also increased with increasing amounts of grafted natural rubber. For MBS modified PVC, the results were similar to that for grafted natural rubber modified PVC. For the grafted natural rubber modified PVC, the effect of different graft copolymer properties (GNR 01, GNR 03, and GNR 04) on the change in ultimate elongation of the blends was very small. The increase in ultimate elongation can be explained that PVC is brittle thermoplastic, therefore the rubber component in grafted natural rubber and MBS improved this elongation property of PVC [29].

b) Impact Strength

The impact strength of graft copolymer modified PVC and NR modified PVC are shown in Figure 4.13c. It was found that the unmodified PVC had a lower impact strength than the modified PVC. The impact strength of PVC blends increased with increasing graft copolymer content. This results may be explained that incorporating rubbery particulate graft copolymer into rigid PVC enhanced the toughness of PVC. So, the increase in impact modifier content made the crack propagation more difficult, leading to the increase impact strength.

For GNR 03 modified PVC, the impact strength increased to 42.9 kg-cm/cm (118%) when the GNR 03 was increased up to 10 phr. For MBS modified PVC, the impact strength increased to 37.2 kg-cm/cm (89%) when MBS was increased up to 10 phr. Comparison between GNR 03 and MBS graft copolymers (Figure 4.13c), impact strength of GNR 03 modified PVC were higher than that of MBS modified PVC in the range of 5 and 10 phr of graft copolymer content. But for further increase in graft copolymer content (15 phr), the impact strength of MBS modified PVC were much higher than that of GNR 03 modified PVC.

The comparison of impact strength of PVC modified with graft copolymers (GNR 03 and MBS) and NR suggested that the graft copolymers were more compatible to PVC than NR, though NR could increase impact strength of the blends. For natural rubber modified PVC, the impact strength increased to 30.6 kg-cm/cm (56%) when the natural rubber was increased up to 10 phr. This can be explained that the NR was incompatible with PVC and formed a distinct disperse phase. For the grafted natural rubber, the NR particulate usually had a grafted outer glassy shell to achieve the desired controlled compatibility with the PVC matrix and good dispersion. Grafting of each rubber particle was essential for attaching the rubber particles to the surrounding glassy matrix. This allowed the transfer of energy necessary for the rubber particles to dissipate impact energy.

The impact strength of grafted natural rubber modified PVC at various percentage grafted natural rubber is shown in Figure 4.14c. It was found that, for all grafted natural rubbers modified PVC, the impact strength of the blends increased as grafted natural rubber content increased. However, the highest increase in impact strength of the blends was obtained for the GNR 03. It can be explained that the higher percentage grafted natural rubber exhibited the better impact strength due to the better adhesion between the components in the compatibilized system. Styrene/methyl methacrylate copolymers were used in formation of the shell for grafted natural rubber. When incorporated into the PVC matrix, the rubber core serves as a toughening agent whereas the glassy layer serves as a compatibilizing agent with the PVC phase [13]. Grafted natural rubbers with high level of non rubbery component (high grafting efficiency) exhibited better adhesion between the ST/MMA shell and the PVC and this resulted in better transfer of energy between the hard PVC phase and the rubbery phase [19].

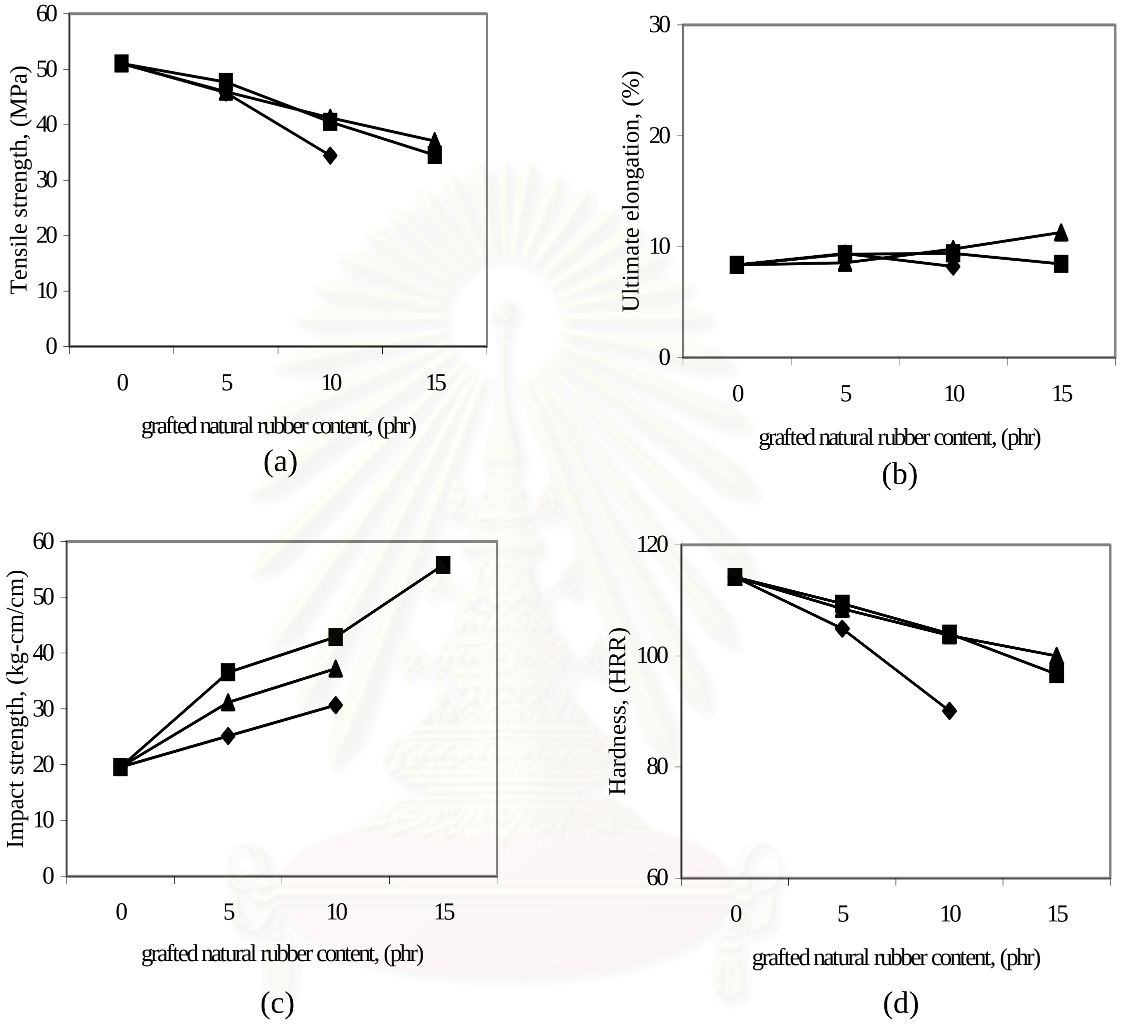
The more grafted natural rubber and MBS contents, the higher the impact strength of the blends. The grafted natural rubber could be used as an impact modifier for PVC to form grafted natural rubber modified PVC by mechanical blending and compression molding. The good mechanical properties of blends were obtained at 10 phr of the grafted natural rubber.

c) Hardness

The hardness of grafted natural rubber modified PVC, MBS modified PVC, and NR modified PVC at various amounts of impact modifier is presented in Figure 4.13d. The hardness of the blends decreased with increasing rubber content. This results may be explained that the rubber component of the graft copolymer (grafted natural rubber and MBS) and NR had more elastic properties, consequently the blends were deformed easily. The hardness of graft copolymer modified PVC were higher than that of NR modified PVC. This can be noted that NR modified PVC were deformed easily because of high level of elasticity of NR. The hardness of grafted natural rubber modified PVC at various percentage grafted natural rubber is shown in Figure 4.14d. It was found that, for all percentage grafted natural rubber modified PVC, the hardness of the blends decreased as grafted natural rubber content increased. However, the least decrease in hardness of the blends was obtained for the GNR 01. The explaination is similar to that for the results of tensile properties. GNR 01 modified PVC had a high level of free copolymer content exhibited the higher hardness than that of GNR 03 and GNR 04 modified PVC.

Table 4.7 Properties of graft copolymers modified PVC and NR modified PVC

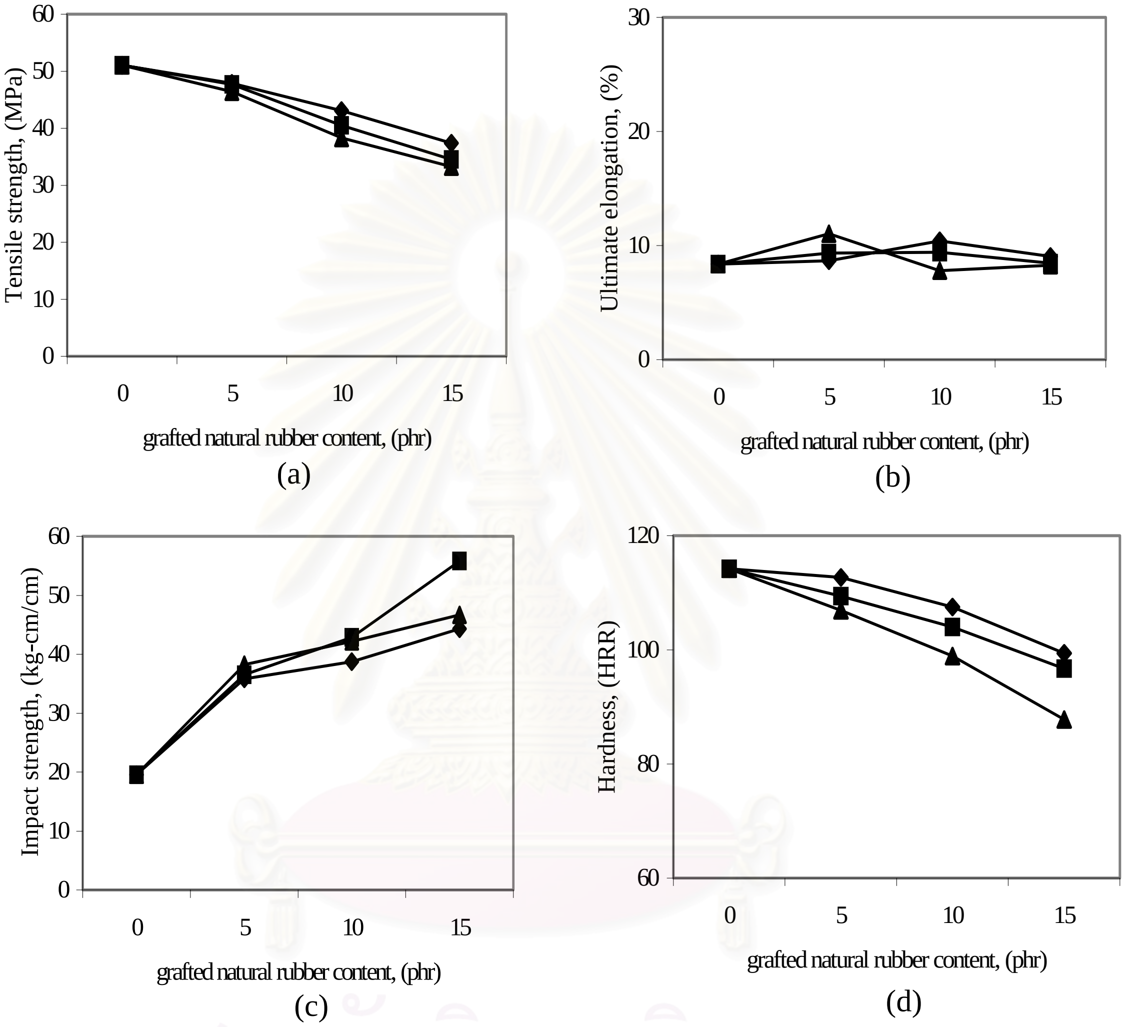
	Amount (phr)	Tensile Strength (MPa)	Ultimate Elongation (%)	Impact Strength (kg-cm/cm)	Hardness (HRR)
Unmodified					
PVC	0	51.0	8.4	19.6	114.2
MBS	5	45.9	8.6	31.1	108.5
	10	41.2	9.8	37.2	103.7
	15	37.0	11.3	100.6	100.0
GNR 03	5	47.7	9.3	36.5	109.4
	10	40.5	9.4	42.9	104.0
	15	34.5	8.4	55.8	96.7
GNR 04	5	46.4	11.0	38.2	106.9
	10	38.3	7.8	42.2	98.9
	15	33.3	8.3	46.7	87.8
GNR 01	5	47.9	8.7	35.8	112.7
	10	43.1	10.4	38.7	107.5
	15	37.4	9.0	44.3	99.4
NR	5	45.8	9.4	25.1	104.9
	10	34.4	8.2	30.6	90.1



(a) (b)

(c) (d)

Figure 4.13 Effect of graft copolymer on the mechanical properties of PVC; (♦) NR, (■) GNR 03, (▲) MBS.



(a) (b)

(c) (d)

Figure 4.14 Effect of grafted natural rubber on the mechanical properties of PVC; (♦) GNR 01, (■) GNR 03, (▲) GNR 04.

4.7 Scanning Electron Microscopy (SEM)

The scanning electron microscope was employed to investigate the fracture surface of the specimen from the tensile properties test. Figure 4.15a shows the fracture surface of unmodified PVC. The influence of NR on the morphology of modified PVC is shown in Figures 4.15b-4.15c. The fracture surface of the NR modified PVC shows the nonhomogeneous phase and poor adhesion between the rubber phases and PVC phase. This similar observation were also made for unmodified PVC. Figures 4.16-4.17 show the fracture surface of grafted natural rubber modified PVC and MBS modified PVC. The fracture surfaces had root whiskers when the grafted natural rubber and MBS were dispersed to PVC matrix. The root whiskers on the fracture surface of the blends show the signs of good interfacial adhesion between the two phases. For 5-10% grafted natural rubber content, the good distribution of grafted natural rubber in PVC matrix could be observed. With 15% grafted natural rubber content, large domains of grafted natural rubber were clearly observed where the agglomeration of grafted natural rubber occurred due to the incompatibility between the phases, which led to cavity formation. For the comparison between grafted natural rubber and MBS, the root whiskers on the fracture surface of the MBS modified PVC were less and shorter than that of grafted natural rubber modified PVC in the range of 5 and 10 phr of graft copolymer content. For further increase in graft copolymer content (15 phr), the root whiskers of the grafted natural rubber modified PVC were less and shorter than that of MBS modified PVC. The change in morphology of the fracture surface corresponds to the increase of impact strength (see Figure 4.13c), therefore addition of graft copolymers improved the impact strength of PVC.

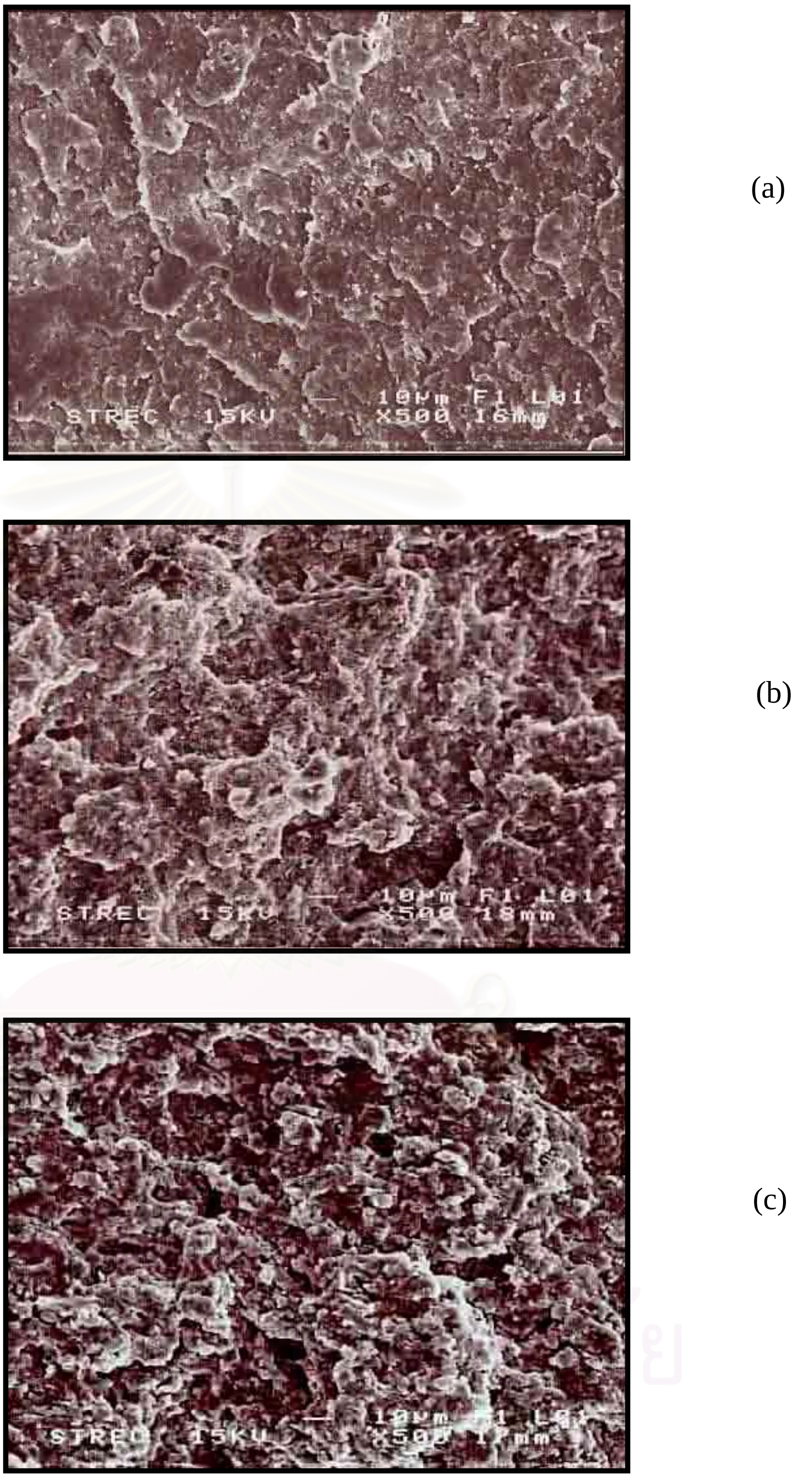


Figure 4.15 SEM photographs of PVC with NR at (a) 0 phr, (b) 5 phr, and (c) 10 phr (x 500).

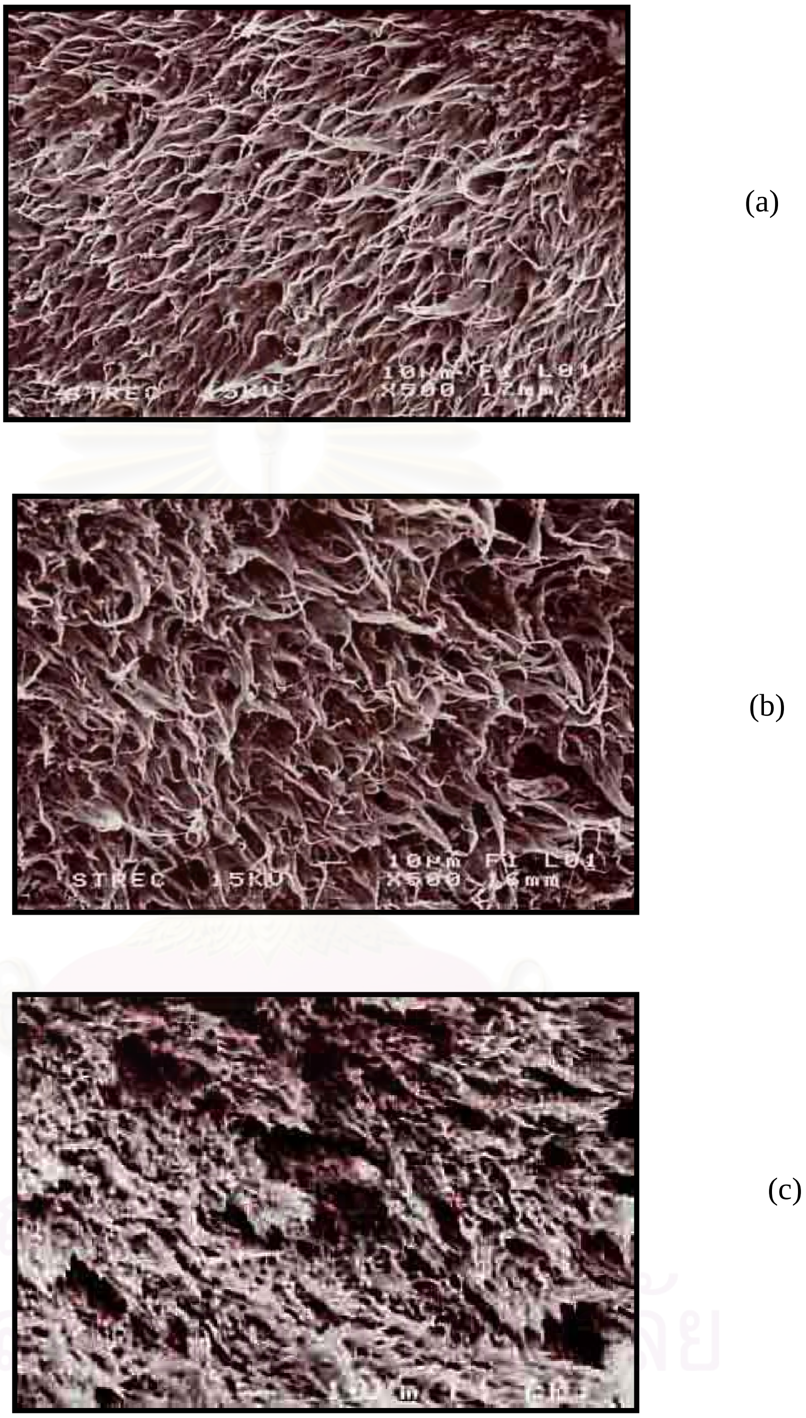


Figure 4.16 SEM photographs of PVC modified with grafted natural rubber product (GNR 03) at (a) 5 phr, (b) 10 phr, and (c) 15 phr (x 500).

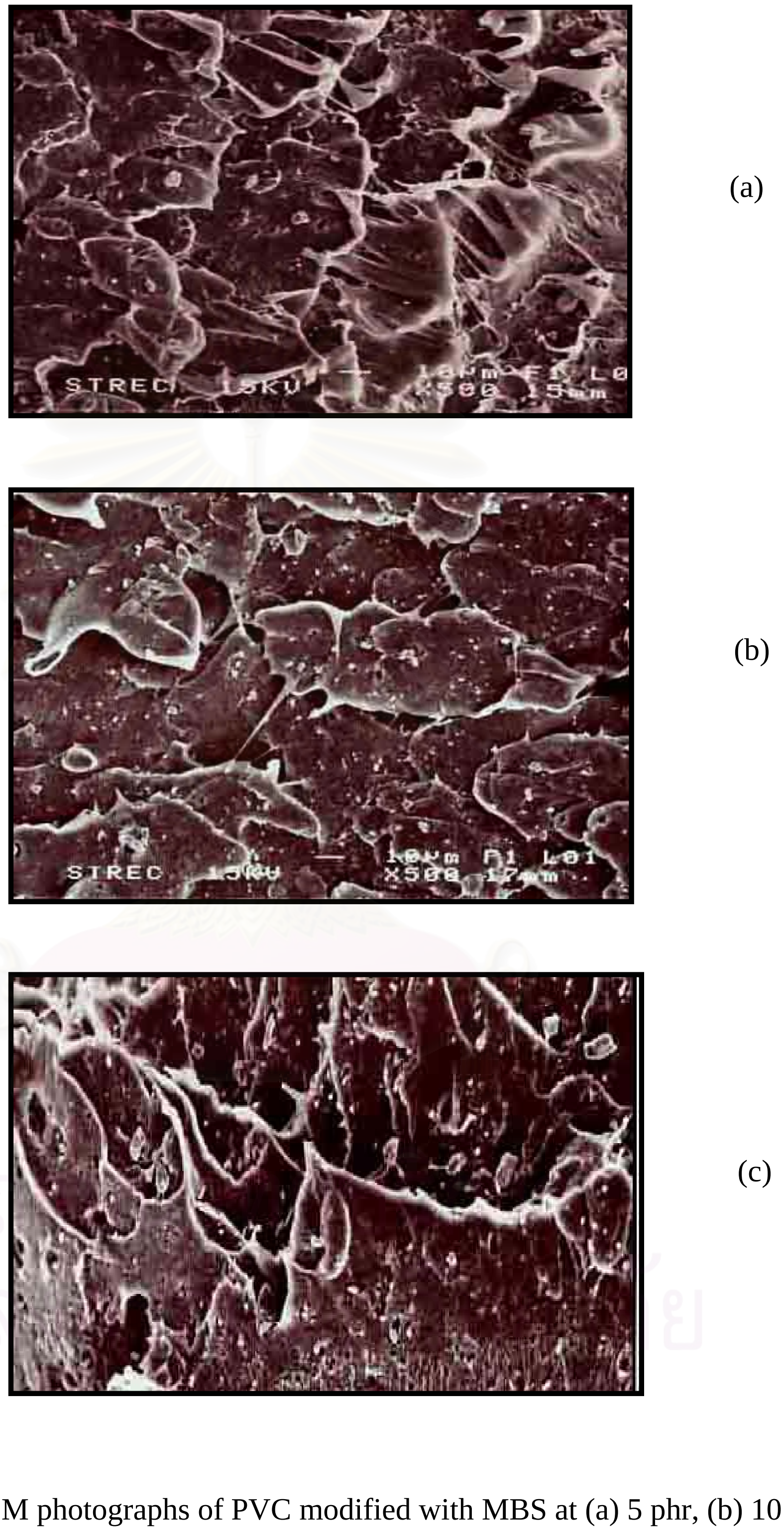


Figure 4.17 SEM photographs of PVC modified with MBS at (a) 5 phr, (b) 10 phr, and (c)15 phr (x 500).

4.8 Dynamic Mechanical Analysis (DMA)

The results of dynamic mechanical measurements are given in Figures 4.18-4.19 and Table 4.8. Tan δ curves for pure natural rubber and grafted natural rubber are shown in Figure 4.18a. The temperature at the maximum point of the tan δ peak was taken as the measure of glass transition temperature (T_g). From Figure 4.18a, natural rubber has higher damping than grafted natural rubber because of its rubbery nature. The intensity of tan δ decreased upon grafting and an increase in breadth of tan δ was observed because of an increase in molecular entanglement [31]. The T_g of grafted natural rubber was observed to shift to lower temperature because the rubbery chain was partially immobilized by grafting.

Dynamic mechanical investigations were used to predict the miscibility of polymer systems by some researchers [32]. The tan δ curve for the grafted natural rubber modified PVC prepared by mechanical blending are shown in Figure 4.18b. It was found that for grafted natural rubber modified PVC at various contents of grafted natural rubber, the peak appeared at about -62°C. This peak is due to the existence of grafted natural rubber. It should be noted that the three-point bending mode used, it was not able to determine the glass transition temperature of PVC (T_{g1}). The curves of grafted natural rubber modified PVC also had a broad peak centered at about -20°C [31]. This broad region indicated some phase mixing, which implied that the hard segments (grafted or ungrafted) in this sample was well mixed in some parts of the natural rubber phase. It was also found that the tan δ increased with increasing grafted natural rubber content in PVC. The intensity of the tan δ peak at the T_g reflected the extent of mobility of the macromolecular chain segments at that temperature [31]. This indicated that the mobility of the grafted natural rubber molecules in modified PVC were affected by the increase in grafted natural rubber content in the blends.

Figure 4.19a shows the dependence of the storage modulus on temperature for natural rubber and grafted natural rubber. Below the T_g region natural rubber had a higher storage modulus than grafted natural rubber and this phenomenon was reversed above the T_g. As natural rubber and grafted natural rubber undergo the transition from the fully glassy state to the rubbery state, the storage modulus decreased considerably.

The storage modulus curves for the unmodified and modified PVC are shown in Figure 4.19b. A drop in storage modulus below the T_{g2} of grafted natural rubber modified PVC was observed when grafted natural rubber content decreased.

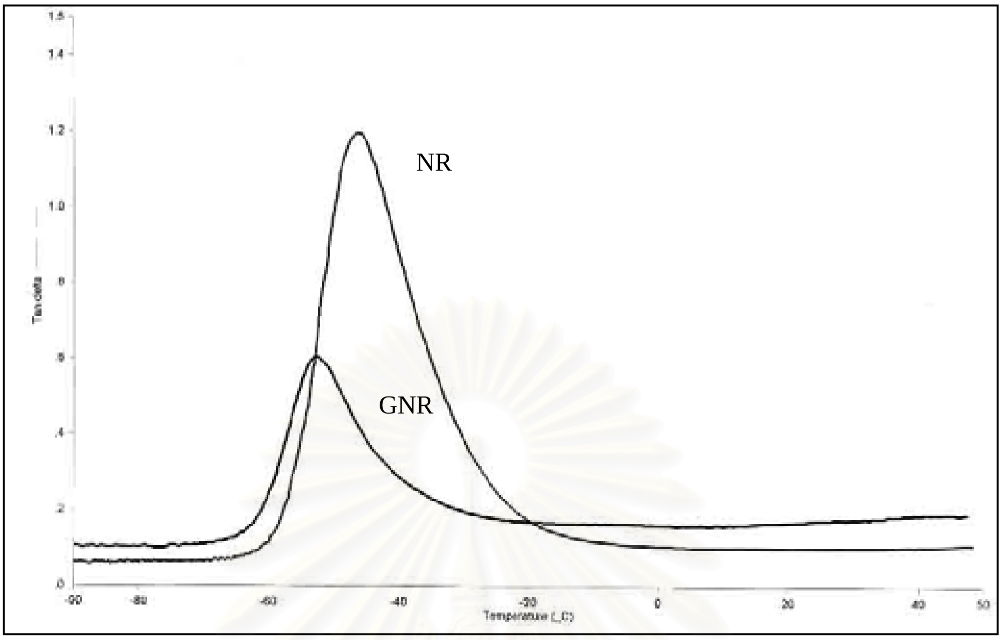
Table 4.8 Glass transition temperature and tan δ of the grafted natural rubber and grafted natural rubber modified PVC

Materials	T_{g1}^{a} (°C)	T_{g2}^{b} (°C)	tan δ_2^{b}
Natural rubber	-	-46.3	1.20
Grafted natural rubber (GNR)	-	-52.9	0.60
Poly(vinyl chloride) (PVC)	80.6	-	-
PVC/GNR 5 phr	84.1	-61.9	0.10
PVC/GNR 10 phr	80.2	-63.9	0.11
PVC/GNR 15 phr	79.3	-62.4	0.14

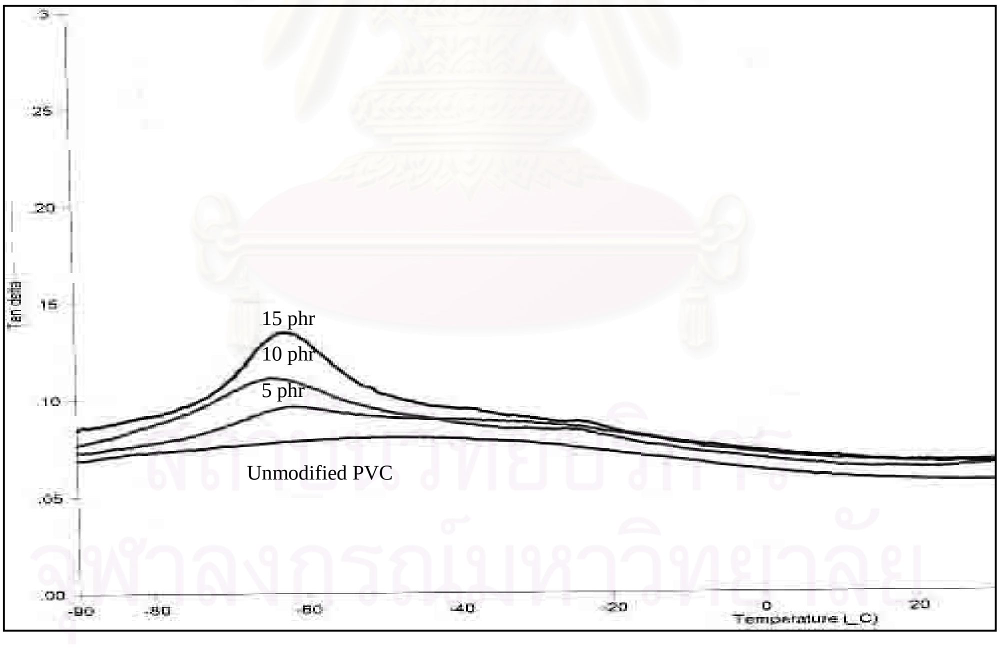
[a] = Taken from DSC technique [b] = Taken from DMA technique

4.9 Differential Scanning Calorimetry (DSC)

The DSC thermograms of unmodified PVC and grafted natural rubber modified PVC at various grafted natural rubber content are shown in Figure 4.20. The results of glass transition temperature (T_{g1}) are given in Table 4.8. All blends show T_{g1}'s of the PVC-rich phase. The increase in T_g of the blends at a low grafted natural rubber content may be attributed due to the graft of poly(styrene-*co*-methyl methacrylate) formed on the natural rubber chain, which was miscible with PVC. At higher contents of grafted natural rubber product (10 and 15 phr), the T_{g1} of the blends was observed to shift slightly to lower temperatures. It shows that the brittleness temperature of PVC was lowered progressively by addition of grafted natural rubber. It can be explained that higher contents of grafted natural rubber (high elastomer concentration) induced more entanglements. The change of T_{g1} must obviously increase the ductility of grafted natural rubber modified PVC, therefore, the grafted natural rubber improved the impact strength of PVC.

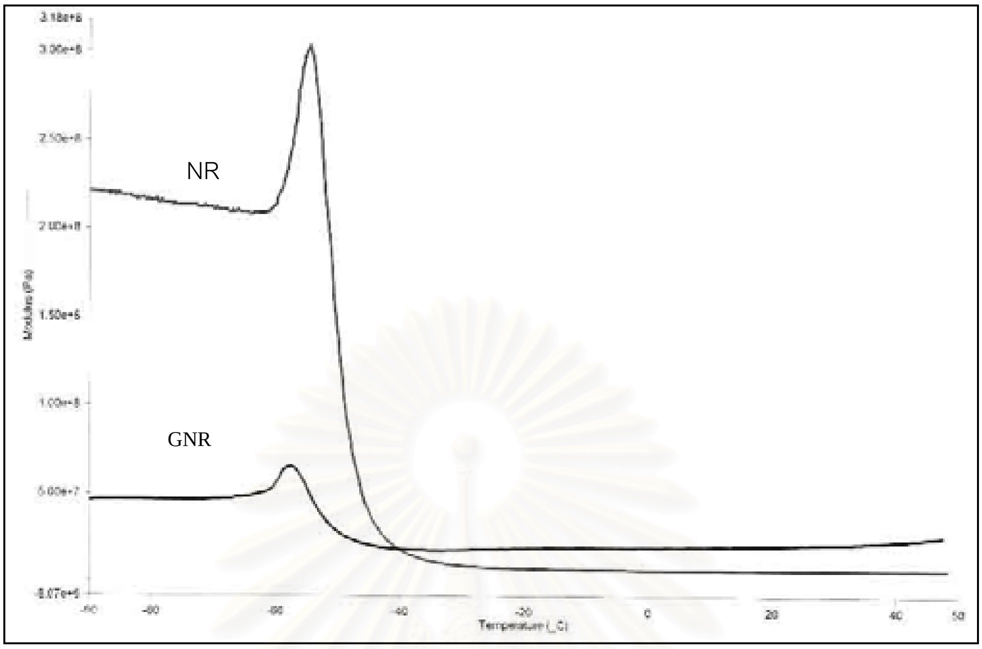


(a)

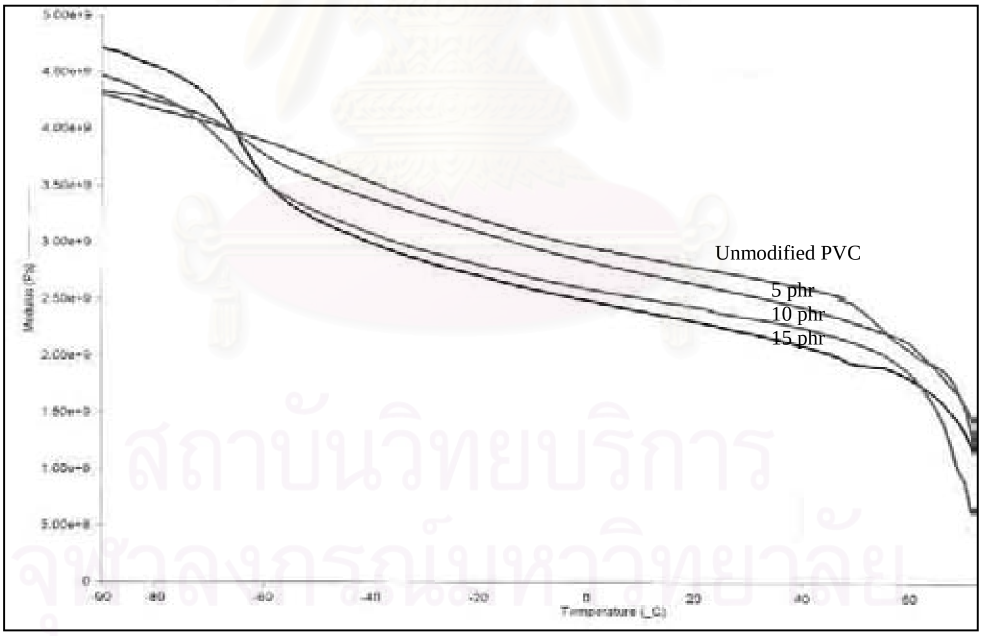


(b)

Figure 4.18 Loss factor (tan δ) of polymer; (a) natural rubber and grafted natural rubber and (b) grafted natural rubber modified PVC.



(a)



(b)

Figure 4.19 Storage modulus of polymer; (a) natural rubber and grafted natural rubber and (b) grafted natural rubber modified PVC.

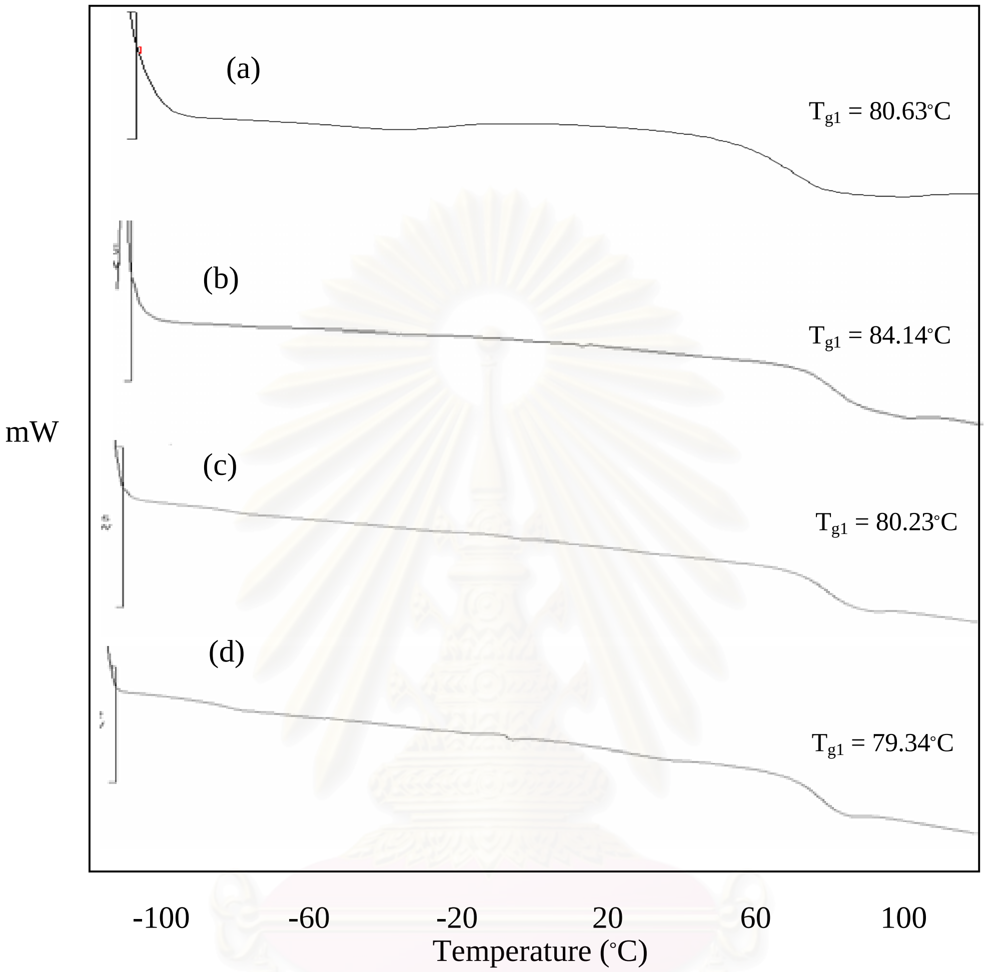


Figure 4.20 DSC thermograms of PVC modified with grafted natural rubber product (GNR 03) at (a) 0 phr, (b) 5 phr, (c) 10 phr, and (d) 15 phr.

CHAPTER V

CONCLUSION AND SUGGESTION

5.1 Conclusion

The graft copolymerization of styrene and methyl methacrylate onto natural rubber latex were prepared by emulsion polymerization using redox initiator. The two level factorial design experimental method had demonstrated to be a very useful tool in order to study the influence of the process variables on grafting efficiency, percentage graft copolymer, and percentage free copolymer. Statistical analysis of the data showed that initiator concentration, reaction temperature, and ratio of monomer to natural rubber had a significant effect on grafting efficiency. The reaction temperature and ratio of monomer to natural rubber had a significant effect on percentage graft copolymer. The three main effects of initiator concentration, reaction temperature, and ratio of monomer to natural rubber had a significant effect on percentage free copolymer. For the effects of process variables, the results are summarized as follows:

- The mean grafting efficiency and mean percentage graft copolymer increased with increasing reaction temperature, whereas the mean percentage free copolymer decreased with increasing reaction temperature.
- The mean grafting efficiency and mean percentage graft copolymer decreased with increasing initiator concentration and M/R ratio, whereas the mean percentage free copolymer increased with increasing initiator concentration and M/R ratio

From TEM micrographs, the grafted natural rubber showed the core-shell formation. The glass transition temperature of grafted natural rubber determined by DMA technique was –52.9°C. The grafted natural rubber product could be used as an impact modifier in rigid PVC. The impact strength of grafted natural rubber modified PVC exhibited considerable improvement by the addition of the grafted natural rubber product.

The good mechanical properties was obtained at 10 phr of grafted natural rubber product. For PVC modified with 10 phr grafted natural rubber, impact strength was increased 118% and tensile strength was decreased 20% from unmodified PVC. From SEM photographs, the fracture surface of grafted natural rubber modified PVC showed good interfacial adhesion by the addition of grafted natural rubber product. For DMA technique, the curves of grafted natural rubber modified PVC also had broad peak centered at about -20°C that indicated some phase mixing due to partially miscible blends. From DSC technique, the T_{g1} of the blends was observed to shift slightly to lower temperature when the grafted natural rubber was increased in PVC.

5.2 Suggestion for Future Work

In the area of modification of natural rubber latex and polymer blends, it should be studied further in the following aspects:

1. To prepare the graft copolymerization of styrene and methyl methacrylate onto natural rubber by using different redox initiators, e.g. tert-butyl hydroperoxide.
2. To apply the grafted natural rubber product as impact modifier for other rigid polymer, e.g. polystyrene, polymethyl methacrylate.

REFERENCES

1. Rubber Research Institute of Thailand: Department of Agriculture. Encyclopedia of Rubber. 3rd ed., Bangkok, 2002, p. 9.
2. Williams, P. H. The Science of Rubber. Malasia: Dunlop Limited, 1975, pp. 1-9.
3. Brydson, J. A. Rubber Chemistry. Essex: Applied Science Publishers Ltd., 1978, pp. 11-24.
4. Morton, M. Rubber Technology. 2nd ed., New York: Van Nostrand Reinhold Company, 1973, pp. 162-164.
5. Duck, E. W., and Daniels, D. J. Plastics and Rubber. London: Page Bros (Nerwich) Ltd., 1971, pp. 48-54.
6. Calvin, E. S. Polymerization Processes. New York: John Wiley & Sons, 1977, pp. 228-246.
7. Roberts, A. D. Natural Rubber Science and Technology. New York: Oxford University Press, 1990, pp. 679-684.
8. Mark, J. E., Erman, B., and Eirich, F. R. Science and Technology of Rubber. 2nd ed., London: Academic Press, 1994, pp. 533-540.
9. Lovell, P. A., and EL-Aasser, M. S. Emulsion Polymerization and Emulsion Polymers England: John Wiley & Sons, 1997, pp. 207-234.
10. Gasperowicz, A., Kolendowicz, M., and Skowronski, T. Grafting of Styrene onto Poly(butyl acrylate) in Emulsion. Polymer 23 (1982): 839-842.
11. Aerdts, A. M., DE-Krey, J. E. D., Kurja, J., and German, A. L. Emulsifier Free Grafting of Styrene and Methyl Methacrylate Concurrently onto Polybutadiene and Determination of the Copolymer Microstructure. Polymer 35 (1994): 1636-1647.
12. Daniels, E. S., Dimonie, V. L., EL - Aasser, M. S., and Vanderhoff, J. W. Preparation of ABS Latexes Using Hydroperoxide Redox Initiators. J. Appl. Polym. Sci. 41 (1990): 2463-2477.
13. Arayapranee, W., Prassarakich, P., and Lempel, G. L. Synthesis of Graft Copolymers from Natural Rubber Using Cumene Hydroperoxide Redox Initiator. J. Appl. Polym. Sci. 83 (2002): 2993-3001.

14. Razzak, M. T., Yoshii, F., Makuuchi, K., and Ishigaki, I. Thermoplastic Elastomer by Radiation Grafting. I. Evaluation of Processability of Natural Rubber Grafted Methyl Methacrylate. J. Appl. Polym. Sci. 43 (1991): 883-890.

15. Sundardi, F., and Kadariah, S. Radiation Grafting of Methyl Methacrylate Monomer on Natural Rubber Latex. J. Appl. Polym. Sci. 29 (1984): 1551-1521.

16. Gilbert, R.G. Emulsion Polymerization. London: Academic Press, 1995, pp. 1-11.

17. Ebewele, R. O. Polymer Science and Technology. New York: CRC Press, 2000, pp. 348-349, 426-427.

18. Gachter, R., and Muller, H. Plastics Additive Handbook. 3rd ed., New York: Oxford University Press, 1990, pp. 501-516.

19. Nass, L. I., and Heiberger, C. A. Encyclopedia of PVC. 2nd ed., Vol. 2, New York: Marcel Dekker, Inc., 1988, pp. 409-470.

20. Autofina, Plastic Additive Europe, 2003. Available from: **http://www.plasticadditives.atofina.com/plasticadd/europe/frameset.cmf**.

21. Titow, W. V. PVC Technology. 4th ed., London: Elsevier Applied Science Publishers, 1984, p. 395.

22. Zhao, J., Yuan, H., and Pan, Z. Grafting Mechanism in SBR-St-MMA Core-Shell Emulsion Copolymerization. J. Appl. Polym. Sci. 53 (1994): 1447-1452.

23. Aerdts, A. M., Theelen, S. J. C., Smit, T. M. C., and German, A. L. Grafting of Styrene and Methyl Methacrylate Concurrently onto Polybutadiene in Semicontinuous Emulsion Processes and Determination of Copolymer Microstructure. Polymer 35 (1994): 1648-1653.

24. Lenka, S., Nayak, P. L., and Das, A. P. Graft Copolymerization onto Rubber. VII. Graft Copolymerization of Methyl Methacrylate onto Rubber Using Potassium Peroxydisulfate Catalyzed by Silver Ion. J. Appl. Polym. Sci. 30 (1985): 2753-2759.

25. Markel, M. P., Dimonie, V. L., EL - Aasser, M. S., and Vanderhoff, J. W. Process Parameters and Their Effect on Grafting Reactions in Core/Shell Latexes. J. Polym. Sci. : Part A : Polym. Chem. 25 (1987): 1755-1767.

26. Brydon, A., Burnett, G. M., and Cameron, G. G. Free Radical Grafting of Monomers to Polydienes. I. Effect of Reaction Conditions on Grafting of Styrene to Polybutadiene. J. Polym. Sci: Polym. Chem. 11 (1973): 3253-3269.

27. Dompas, D., Groeninckx, G., Isogawa, M ., Hasegawa, T., and Kadokura, M. Toughening Behaviour of Rubber - Modified Thermoplastic Polymers Involving very Small Rubber Particles : III. Impact Mechanical Behaviour of Poly(vinyl chloride)/Methyl Methacrylate-Butadiene-Styrene Graft Copolymer Blends. Polymer 35 (1994): 4760-4765.

28. Prasassarakich, P., Sintoorahat, P., and Wongwisetsirikul, N. Enhanced Graft Copolymerization of Styrene and Acrylonitrile onto Natural Rubber. J. Chem. Eng. 34 (2001): 249-253.

29. Charmondusit, K., Kiatkamjornwong, S., and Prasassarakich, P. Grafting of Methyl Methacrylate and Styrene onto Natural Rubber. J. Sci. Chula. Univ. 23 (1998): 167-181.

30. Montgomery, D. C. Design and Analysis of Experiments. 5th ed., New York: John Wiley & Sons, 2001, pp. 218-287.

31. Lee, D. Y., Subramaniam, N., Fellows, C. M., and Gilbert, R. G. Structure-Property Relationships in Modified Natural Rubber Latexes Grafted with Methyl Methacrylate and Vinyl neo-Decanoate. J. Polym. Sci.: Part A: Polym. Chem. 40 (2002): 809-822.

32. Perera, M. C. Structure and Dynamics of MG Rubber Studied by Dynamic Mechanical Analysis and Solid-State NMR. J. Polym. Sci.: Part B: Polym. Phy. 37 (1999): 1141-1153.

APPENDICES

APPENDIX A

Table A-1 Effect of initiator concentration, reaction temperature, styrene to methyl methacrylate ratio, and monomer to rubber ratio on the conversion, percentage grafted natural rubber, and grafting efficiency

Exp.	NR (g)	product	%DRC	NR content	% conv.	Sample	wt.A	wt.B	% free NR	% free ST/MMA	% grafted NR	total ST/MMA	free ST/MMA	grafted ST/MMA	% GE
GNR 01	50.06	49.75	60.14	30.04	87.60	2.0232	0.6033	0.5967	29.82	29.49	40.69	19.71	14.67	5.04	25.56
	50.89	49.52	60.14	30.53	84.36	2.0346	0.4844	0.6003	23.81	29.50	46.69	18.99	14.61	4.38	23.07
GNR 02	50.28	52.49	60.14	30.17	99.16	2.0128	0.5090	0.7071	25.29	35.13	39.58	22.32	18.44	3.88	17.38
	50.20	51.68	60.14	30.12	95.78	2.0524	0.4778	0.7028	23.28	34.24	42.48	21.56	17.70	3.86	17.92
GNR 03	50.68	45.32	60.14	30.41	66.24	2.0092	0.4822	0.3027	24.03	15.07	60.90	14.91	6.83	8.08	54.21
	50.33	44.92	60.14	30.20	65.39	2.0085	0.4656	0.2641	23.18	13.15	63.67	14.72	5.91	8.81	59.87
GNR 04	50.17	44.82	60.14	30.10	65.39	2.0420	0.4160	0.3372	20.37	16.51	63.12	14.72	7.40	7.32	49.73
	50.02	45.00	60.14	30.01	66.65	2.0040	0.4227	0.3772	21.09	18.82	60.09	14.99	8.47	6.52	43.50
GNR 05	50.14	49.73	60.14	30.08	87.33	2.0612	0.4616	0.5778	22.39	28.03	49.58	19.65	13.94	5.71	29.06
	50.25	49.98	60.14	30.15	88.13	2.0580	0.3593	0.5880	17.46	28.57	53.97	19.83	14.28	5.55	27.99
GNR 06	50.08	51.95	60.14	30.05	97.29	2.0916	0.4398	0.6925	21.03	33.11	45.86	21.90	17.20	4.70	21.46
	50.06	52.19	60.14	30.04	98.40	2.0017	0.4087	0.6978	20.42	34.86	44.72	22.15	18.19	3.96	17.86
GNR 07	50.13	44.60	60.14	30.08	64.53	2.0248	0.4509	0.2906	22.27	14.35	63.38	14.52	6.40	8.12	55.92
	50.38	44.71	60.14	30.23	64.38	2.0251	0.3542	0.2790	17.49	13.78	68.73	14.48	6.16	8.32	57.45
GNR 08	50.08	45.00	60.14	30.05	66.56	2.0070	0.4436	0.3431	22.10	17.10	60.80	14.95	7.70	7.25	48.54
	50.19	45.72	60.14	30.11	69.32	2.0565	0.4220	0.4079	20.52	19.83	59.65	15.61	9.07	6.54	41.92

wt.A = Grafted product was extracted by light petroleum ether for 24 hrs.

Wt.B = Grafted product was extracted by light petroleum ether for 24 hrs and then extracted by the mixture of MEK/acetone(50:50(v/v)) for 24 hrs.

Table A-1 (Continued)

Exp.	NR (g)	product	%DRC	NR content	% conv.	Sample	wt.A	wt.B	% free NR	% free ST/MMA	% grafted NR	total ST/MMA	free ST/MMA	grafted ST/MMA	% GE
GNR 09	50.13	54.60	60.14	30.08	81.76	2.0300	0.6584	0.7079	32.43	34.87	32.70	24.52	19.04	5.48	22.35
	50.05	55.11	60.14	30.03	83.60	2.0333	0.5831	0.7134	28.68	35.09	36.23	25.08	19.34	5.74	22.89
GNR 10	50.31	59.53	60.14	30.19	97.83	2.0199	0.5335	0.8045	26.41	39.83	33.76	29.34	23.71	5.63	19.19
	50.25	58.93	60.14	30.15	95.97	2.0257	0.5342	0.8057	26.37	39.77	33.86	28.78	23.44	5.34	18.55
GNR 11	50.08	48.87	60.14	30.05	62.75	2.0939	0.5024	0.4462	23.99	21.31	54.70	18.82	10.41	8.41	44.66
	50.13	48.57	60.14	30.08	61.65	2.0382	0.5067	0.4177	24.86	20.47	54.67	18.49	9.94	8.55	46.22
GNR 12	50.30	49.49	60.14	30.18	64.37	2.0585	0.3517	0.5338	17.09	25.93	56.98	19.31	12.83	6.48	33.54
	50.39	49.02	60.14	30.23	62.63	2.0031	0.3039	0.4704	15.17	23.48	61.35	18.79	11.51	7.28	38.74
GNR 13	50.21	54.18	60.14	30.13	80.19	2.0320	0.3966	0.7088	19.52	34.88	45.60	24.05	18.90	5.15	21.42
	50.84	55.13	60.14	30.50	82.10	2.0133	0.3482	0.7122	16.41	35.37	48.22	24.63	19.50	5.13	20.83
GNR 14	50.05	56.97	60.14	30.03	89.80	2.0330	0.5251	0.8140	25.83	40.04	34.13	26.94	22.81	4.14	15.33
	50.73	57.75	60.14	30.44	91.03	2.0563	0.4528	0.8002	22.02	38.91	39.07	27.31	22.47	4.84	17.72
GNR 15	50.14	49.31	60.14	30.08	64.10	2.0438	0.5056	0.4716	24.74	23.07	52.19	19.23	11.38	7.85	40.84
	50.11	49.53	60.14	30.07	64.87	2.0909	0.5688	0.4642	27.20	22.20	50.60	19.46	11.00	8.46	43.50
GNR 16	50.16	49.70	60.14	30.10	65.33	2.0060	0.4439	0.4680	22.13	23.33	54.54	19.60	11.60	8.00	40.84
	50.11	49.57	60.14	30.07	65.04	2.0344	0.3582	0.5079	17.61	24.97	57.42	19.50	12.38	7.12	36.52

wt.A = Grafted product was extracted by light petroleum ether for 24 hrs.

Wt.B = Grafted product was extracted by light petroleum ether for 24 hrs and then extracted by the mixture of MEK/acetone(50:50(v/v)) for 24 hrs.

Table A-2 The average of the conversion, percentage grafted natural rubber, percentage free NR, percentage free ST/MMA, and grafting efficiency

Exp.	Avg. Conversion (%)	Avg. Free NR (%)	Avg. Free ST/MMA (%)	Avg. Grafted NR (%)	Avg. GE (%)
GNR 01	85.98	26.81	29.50	43.69	24.32
GNR 02	97.47	24.28	34.69	41.03	17.65
GNR 03	65.82	23.60	14.11	62.29	57.04
GNR 04	66.02	20.73	17.67	61.61	46.62
GNR 05	87.73	19.92	28.30	51.78	28.53
GNR 06	97.85	20.72	33.99	45.29	19.66
GNR 07	64.46	19.88	14.07	66.06	56.69
GNR 08	67.94	21.31	18.47	60.23	45.23
GNR 09	82.68	30.55	34.98	34.47	22.62
GNR 10	96.90	26.39	39.80	33.81	18.87
GNR 11	62.20	24.42	20.89	54.69	45.44
GNR 12	63.50	16.13	24.71	59.17	36.14
GNR 13	81.15	17.96	35.13	46.91	21.13
GNR 14	90.42	23.92	39.48	36.60	16.53
GNR 15	64.49	25.97	22.64	51.40	42.17
GNR 16	65.19	19.87	24.15	55.98	38.68

APPENDIX B

1 Experimental Designs [30]

Factorial designs are most efficient for the study of the effects of two or more factors in relatively few experiments as compared to the one-factor-at-a-time technique. The one-factor-at-a-time technique, varying one factor while keeping the other factors at a constant level, is tedious when a large number of factors have to be investigated, whereas statistically based experimental designs are more efficient approach to deal with a large number of variables. Moreover, if there are statistical interaction between factors, that is where the effect of one factor is dependent on the value of another factor, then this information will not be obtained using the one-factor-at-a-time technique.

Factorial designs allow one to study a large number of variables simultaneously, while a large amount of information is obtained with a reduced experimental effort. The clarification of experimental kinetics is an iterative process involving seven steps. These steps are recognition of and statement of the problem, choice of factors and levels, selection of a response variable, choice of experimental design, performing the experiment, data analysis, and conclusions. Within the choice of experimental design, it is always necessary to maintain a balance between statistical accuracy and cost.

A factorial design assumes that the factor are fixed, the designs are completely randomized, and the usual normality assumptions are satisfied. The 2^k design is particularly useful in the early stages of experimental work, when there are likely to be many factors to be investigated. It provides the smallest number of runs which k factors can be studied in a complete factorial design. Consequently, these designs are widely used in factor screening experiments.

1.1 Calculation of Experimental

This research begin the analysis of experimental data constructing a normal probability plot of the effect estimates. The table of plus and minus signs for the contrast constants for the 2^4 design are shown in Table B-1. From these contrasts, we may estimate the 15 factorial effects and the sum of squares show in Tables B-2.

Table B-1 Design factor levels for factorial designed experiment

Run Number	Factor A	B	C	D	Run Label	Grafting Efficiency (%)
1	-	-	-	-	(1)	24.32
2	+	-	-	-	a	17.65
3	-	+	-	-	b	57.04
4	+	+	-	-	ab	46.62
5	-	-	+	-	c	28.53
6	+	-	+	-	ac	19.66
7	-	+	+	-	bc	56.69
8	+	+	+	-	abc	45.23
9	-	-	-	+	d	22.62
10	+	-	-	+	ad	18.87
11	-	+	-	+	bd	45.44
12	+	+	-	+	abd	36.14
13	-	-	+	+	cd	21.13
14	+	-	+	+	acd	16.53
15	-	+	+	+	bcd	42.17
16	+	+	+	+	abcd	38.68

Table B-2 Contrast constants for the 2^4 design

	A	B	AB	C	AC	BC	ABC	D	AD	BD	ABD	CD	ACD	BCD	ABCD	% GE
(1)	-	-	+	-	+	+	-	-	+	+	-	+	-	-	+	24.32
a	+	-	-	-	-	+	+	-	-	+	+	+	+	-	-	17.65
b	-	+	-	-	+	-	+	-	+	-	+	+	-	+	-	57.04
ab	+	+	+	-	-	-	-	-	-	-	-	+	+	+	+	46.62
c	-	-	+	+	-	-	+	-	+	+	-	-	+	+	-	28.53
ac	+	-	-	+	+	-	-	-	-	+	+	-	-	+	+	19.66
bc	-	+	-	+	-	+	-	-	+	-	+	-	+	-	+	56.69
abc	+	+	+	+	+	+	+	-	-	-	-	-	-	-	-	45.23
d	-	-	+	-	+	+	-	+	-	-	+	-	+	+	-	22.62
ad	+	-	-	-	-	+	+	+	+	-	-	-	-	+	+	18.87
bd	-	+	-	-	+	-	+	+	-	+	-	-	+	-	+	45.44
abd	+	+	+	-	-	-	-	+	+	+	+	-	-	-	-	36.14
cd	-	-	+	+	-	-	+	+	-	-	+	+	-	-	+	21.13
acd	+	-	-	+	+	-	-	+	+	-	-	+	+	-	-	16.53
bcd	-	+	-	+	-	+	-	+	-	+	-	+	-	+	-	42.17
abcd	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	38.68

Table B-2 (Continued)

	A	B	AB	C	AC	BC	ABC	D	AD	BD	ABD	CD	ACD	BCD	ABCD	% GE
(1)	-24.32	-24.32	+24.32	-24.32	+24.32	+24.32	-24.32	-24.32	+24.32	+24.32	-24.32	+24.32	-24.32	-24.32	+24.32	24.32
a	+17.65	-17.65	-17.65	-17.65	-17.65	+17.65	+17.65	-17.65	-17.65	+17.65	+17.65	+17.65	+17.65	-17.65	-17.65	17.65
b	-57.04	+57.04	-57.04	-57.04	+57.04	-57.04	+57.04	-57.04	+57.04	-57.04	+57.04	+57.04	-57.04	+57.04	-57.04	57.04
ab	+46.62	+46.62	+46.62	-46.62	-46.62	-46.62	-46.62	-46.62	-46.62	-46.62	-46.62	+46.62	+46.62	+46.62	+46.62	46.62
c	-28.53	-28.53	+28.53	+28.53	-28.53	-28.53	+28.53	-28.53	+28.53	+28.53	-28.53	-28.53	+28.53	+28.53	-28.53	28.53
ac	+19.66	-19.66	-19.66	+19.66	+19.66	-19.66	-19.66	-19.66	-19.66	+19.66	+19.66	-19.66	-19.66	+19.66	+19.66	19.66
bc	-56.69	+56.69	-56.69	+56.69	-56.69	+56.69	-56.69	-56.69	+56.69	-56.69	+56.69	-56.69	+56.69	-56.69	+56.69	56.69
abc	+45.23	+45.23	+45.23	+45.23	+45.23	+45.23	+45.23	-45.23	-45.23	-45.23	-45.23	-45.23	-45.23	-45.23	-45.23	45.23
d	-22.62	-22.62	+22.62	-22.62	+22.62	+22.62	-22.62	+22.62	-22.62	-22.62	+22.62	-22.62	+22.62	+22.62	-22.62	22.62
ad	+18.87	-18.87	-18.87	-18.87	-18.87	+18.87	+18.87	+18.87	+18.87	-18.87	-18.87	-18.87	-18.87	+18.87	+18.87	18.87
bd	-45.45	+45.45	-45.45	-45.45	+45.45	-45.45	+45.45	+45.45	-45.45	+45.45	-45.45	-45.45	+45.45	-45.45	+45.45	45.45
abd	+36.14	+36.14	+36.14	-36.14	-36.14	-36.14	-36.14	+36.14	+36.14	+36.14	+36.14	-36.14	-36.14	-36.14	-36.14	36.14
cd	-21.13	-21.13	+21.13	+21.13	-21.13	-21.13	+21.13	+21.13	-21.13	-21.13	+21.13	+21.13	-21.13	-21.13	+21.13	21.13
acd	+16.53	-16.53	-16.53	+16.53	+16.53	-16.53	-16.53	+16.53	+16.53	-16.53	-16.53	+16.53	+16.53	-16.53	-16.53	16.53
bcd	-42.17	+42.17	-42.17	+42.17	-42.17	+42.17	-42.17	+42.17	-42.17	+42.17	-42.17	+42.17	-42.17	+42.17	-42.17	42.17
abcd	+38.68	+38.68	+38.68	+38.68	+38.68	+38.68	+38.68	+38.68	+38.68	+38.68	+38.68	+38.68	+38.68	+38.68	+38.68	38.68
Contrast	-58.56	198.70	-10.78	-0.08	1.72	-4.86	7.82	-54.16	16.28	-32.14	1.90	-9.04	8.20	11.06	5.50	
Effect estimate	-7.32	24.84	-1.35	-0.01	0.21	-0.61	0.98	-6.77	2.04	-4.02	0.24	-1.13	1.03	1.38	0.69	
Sum of square	214.33	2467.61	7.26	0.00	0.18	1.48	3.82	183.33	16.56	64.56	0.23	5.11	4.20	7.65	1.89	

ΣSS = 2978.21

$$\text{Contrast} \quad = \quad \text{Total of treatment combination}$$

Once the contrasts for the effects have been computed, we may estimate the effects and compute the sums of squares according to

$$AB\ldots K \quad = \quad \frac{2}{n \times 2^k}\,(\text{Contrast}_{AB\ldots K})$$

and

$$SS_{AB\ldots K} \quad = \quad \frac{1}{n \times 2^k}\,(\text{Contrast}_{AB\ldots K})^2$$

respectively, where n denotes the number of replicates.

Table B-3 The analysis of variance

Effect Name	Sum of Square	Degree of Freedom	Mean Square	F_0
A	SS_A	a - 1	$MS_A = \frac{SS_A}{a-1}$	$F_0 = \frac{MS_A}{MS_E}$
B	SS_B	b - 1	$MS_B = \frac{SS_B}{b-1}$	$F_0 = \frac{MS_B}{MS_E}$
D	SS_D	d - 1	$MS_B = \frac{SS_D}{d-1}$	$F_0 = \frac{MS_D}{MS_E}$
BD	SS_{BD}	(b – 1)(d – 1)	$MS_{BD} = \frac{SS_{BD}}{(b-1)(d-1)}$	$F_0 = \frac{MS_{BD}}{MS_E}$
Error	SS_E	abc(n – 1)	$MS_E = \frac{SS_E}{abc(n-1)}$	
Total	SS_T	abcn-1		

Where SS_T = Total of summation of square

$SS_E = SS_T - SS_A - SS_B - SS_D - SS_{BD}$

APPENDIX C

1. Residuals and Model Adequacy

The usual diagonostic checks should be applied to the residuals of a 2^4 design. Our analysis indicates that the only significant effects are A = -7.32, B = 24.84, D = -6.77, and BD = -4.02. If this is true, the estimated grafting efficiency are given by

$$\hat{Y} = 33.57 + (-7.32/2)X_1 + (24.84/2)X_2 + (-6.77/2)X_4 + (-4.02/2)X_2X_4$$

This regression model can be used to obtain the predicted or fitted value of Y at the sixteen points in the design. The residuals are the differences between the observed and fitted values of Y. For example, when the A is at the low level (X_1= -1), the B is at the low level (X_2 = -1), and the D is at the low level (X_4 = -1), the predicted yield is

$$\begin{aligned}\hat{Y} &= 33.57 + (-7.32/2)(-1) + (24.84/2)(-1) + (-6.77/2)(-1) + (-4.02/2)(-1)(-1) \\ &= 26.18\end{aligned}$$

There is one observation at this treatment combination, and the residual is

$$\begin{aligned}\varepsilon &= Y - \hat{Y} \\ \varepsilon &= 24.32 - 26.18 \\ &= -1.86\end{aligned}$$

Where Y is observed values

$\hat{Y}$ is fitted values

Table C-1 The values of observed, fitted, and residual for all sixteen observations

Run Label	X_1	X_2	X_4	X_2X_4	%GE (Y)	$\hat{Y}$	Residual (ε)
(1)	-1	-1	-1	+1	24.32	26.18	-1.86
a	+1	-1	-1	+1	17.65	18.86	-1.21
b	-1	+1	-1	-1	57.04	55.04	1.99
ab	+1	+1	-1	-1	46.62	47.72	-1.10
c	-1	-1	-1	+1	28.53	26.18	2.34
ac	+1	-1	-1	+1	19.66	18.86	0.79
bc	-1	+1	-1	-1	56.69	55.04	1.64
abc	+1	+1	-1	-1	45.23	47.72	-2.49
d	-1	-1	+1	-1	22.62	23.43	-0.81
ad	+1	-1	+1	-1	18.87	16.11	2.75
bd	-1	+1	+1	+1	45.44	44.25	1.18
abd	+1	+1	+1	+1	36.14	36.93	-0.79
cd	-1	-1	+1	-1	21.13	23.43	-2.30
acd	+1	-1	+1	-1	16.53	16.11	0.41
bcd	-1	+1	+1	+1	42.17	44.25	-2.08
abcd	+1	+1	+1	+1	38.68	36.93	1.74

APPENDIX D

Mechanical Properties of Grafted Natural Rubber Modified PVC, MBS Modified PVC, and NR Modified PVC

Table D-1 Tensile strength of grafted natural rubber modified PVC, MBS modified PVC, and NR modified PVC

	Unmodified	PVC/GNR 01			PVC/GNR 04			PVC/GNR 03			PVC/MBS			PVC/NR	
		5	10	15	5	10	15	5	10	15	5	10	15	5	10
Tensile strength	51.85	47.42	43.10	37.71	47.89	37.98	33.50	46.82	41.77	34.21	45.96	41.42	37.36	45.05	35.66
(Mpa)	51.72	48.33	43.18	36.66	45.07	38.15	33.51	48.07	40.12	34.42	45.79	40.96	36.29	46.40	33.93
	49.52	47.86	43.00	37.76	46.21	38.73	32.79	48.19	39.59	34.94	46.06	41.34	37.51	45.87	33.93
Mean	51.03	47.87	43.09	37.38	46.39	38.29	33.27	47.69	40.49	34.52	45.94	41.24	37.05	45.77	34.43

Table D-2 Ultimate elongation of grafted natural rubber modified PVC, MBS modified PVC, and NR modified PVC

	Unmodified	PVC/GNR 01			PVC/GNR 04			PVC/GNR 03			PVC/MBS			PVC/NR	
		5	10	15	5	10	15	5	10	15	5	10	15	5	10
Ultimate elongation	8.91	8.67	9.72	9.23	11.80	7.89	7.65	8.10	9.23	8.98	8.10	8.93	12.07	8.68	7.94
(%)	8.11	9.47	11.80	7.90	10.78	7.89	9.00	10.49	9.50	7.91	8.40	11.28	9.76	9.74	8.22
	8.10	7.86	9.71	10.02	10.51	7.61	8.19	9.45	9.50	8.45	9.18	9.19	12.08	9.75	8.51
Mean	8.37	8.67	10.41	9.05	11.03	7.80	8.28	9.35	9.41	8.45	8.56	9.80	11.30	9.39	8.22

Table D-3 Impact strength of grafted natural rubber modified PVC, MBS modified PVC, and NR modified PVC

	Unmodified	PVC/GNR 01			PVC/GNR 04			PVC/GNR 03			PVC/MBS			PVC/NR	
		5	10	15	5	10	15	5	10	15	5	10	15	5	10
Impact strength	17.15	40.03	33.99	45.82	32.05	46.36	37.40	35.60	48.35	79.43	36.17	38.53	112.12	24.87	27.61
(kg-cm/cm)	22.78	31.21	37.08	42.84	33.98	47.38	69.95	32.22	44.38	51.38	28.15	39.33	106.47	25.60	25.18
	17.20	40.63	48.44	45.95	44.38	33.58	38.58	30.62	42.64	50.63	34.09	35.60	111.68	26.18	39.38
	21.09	31.35	35.28	42.62	42.11	41.35	40.77	47.64	36.13	41.71	26.19	35.38	72.34	23.80	30.40
Mean	19.56	35.81	38.70	44.31	38.13	42.17	46.68	36.52	42.88	55.79	31.15	37.21	100.65	25.11	30.64

Table D-4 Hardness of grafted natural rubber modified PVC, MBS modified PVC, and NR modified PVC

	Unmodified	PVC/GNR 01			PVC/GNR 04			PVC/GNR 03			PVC/MBS			PVC/NR	
		5	10	15	5	10	15	5	10	15	5	10	15	5	10
Hardness	113.5	112.6	107.8	99.1	107.4	99.6	87.2	109.6	102.7	97.6	108.0	102.9	99.5	105.7	90.8
(HRR)	113.0	112.6	107.5	99.4	107.4	98.5	87.7	109.6	104.1	96.5	109.2	104.6	100.6	105.2	89.5
	114.6	113.0	107.5	99.8	106.9	98.5	88.5	109.1	104.0	96.1	107.2	103.0	100.9	104.6	90.2
	115.6	112.4	107.9	99.0	106.4	98.5	88.2	109.6	105.0	96.4	109.0	103.5	98.5	104.1	89.5
	114.2	112.7	106.7	99.6	106.2	99.6	87.6	109.2	104.2	97.1	109.1	104.6	100.6	104.7	90.3
Mean	114.2	112.7	107.5	99.4	106.9	98.9	87.8	109.4	104.0	96.7	108.5	103.7	100.0	104.9	90.1

APPENDIX E

Dynamic Mechanical Properties of Polymer

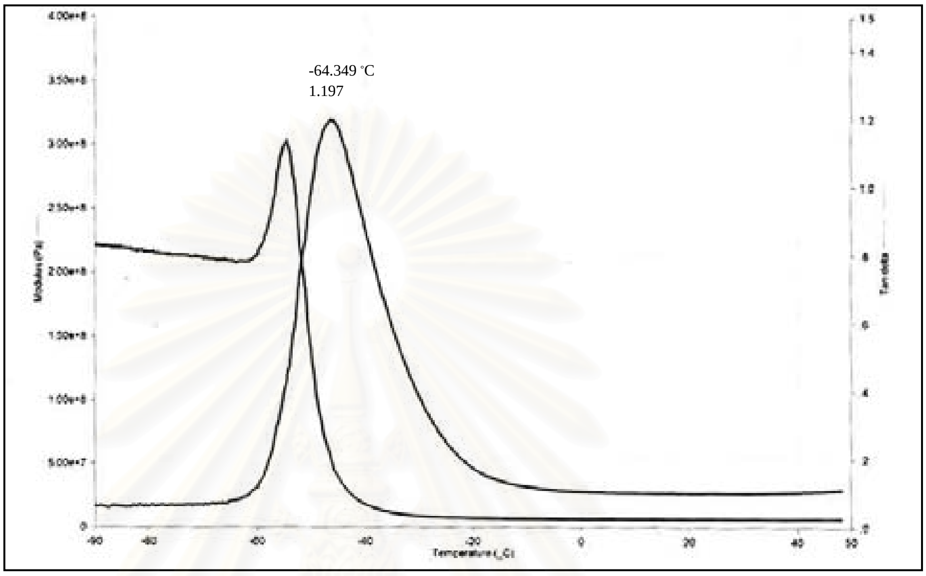


Figure E-1 Dynamic mechanical properties of natural rubber

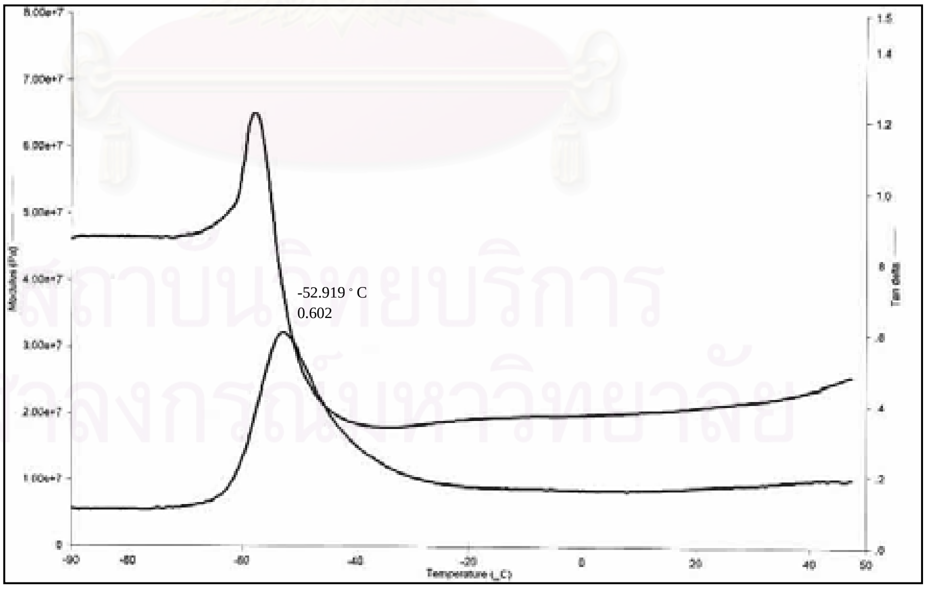


Figure E-2 Dynamic mechanical properties of grafted natural rubber

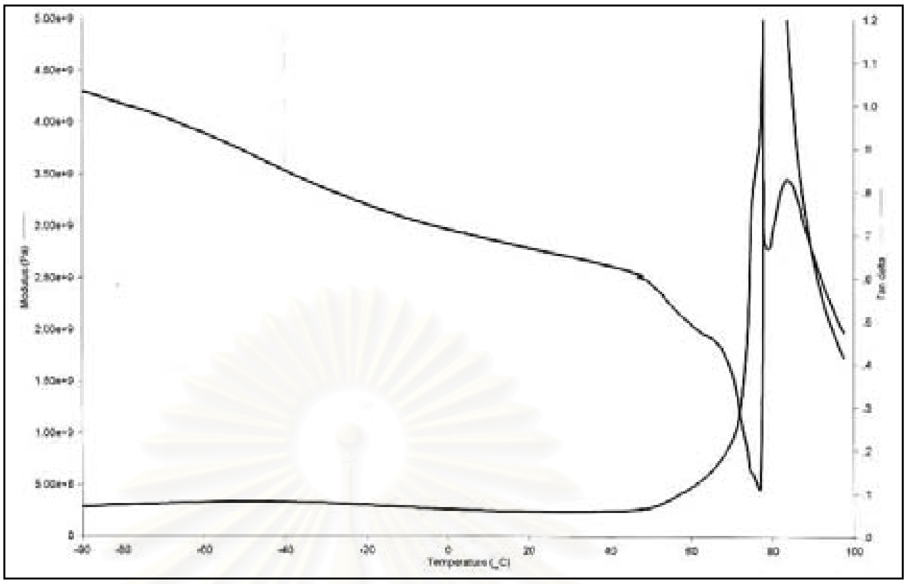


Figure E-3 Dynamic mechanical properties of unmodified PVC

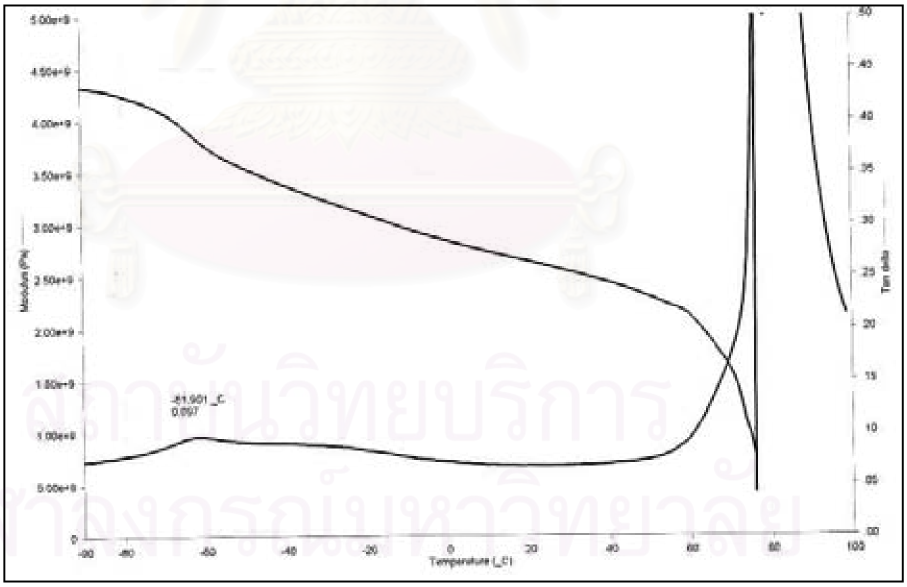


Figure E-4 Dynamic mechanical properties of PVC modified with grafted natural rubber at 5 phr

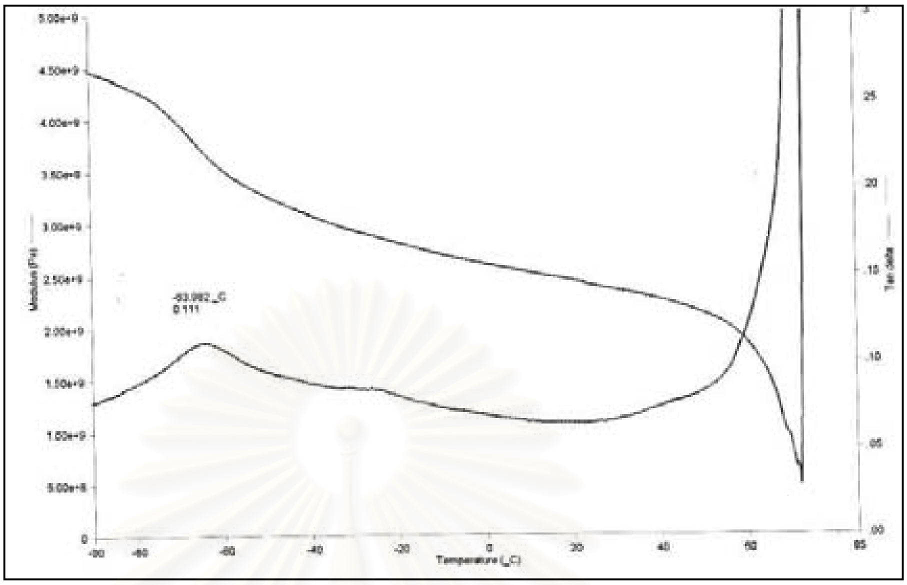


Figure E-5 Dynamic mechanical properties of PVC modified with grafted natural rubber at 10 phr

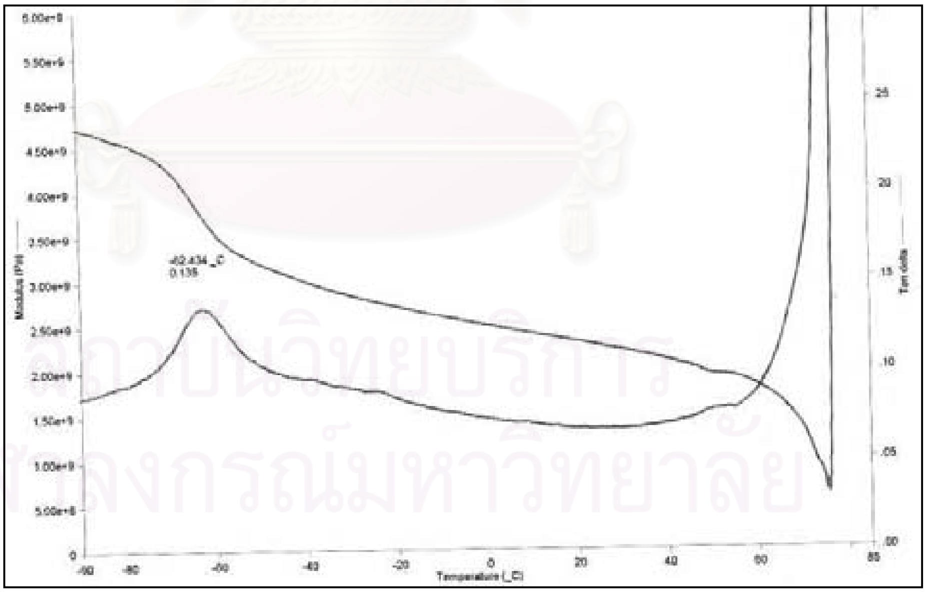


Figure E-6 Dynamic mechanical properties of PVC modified with grafted natural rubber at 15 phr

APPENDIX F

Thermal Properties of Unmodified and Modified PVC

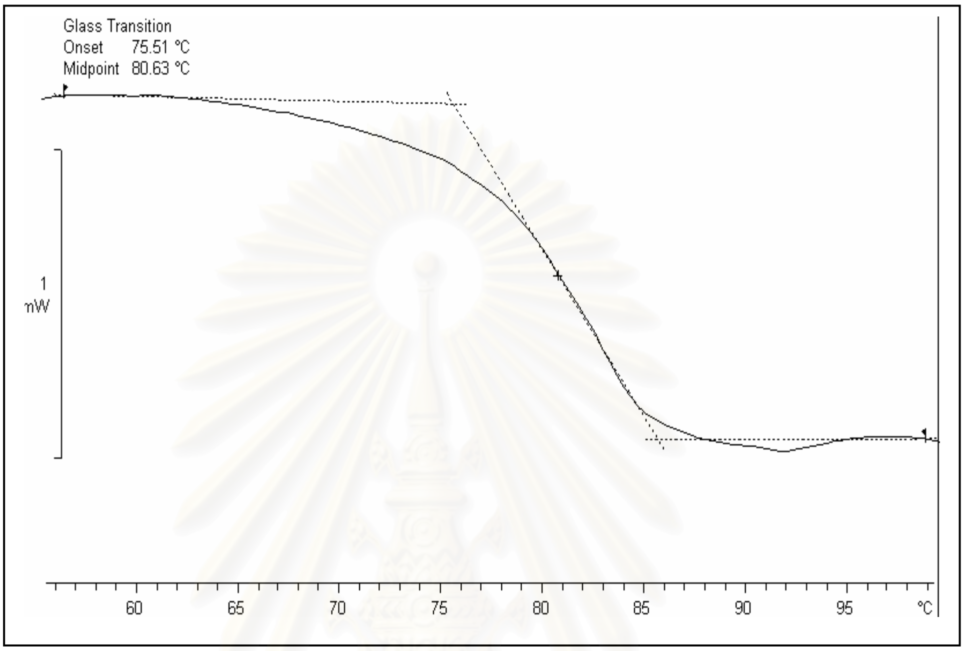


Figure F-1 DSC thermogram of unmodified PVC

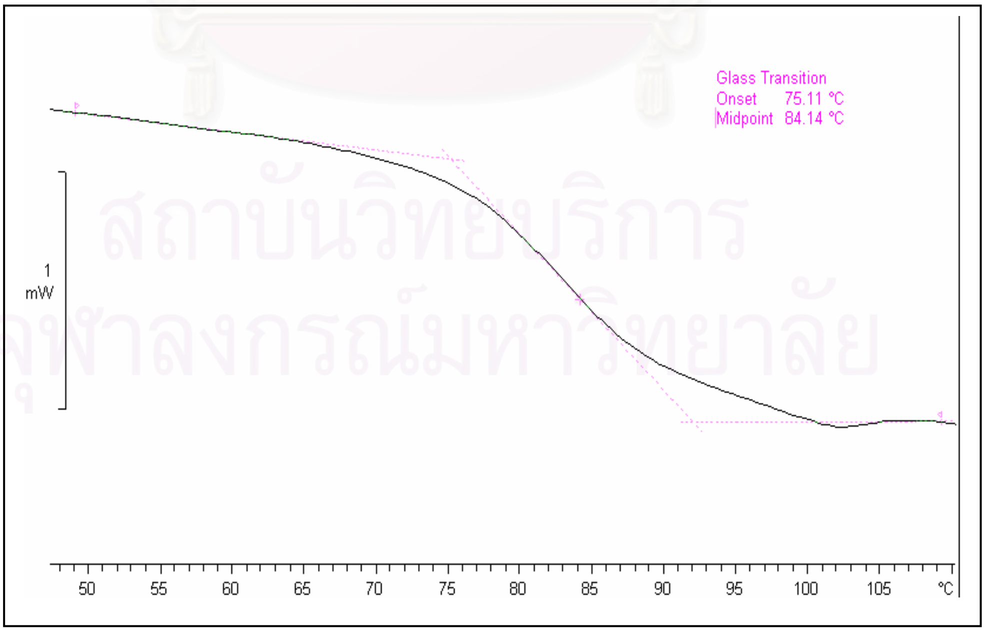


Figure F-2 DSC thermogram of PVC modified with grafted natural rubber at 5 phr

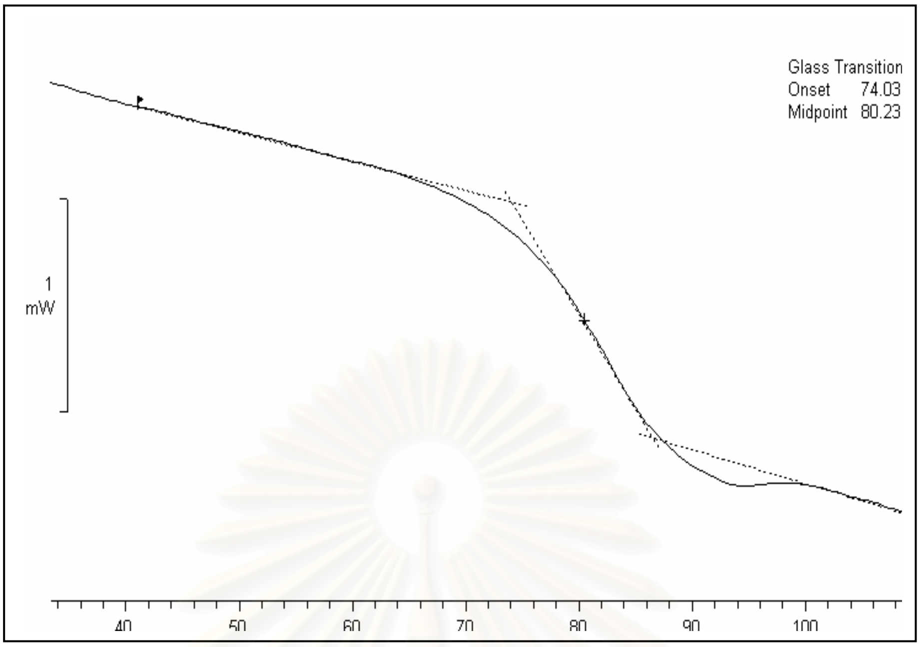


Figure F-3 DSC thermogram of PVC modified with grafted natural rubber at 10 phr

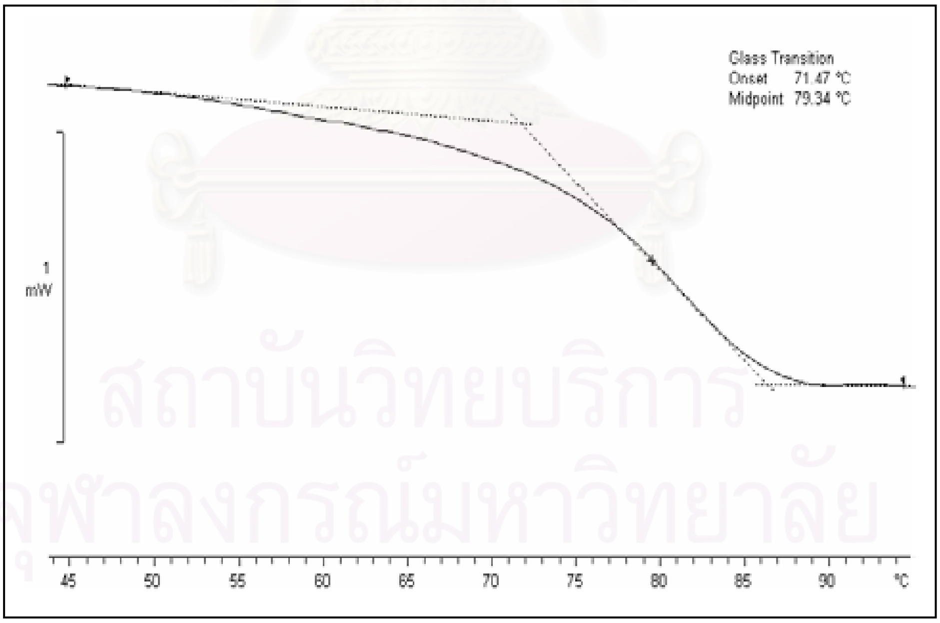


Figure F-4 DSC thermogram of PVC modified with grafted natural rubber at 15 phr

VITAE

Miss Kanchana Eawsuwan was born on December 20, 1976 in Ratchaburi, Thailand. She received her Bachelor’s degree in Industrial Chemistry, from the Faculty of Science, King Mongkut’s Institute of Technology Ladkrabang in 1999. She has pursued Master’s Degree in Petrochemistry and Polymer Science, Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University since 2001 and finished her study in 2003.