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GRAFTING OF STYRENE AND METHYL METHACRYLATE ONTO NATURAL RUBBER IN BATCH EMULSION PROCESS

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งานวิจัยนี้เป็นการศึกษากราฟต์โคพอลิเมอไรเซชันของผสมสไตรีนและเมทิลเมทาคริเลตบนไดอีนพอลิเมอร์ซีดลาเท็กซ์ โดยใช้คูมีนไฮโดรเปอร์ออกไซด์เป็นตัวริเริ่มแบบรีดอกซ์ ไดอีนพอลิเมอร์ที่ใช้คือ ยางธรรมชาติ ยางสไตรีน-บิวทาไดอีน และ พอลิบิวทาไดอีน งานการทดลองใช้เทคนิคการวางแผนการทดลองแฟกทอเรียลทำเพียงบางส่วนเพื่อศึกษาการเปลี่ยนมอนอเมอร์ องค์ประกอบของกราฟต์โคพอลิเมอร์ และประสิทธิภาพการกราฟต์ กราฟต์โคพอลิเมอร์ที่สังเคราะห์ได้ทำให้บริสุทธิ์และองค์ประกอบของกราฟต์โคพอลิเมอร์หาได้ด้วยนิวเคลียร์แมกเนติกเรโซแนนซ์สเปกโทรสโกปีและ ดิฟเฟอเรนเชียลสแกนนิงแคลอริมิทรีย์ และศึกษาสัณฐานวิทยาของกราฟต์โคพอลิเมอร์ด้วยทรานสมิสชันอิเลคตรอนไมโครสโกปี ในงานวิจัยนี้ศึกษาผลของแฟกเตอร์กระบวนการ 6 ตัวและปฏิกิริยาสัมพันธ์ของแฟกเตอร์เหล่านี้ต่อประสิทธิภาพการกราฟต์ แฟกเตอร์ที่ศึกษาคือ ความเข้มข้นของตัวริเริ่ม สารก่ออิมัลชัน และสารถ่ายโอนสายโซ่ อัตราส่วนสไตรีนต่อเมทิลเมทาคริเลต อัตราส่วนมอนอเมอร์ต่อยาง และอุณหภูมิ การวิเคราะห์ผลจากการออกแบบการทดลองพบว่า ความเข้มข้นของสารถ่ายโอนสายโซ่และอุณหภูมิของปฏิกิริยาในช่วงการทดลองเป็นปัจจัยที่สำคัญต่อประสิทธิภาพการกราฟต์ เมื่อศึกษากลไกกราฟต์โคพอลิเมอไรเซชันปรากฏว่ากราฟต์โคพอลิเมอร์เกิดขึ้นที่พื้นผิวของอนุภาคลาเท็กซ์โดยผ่านกระบวนการการถ่ายโอนสายโซ่ งานวิจัยนี้มีการนำกราฟต์โคพอลิเมอร์มาใช้เป็นสารเสริมการทนแรงกระแทกในพีวีซี โดยการเตรียมพลาสติกผสมของกราฟต์โคพอลิเมอร์กับพีวีซี ศึกษาผลของกราฟต์โคพอลิเมอร์ต่อความทนแรงดึง และความทนแรงกระแทกไอซอด

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KEY WORD: GRAFT COPOLYMERIZATION / TWO FRACTIONAL FACTORIAL DESIGN TECHNIQUE / STYRENE / METHYL METHACRYLATE / REDOX INITIATOR

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The graft copolymerization of styrene/methyl methacrylate mixtures onto diene-based polymer seed latex has been carried out using cumene hydroperoxide redox initiator. The diene-based polymers were natural rubber, styrene-butadiene rubber and polybutadiene. The experiments were designed using two fractional factorial design techniques. The monomer conversion, graft copolymer composition and grafting efficiency were determined. The synthesized graft copolymers were purified and then characterized by proton nuclear magnetic resonance (^{1}H-NMR) analysis and differential scanning calorimetry (DSC). Transmission electron microscopy (TEM) was used to study the morphology of the graft copolymers. Grafting efficiency is discussed with respect to the influence of six process factors and the interaction of these factors. The factors studied include the amount of initiator, emulsifier and chain-transfer agent, styrene-to-methyl methacrylate ratio, monomer-to-rubber ratio, and temperature. The analysis of the results from the design showed that only the amount of chain transfer agent and temperature in the range of test had significant effects on grafting efficiency. The mechanism of graft copolymerization has been studied. It appears that the formation of graft copolymers occurs on the surface of the latex particles through a chain-transfer process. The graft copolymer products could be used as an impact modifier for PVC, thus, blends of the graft copolymer products and PVC were prepared. Izod impact strength and tensile properties of the graft copolymer products were investigated.

Department	Chemical Technology	Student's signature…………………….
Field of study	Chemical Technology	Advisor's signature……………………
Academic year	2000	Co-advisor's signature…………………

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NOMENCLATURE

H : α-Methylenic Hydrogen Atom

M : Vinyl Monomer

$M^{\bullet}_n$: Vinyl Polymer Radical

NR-H : Natural Rubber

$NR^{\bullet}$: Polyisoprene Radical

$NR\text{-}M^{\bullet}_n$: The Growing Graft Polymer Radical Chain

P_r : Polymer Rubber

$P_r^{\bullet}$: Macromolecule Radical

$P_r\text{-}M^{\bullet}_n$: The Growing Graft Copolymer

$R^{\bullet}$: Primary Radical

$RO^{\bullet}$: Alkoxy Radical

Acronyms

ASTM : American Standard of Testing Material

CHPO : Cumene Hydroperoxide

CTA : Chain-transfer Agent

DRC : Dry Rubber Content

DSC : Differential Scanning Calorimetry

EDTA : Ethylenediamine Tetraacetic

EMUL : Emulsifier

GE : Grafting Efficiency

GL : Grafting Level

GPB : Grafted Polybutadiene

GNR : Grafted Natural Rubber

GSBR : Grafted Styrene-Butadiene Rubber

^{1}H-NMR : Proton Nuclear Magnetic Resonance

INT : Initiator

KPS : Potassium Persulfate

NR : Natural Rubber

MMA : Methyl Methacrylate

M/R : Monomer to Rubber Ratio

PVC : Poly(Vinyl Chloride)

ST : Styrene

SDS : Sodium Dodecyl Sulfate

SFS : Sodium Formaldehyde Sulfoxylate

TEM : Transmission Electron Microscopy

TEMP : Temperature

TEPA : Tetraethylenepentamine

T_g : Glass Transition Temperature

nDM : n-Dodecyl Mercaptan

phr : Part per Hundred

Greek Symbols

β : Transition Temperature

α' : Transition Temperature

CHAPTER 1

INTRODUCTION

1.1 General Introduction

The history of modification of polymeric materials is nearly as old as that of polymers. Since the first synthetic polymer was produced, people have been trying to improve its properties. Some of the most important commercial polymers are diene polymers, e.g., natural rubber (NR), polybutadiene (PB), and styrene butadiene rubber (SBR). Their usefulness to scientists and engineers comes not only from their desirable physical properties, but also because they may be used as a base for a variety of chemical modification reactions that are made possible because of the presence of olefinic groups within the polymers. The modification of polymeric materials can be achieved either by the synthesis of new polymers, by new polymerization processes, or by the combination of existing polymers having various properties. Chemical modification of polymers is a post polymerization process. In the broadest sense, chemical modification could include reactions such as cross-linking (vulcanization and curing), grafting, degradation, oxidation, isomerization, hydrogenation, cyclization, etc.

Graft copolymerization is a process by which a polymer chain (the backbone) has attached to it, polymeric side chains (the grafts) of a different chemical nature; graft copolymers show branched molecular structures and usually the side chains distribute randomly. High impact modified resistance polymers are based on two-phase polymers systems, comprising a continuous glassy phase containing finely dispersed rubbery domains. Stabilization of these two domains is achieved by grafting the monomer in the second stage polymerization onto the performed rubber, usually by solution or emulsion polymerization. Many latex applications such as adhesives, coatings, impact modification, and toughening of polymers can be carried out in stages, such that previously formed latex particles or "seed" particles are grafted in further polymerization steps. Using emulsion polymerization techniques, however, there is a great degree of control over these properties due to the particulate nature of the polymerization. Essentially, altering the polymerization conditions can vary particle size and morphology. Emulsion polymerization is the process of choice for a number of toughened plastic, notably ABS (acrylonitrile-butadiene-styrene), MBS (methacrylate-butadiene-styrene) and toughened PMMA [1]. In the manufacture of these impact-resistant plastics, the rubbery latex is emulsion polymerized first, and the further monomer (e.g. acrylonitrile and styrene) is polymerized in the presence of the preformed rubbery latex. It has been reported that block or graft copolymer can be used effectively as a modifier [2,3]. Usually, improvement of the impact strength of rigid plastics can be reached by the addition of polymeric modifiers such as chlorinated polyethylene (CPE), ethylene-vinyl acetate copolymers, nitrile rubbers, and acrylonitrile-butadiene-styrene copolymer (ABS) or methyl methacrylate-butadiene-styrene (MBS) [4-8]. The manufacture of Cycolac brand by ABS Borg-Warner was one of the most successful emulsion graft polymerization processes [9].

On the other hand, the emulsion polymerization method employs various possibilities to prepare particles with controlled morphologies and surface properties. Core-shell arrangements are 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 that has been synthesized in a previous polymerization. The layered particle structure gives the impact modifier novel properties, which can not be duplicated by a simple blend of the two polymers or copolymerization of the respective monomers. The core-shell latex systems can have differing morphologies; for instance, the latex particle can have a rubbery core and a glassy shell or a glassy core and rubbery shell. The core and shell can be composed of either homopolymers or copolymers. Such core-shell latex with a glassy core and rubbery shell can be used in coating and adhesive formulation; the shell material forms the continuous film or adhesion points, and the core serves to strengthen the film or improves the cohesive strength. In this work, the latex particles had rubbery cores and glassy shells at room temperature. These core-shell latexes are used as impact modifiers in plastics. The rubber 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 use as model systems in the improvement of impact modification.

Graft copolymers 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 for most applications. The purpose of adding the rubber is to improve the brittle characteristics of the basic polymer and to improve the mechanical properties of the material, in particular, impact resistance. Impact modifiers are used to enhance the toughness of rigid vinyl matrix by providing a finely dispersed rubbery phase to absorb energy and thus minimize fracture of the otherwise brittle vinyl matrix. Toughness may be defined as resistance to impact. Rigid PVC compounds require the addition of rubbery impact modifiers to meet most fabrication or end-use needs. Applications of these materials include item such as shatterproof clear bottles, pipe, window and house siding.

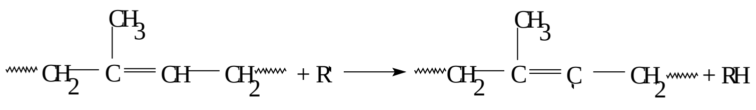
Polymer blends are of considerable importance since the blending may provide a means for improving mechanical properties as well as processibility. It is well known that plastics are blended with rubbery polymers to improve the impact strength, thus making them suitable for marsh application. The introduction of a small amount of modifier can lead to major changes in mechanical properties [10,11]. Furthermore, considerable attention has been devoted to the modification of PVC, including plasticization, enhancement of impact strength, increase of heat distortion temperature, and improvement of processibility [12-13]. A great body of knowledge exists on the toughening of plastics by rubber modification. The effect of finely divided rubber inclusions on the impact resistance of plastics has been recognized for some time and represents a well-developed technology.

1.2 Literature Review

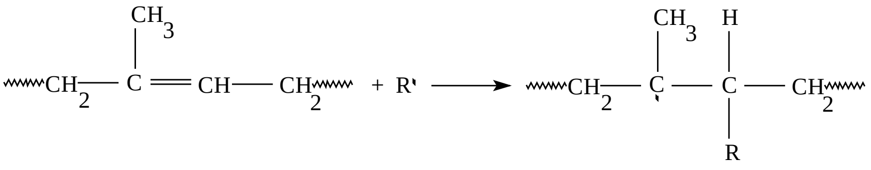
The terms "graft", "grafting" and " graft copolymer" were first used by Mark [14]. Historically, the development and later exploitation of graft copolymers became evident by the work of Houtz and Askins [15]. They observed that a dead polymer molecule in the presence of growing polymer chains was capable of increasing its molecular size. Flory suggested that branched vinyl polymers could result from chain transfer reactions involving polymer molecules and growing polymer chains [16]. The mechanism describes a chain transfer process of a growing polymeric radical to an existing formed polymer. Chain transfer reactions usually, but not necessarily, involve hydrogen abstraction. The extent of the chain transfer reaction is dependent on a number of parameters such as temperature, monomer/polymer ratio, the lability of the atom being abstracted, the type and concentration of initiator, and the type and structure of the monomer and polymer. Of all the methods to prepare graft copolymers mentioned above, the chain transfer method is the most practiced route. Chain transfer has been applied to solution, suspension, bulk and emulsion polymerizations. Graft copolymer and linear homopolymers are formed during the polymerization depending on process parameters. Mayo also proposed that growing polymer chains could undergo chain transfer reactions with polymer molecules [17]. Based on this chain transfer mechanism, Carlin and Shakespeare found that a solution of poly(methyl methacrylate) in *p*-chlorostyrene polymerized at 50^{o}C would produce some graft copolymer which contained units of both types [18].

Graft copolymers can also be formed by direct attack on unsaturated polymer as described by Battaerd and Tregear [19]. The most common natural and synthetic polymers, containing residual double bonds on the carbon backbone, are rubbers. Extensive work dealing with grafting to rubber polymers is extensively reported in the literature.

Allen et al. investigated in detail the grafting mechanism by using tracer methods for the graft polymerization of methyl methacrylate onto gutta-percha (tran-1,4-polyisoprene) in benzene solution at 60 °C [20]. The reaction mechanism is schematically represent by the following equation:



$$\sim\!CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH-CH_2\!\sim + R^{\cdot} \longrightarrow \sim\!CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}}=\underset{\cdot}{C}-CH_2\!\sim + RH \qquad (1.1)$$



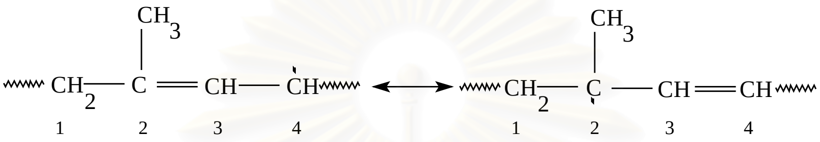
$$\sim\!CH_2-\underset{}{\overset{CH_3}{\overset{|}{C}}}=CH-CH_2\!\sim \;+\; R^{\bullet} \longrightarrow \;\sim\!CH_2-\overset{CH_3}{\overset{|}{\dot{C}}}-\overset{H}{\overset{|}{\underset{\underset{R}{|}}{C}}}-CH_2\!\sim \qquad (1.2)$$

Natural Rubber (radical)

The addition reaction (1.2) plays a minor role in relation to the transfer reaction (1.1). The equations explain also the mechanism in solution or in solid rubber, swollen with a monomer containing the initiator.

Brydon et al. studied the grafting of styrene monomer onto polybutadiene in benzene solution at 60^{o}C with benzoyl peroxide as initiator [21,22]. They proposed a primary radical initiated grafting mechanism and found the rate coefficient for the primary radical attacking a monomer molecule was slightly greater than that for a primary radical attacking backbone polymer.

Cameron and Quereshi studied the grafting reaction of styrene onto polyisoprene (PIP) in benzene solution at 60^{o}C [23,24]. They found that the proportion of polystyrene incorporated as graft was independent of the initiator (benzoyl peroxide) concentration. The graft fraction of polystyrene, which was higher than in the corresponding styrene-polybutadiene system, reflected the higher reactivity of PIP toward radicals. Azobisisbutyronitrile produced no graft copolymer in this system. The difference between the polydienes could be attributed to the methyl side groups in PIP, which made the polyisoprenyl radical somewhat more stable than the corresponding polybutadienyl radical. The two methylene groups in the isoprene residue were not equivalent and it seemed likely that the attack occurs preferentially at carbon 4 so that the methyl group could exert the greatest stabilizing influence on the resulting allylic radical. The preference for initiator attack on the rubber in PIP-styrene systems explained why grafting was more efficient in this case than with polybutadiene, (PBD). The greater reactivity of PIP compared with PBD toward hydrogen atom abstraction was also reflected in the higher graft densities of the former.



$$\sim\underset{1}{CH_2}-\underset{2}{\overset{CH_3}{\overset{|}{C}}}=\underset{3}{CH}-\underset{4}{\dot{C}H}\sim \longleftrightarrow \sim\underset{1}{CH_2}-\underset{2}{\overset{CH_3}{\overset{|}{\dot{C}}}}-\underset{3}{CH}=\underset{4}{CH}\sim \qquad (1.3)$$

Manaresi et al. grafted styrene onto polybutadiene in bulk at 100°C containing α-dicumyl peroxide as initiator [25]. They also proposed a mechanism and mentioned that the grafting was likely to occur by primary radical attack on polybutadiene, but the chain transfer reaction between polystyryl radicals and polybutadiene could not be neglected at this high reaction temperature. They reported that the rate coefficient for the primary radical attacking backbone polymer was greater than that of the primary radical attacking the monomer molecule.

Huang and Sunberg have studied grafting reactions of three-vinyl monomers-styrene, benzyl methacrylate, and benzyl acrylate onto *cis*-polybutadiene [26-29]. They show that benzoyl peroxide, PBO, is a more effective initiator for graft copolymerization than is azobisisbutyronitrile, AIBN, for styrene and benzyl methacrylate but that both initiators are about equally efficient for benzyl acrylate. They postulate, in agreement with previous workers (Brydon et al. [21,22] and Cameron and Qureshi [23,24]), that BPO functioned by removal of an allylic hydrogen atom. The efficiency of grafting of benzyl acrylate initiated by AIBN suggested that this reaction occurred by addition across the double bond.

Estenoz and Meira theoretically estimated the detailed molecular macrostructure of the polymer mixture (including branching and crosslinking) generated in a solution polymerization of styrene in the presence of polybutadiene [30]. Their analysis was limited to termination by recombination and graft site initiation via primary radical attack onto the backbone polymer.

Lenka et al. studied the grafting reaction of methyl methacrylate onto natural rubber using redox system [31-33]. The free radicals ($\mathrm{R}^{\bullet}$) might interact with the natural rubber molecule (NR) producing rubber macroradical which initiates grafting. The details of the mechanism are given below.

Initiation:

$$\begin{aligned} \mathrm{NR} + \mathrm{R}^{\bullet} &\xrightarrow{k_i} \dot{\mathrm{N}}\mathrm{R} + \mathrm{RH} \\ \dot{\mathrm{N}}\mathrm{R} + \mathrm{M} &\xrightarrow{k_i'} \mathrm{NR}{-}\mathrm{M}^{\bullet} \end{aligned} \tag{1.4}$$

Propagation:

$$\begin{aligned} \mathrm{NR}{-}\mathrm{M}^{\bullet} + \mathrm{M} &\xrightarrow{k_p} \mathrm{NR}{-}\mathrm{M}^{\bullet}_{1} \\ &\vdots \\ \mathrm{NR}{-}\mathrm{M}^{\bullet}_{n-1} + \mathrm{M} &\xrightarrow{k_p} \mathrm{NR}{-}\mathrm{M}^{\bullet}_{n} \end{aligned} \tag{1.5}$$

Termination:

$$\mathrm{NR}{-}\mathrm{M}^{\bullet}_{m} + \mathrm{NR}{-}\mathrm{M}^{\bullet}_{n} \xrightarrow{k_t} \text{Graft Copolymers} \tag{1.6}$$

Eyiegbulam and Aloka investigated the grafting of methyl methacrylate onto natural rubber in MEK/Toluene solution [34]. The dependence of grafting efficiency and graft level on the concentrations of methyl methacrylate and initiator and also the influence of the grafting characteristics on the hydrodynamics of the graft in MEK/toluene were studied. The grafting efficiency decreased with increasing reaction time and was weakly affected by the temperature of polymerization, and decreased with an increase in the monomer/polymer ratio. An increase in the concentration of methyl methacrylate decreased both the graft level and grafting efficiency but increased the molecular weight of the copolymer. However, an increase in the concentration of benzoyl peroxide initiator decreased the graft level.

. As mentioned previously, extensive R & D in the synthesis of graft copolymers is radiation-induced, specifically in emulsion systems. Grafting efficiencies are high in these systems with little or no homopolymer formation providing an attractive method to synthesize branched copolymers. The graft copolymerization can be initiated by three different types of direct irradiation. The mechanism for the formation of the graft copolymer is generally the same for all types of radiation: α, β, γ or x-ray, since exposure to these various sources results in the formation of free radicals.

Organic molecules with appropriate structures can absorb energy during irradiation, with visible or ultraviolet light, to be raised to be in excited state. This energy-rich molecule can either dissociate into reactive free radicals or dissipate its energy by fluorescence, phosphorescence, or collisional deactivation. For a polymer, the former process can lead to the formation of free radical sites on the polymer backbone, which can be used to initiate block and graft copolymerization in the presence of vinyl monomers. If none of the bonds in the polymer are ruptured by the radiation, the process can be promoted by the addition of photosensitizers. Upon absorption of UV or visible energy, a photosensitizer itself can decompose into active radicals or can transfer its energy to other molecules in the system, thereby promoting the copolymerization reaction. Aliphatic ketones are useful photosensitizers.

Graft copolymerization by photochemical initiation has been extended to emulsion systems by Cooper et al. [35-37]. In spite of the fact that natural rubber latex is practically opaque to ultraviolet light, good yields of graft copolymer were obtained using 1-chloranthroquinone as the photosensitizer. The rates of copolymerization and the efficiencies of grafting were dependent upon the photosensitizer used. The initiation reactions of graft copolymerization are:

$$\mathrm{R} + \gamma \quad \text{--------->} \quad \mathrm{R}^{\bullet} \tag{1.7}$$

and

$$\mathrm{P} + h\nu \quad \text{--------->} \quad \mathrm{P}^{\bullet} \tag{1.8}$$

$$\mathrm{R} + \mathrm{P}^{\bullet} \quad \text{--------->} \quad \mathrm{R}^{\bullet} \tag{1.9}$$

$$\mathrm{R}^{\cdot} + \mathrm{M} \quad \text{--------->} \quad \mathrm{P}_r^{\bullet} \tag{1.10}$$

where R refers to rubber, P to photosensitizer, and M to monomer.

Cooper et al. also proposed a mechanism for these high levels of grafting with minimal homopolymer formation. The reaction rate constant for termination is much greater than that for propagation.

Cockbain et al. studied the grafting of methyl methacrylate onto natural latex using Co-60 γ-irradiation [38]. This latex was compared to an analogous system initiated by a redox catalyst. The investigation involved the evaluation of both the colloidal and film-forming properties. It is interesting to note that the loci of the graft copolymer in the γ-irradiated system is throughout the particle, i.e., more uniformly distributed as opposed to the redox initiated system.

Various researchers have demonstrated that a seed emulsion polymerization of styrene, in the presence of polystyrene, is heterogeneous with regard to the distribution of monomer throughout the polymer particle. Grancio and Williams proposed a core/shell structure model on the basis of a kinetic study coupled with electron micrographs of ultrathin sections of the latex particles [39-40]. The model of the seeded emulsion polymerization consisted of a polymer-rich core, expanding as a function of the degree of conversion and sheathed by a monomer-rich shell. The monomer-rich shell was considered to be the main locus of polymerization. This model was verified by conducting a seeded polymerization of a polystyrene latex in the presence of styrene and butadiene monomer and an electron microscope study. The encapsulation theory proved correct, since doughnut shape morphology was evident as showed by the micrographs [40].

From the study of a variety of monomer-polymer latex systems by Keusch and Williams [41] and Keusch et al. [42], they found that even particles under a state of equilibrium saturation with monomer exhibited two distinct regions within the particles. The heterogeneous system consisted of a monomer-rich shell surrounding a polymer-rich core. Experiments, similar to those of Grancio and Williams [39,40], were conducted employing a three-stage emulsion polymerization process with a trace of butadiene in the monomer in stage 1 and 3. Conditions of equilibrium saturation were achieved in the second and third stage. Microtoming and use of the OsO_4 staining technique of a particle, embedded in epoxy and sliced though the center, depicted the concentric halos, corresponding to each stage of the emulsion polymerization.

Wessling and Gibbs studied the kinetics of seeded emulsion polymerization, for both swelling and non-swelling latex particles, in order to determine the locus of polymerization [43]. The systems investigated were polyvinylidene chloride (non-swelling due to crystallization) and vinylidene chloride-butyl acrylate copolymers (swellling). The kinetic study suggested the polymerization on the periphery of the particles (surface model) to account for the growth of polyvinylidene chloride particles, since vinylidene chloride had a low solubility in the aqueous phase and in its polymer. In this model, the monomer was adsorbed on the surface of the particle, where the site of polymerization is believed to be. Weiner also found that polyvinylidene chloride latex particles adsorb varying amounts of monomer dependent upon the radius of the particle [44].

Gasperowicz et al. investigated the grafting of styrene onto poly(butyl acrylate) in emulsion form [45]. The parameters investigated in relation to the degree of monomer conversion and the grafting efficiency of polystyrene were: time, temperature, the concentration of initiator and emulsifier and the monomer/polymer ratio. The grafting efficiency decreased with increasing time of reaction, was weakly affected by the temperature of polymerization, and decreased with an increase in the monomer/polymer ratio. The grafting efficiency decreased with increasing initiator concentration, although, within the concentration range studied, a maximum grafting efficiency was observed.

Beati and Pegoraro investigated the emulsion polymerization of butadiene and subsequent grafting of methyl methacrylate [46]. In the polymerization of butadiene, two radical initiators were used, namely azobisisobutyronitrile (AIBN) and $(NH_4)_2S_2O_8$. The ratio between the two initiators did not affect the structure of the polybutadiene. During the seeded emulsion polymerization, it was found that, when the water-soluble initiator (potassium persulfate) was used, the grafting efficiency was much lower than that when azobisisobutyronitrile was employed. It was implied that methyl methacrylate was not capable of initiating the growth of the grafted chain by transfer, but occurs by the action of the initiator. On the other hand, Wetton [47] studying the grafting mechanism of methyl methacrylate onto polybutadiene in solution, as well as Dinges and Schuster [48], observed results to the contrary. Bevington reported that azobisisobutyronitrile was not capable of hydrogen abstraction [49]. The inability of azobisisobutyronitrile to abstract a methylene hydrogen, together with the absence of chain transfer from the polymethyl methacrylate radical, has prompted the authors to propose the most probable mechanism of graft copolymer formation. The mechanism involves the addition of the $CN\text{-}\dot{C}\text{-}(CH_3)_2$ radical derived from the initiator decomposition to the double bond of polybutadiene.

Beati and Pegoraro investigated the role of monomer diffusion through the polybutadiene latex and how this affected grafting. This was demonstrated by grafting MMA onto pregrafted polybutadiene latex in steps, carrying each polymerization to completion and the percent grafting was shown to decrease by a factor of two during the three steps. In all experiments, the polybutadiene/polymethyl methacrylate/initiator ratio was held constant. Therefore, polymethyl methacrylate is less chemically bound to the rubber chains upon increasing the number of seeding steps.

Cho and Lee investigated the changes in particle morphology for polymethyl methacrylate/polystyrene composite particle latex employing various seeded emulsion polymerization techniques; batch, batch-swelling (in-situ), and semi-batch [50]. The main factor, in controlling the particle morphology was the anchoring effect exerted by ionic terminal groups introduced by the initiator. Both oil soluble initiators, azobisisobutyronitrile (AIBN) and 4,4′-azobis-(4-cyanovaleric acid) (ABCVA), as well as a water-soluble initiator, $K_2S_2O_8$, were used in the seeded emulsion polymerization. The core/shell latex was observed by electron microscopy. The use of oil-soluble hydrophobic initiators gave rise to an inverted core/shell morphology, whereas the water-soluble hydrophilic initiator gave either halfmoon or sandwich-like morphology.

Sundberg et al. studied the grafting of styrene onto polybutadiene in batch and semi-continuous reactors [51]. The various factors, i.e. monomer/polymer (M/P) ratio, initiator level, degree of conversion and concentration of chain transfer agent governing grafting efficiencies of styrene onto polybutadiene latex were investigated. It was found that the grafting efficiency was invariant throughout the conversion range for a batch reactor for several levels of chain transfer agent. In a semi-continuous process, the grafting was found to be decreasing as a function of the degree of conversion; this was applicable for several levels of crosslinking agent. For both processes, the final level of grafting was virtually identical. The incorporation of chain transfer agent, carbon tetrachloride (CCl_4), was used to create more polymer chains of lower molecular weight, yielding lower grafting efficiencies. The mechanistic scheme included a chain transfer reaction to a chain transfer agent; this reaction was especially important in emulsion polymerization because the chain transfer agent was often used to prevent excessively high molecular weight, yielding lower grafting efficiencies. This trend was evident for the batch and semi-continuous processes. The grafting efficiency increased with temperature for both processes and the reaction rates changed significantly with variation in temperature, especially for a batch polymerization, whereas in a semi-continuous polymerization the reaction rate was restricted in part by the monomer feed rate. Furthermore, the major influence of temperature was that the actual concentration of monomer in the particle could be very low at higher temperatures. This indicates that the styrene/rubber ratio in the rubber phase may be very low throughout the entire reaction process, which should promote higher grafting efficiency. A compilation of the literature for a number of relevant graft copolymers prepared by the emulsion technique is provided in Table 1.1

By manipulation of numerous process parameters in emulsion polymerization, the particle morphology can be controlled. Seeded or multistage emulsion polymerizations are widely employed for the synthesis of structure or core/shell latex particles and can be used for preparing graft copolymers, which can increase the compatibility of two immiscible polymers. Increase in the fraction of graft polymer on the surface of the particle core improves the miscibility of graft polymer on the surface of the particle core with the polymer which forms the shell of particles. The polymerization of styrene with poly(butyl acrylate) (PBA) latex provides and example: the graft PBA/PS copolymer improves the miscibility and adhesion of the core to the shell [60]. Several investigators have suggested that phase separation, during the course of a seeded emulsion polymerization, leads to the development of confetti-like or raspberry-like particles. A number of researchers have observed the manifestation of differences in latex morphology for various polymer systems. O'Connor and Tsaur studied a two-stage system wherein styrene was polymerized in the presence of a poly(butyl acrylate-*co*-divinylbenzene) seed latex [61]. The morphologies obtained upon varying the monomer feed ratio, the seed particle size, and the amount of crosslinker in the seed latex were assessed.

"Core-shell" polymerization or more accurately, two-stage emulsion polymerization has been in use industrially for many years. By making latex particles in consecutive stages, many workers had assumed that a concentric "core-shell" structure would be obtained with the phase polymerized first as the "core" and the phase polymerized last as the "shell". However, it is now well known that such is not necessarily the case. The system is much more complex in reality, and many other

Table 1.1 Graft copolymers prepared by emulsion technique.

Graft copolymers	Reference	Comments
Natural *cis*-1,4-poly(isoprene-*g*-methyl methacrylate)	Cockbain [38]	Film-forming properties of product compared with graft made by chemical initiation
	Cooper and Vaughan [36]	Kinetics of graft reaction studied
	Cooper et al. [35,37]	Graft copolymers from natural rubber latex using high-energy radiation
poly[butadiene-*g*-(methyl methacrylate-*co*-styrene)]	Aerdts et al. [52]	Redox grafting, Effect of Emulsifier concentration and type of initiator
poly[(butadiene-*co*-styrene)-*g*-(methyl methacrylate-*co*-styrene)]	Zhao et al. [53]	Redox grafting, Effect of process parameters
Poly(butadiene-*g*-methyl methacrylate) poly[(butadiene-*co*-styrene)-*g*-methyl methacrylate]	Markel et al. [54]	Effect of composition and structure of the core material and crosslinking agent
Poly(butadiene-*g*-methyl methacrylate)	Markel et al.[55]	Effect of process parameters
Natural *cis*-1,4-Poly(isoprene-*g*-methyl methacrylate) Natural *cis*-1,4-Poly(isoprene-*g*- styrene) Natural *cis*-1,4-Poly(isoprene-*g*-methyl methacrylate-*g*-styrene)	Schneider et al. [56]	Morphological characterization of two-and three component natural rubber-based latex particles

Table 1.1 (continued)

Poly(butadiene-*g*-styrene)	Sundberg et al [51]	Kinetics of graft reaction in batch and semi-continuous reactor
Natural *cis*-1,4-poly(isoprene-*g*-methyl methacrylate)	Hourston and Romaine [57]	Grafting using an Amine-Activated Hydroperoxide, morphology reported
Natural *cis*-1,4-poly(isoprene-*g*-methyl methacrylate)	Perera [3]	A comparison of grafting using chemical initiation and high energy radiation, dynamic mechanical properties determined
Natural *cis*-1,4-poly(isoprene-*g*-styrene)	Tangboriboonrat and Tiyapiboonchaiya [58]	Effect of irradiation dose, rubber content and initiator concentration on the impact property and morphology
Natural *cis*-1,4-poly(isoprene-*g*-styrene)	Fukushima et al [59]	A comparison of grafting of styrene from highly deproteinised natural rubber

factors, as well as the order of addition of monomers, will determine the actual phase distribution in the final particles. The morphology of the particle formed in the presence of seed polymer particles also depends on the mode of polymerizations as reported by Min et al [60]. Okubo et al. reported the formation of a number of unusual latex particle morphologies using seeded emulsion polymerization, i.e. two-stage emulsion polymerization [62-66]. In one case, particles formed by polymerizing styrene in the presence of a PMMA seed latex appeared to contain "voids". Transmission electron microcopy showed the areas of low electron density which appeared as indentations in the particles. Other anomalous particle structures were described as "confetti-like" and "raspberry-like" both structures having many surface nodules giving the particle surface a very uneven appearance. The products obtained from some poly(butyl acrylate) seeded styrene polymerizations exhibited even more unusual morphologies which were dubbed "snowman-like" and "mushroom-like". In this case, the two different polymeric phases were almost completely separated into two distinct lobes. Min et al. also observed such phase-separated morphologies for poly(butyl acrylate)/polystyrene two-stage particles which they described as "dumbbell-shaped" [61], and Stutman et al observed an "acorn-like" morphology for the same system, both very similar to the "mushroom-like" morphologies reported by Okubo et al [67].

Lee and Ishikawa found that "inverted" particle structures could be obtained in which the second-stage polymer formed the core, surrounded by the first-stage polymer "shell" these inverted systems comprised a hydrophilic seed, a copolymer of ethyl acrylate and methacrylic acid, and a hydrophobic second-stage polymer, either styrene or a styrene-butadiene copolymer [68]. The inverted structures were visible in the transmission electron microscope using osmium tetroxide staining of the polybutadiene phase.

From these several examples, it is obvious that two-stage polymerization does not always yield true core-shell morphologies. In the literature, many examples of other phase arrangements like, eg., "raspberry-like", acorn-like", "sandwich-like", "poow", and inverted structured structures have been found [63-69]. These structures are represented schematically in Figure 1.

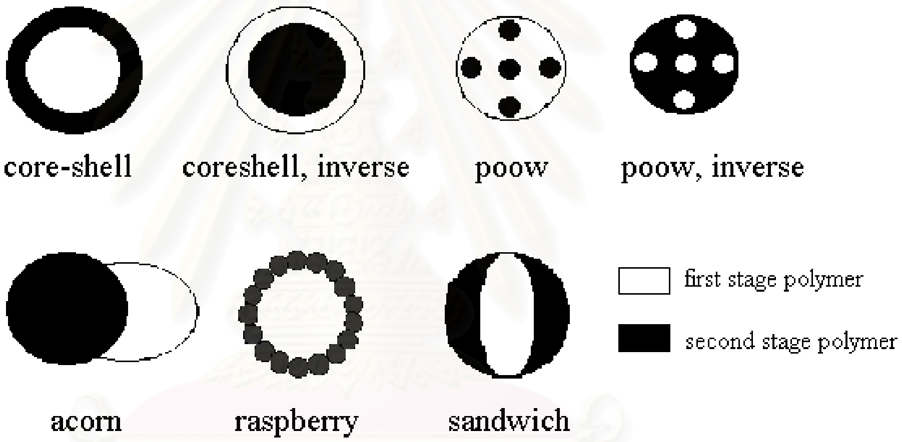


Figure 1.1 Schematic diagrams of various morphologies [56].

The various impact modifiers or toughening agents described in the literature are manufactured by many synthetic approaches and involve numerous chemical compositions. There are several important criteria, however, that must be kept in mind to obtain tough engineering polymers successfully, regardless of the type of elastomer used. These requirements are important for obtaining commercially viable blends useful for demanding engineering applications.

It is recognized that the toughened engineering composites are all multiphase systems that may contain several separate polymer domains in addition to the discrete elastomer particles that enhance blend toughness. Rubber particles need to adhere to the matrix for satisfactory stress transfer in most instances. The adhering rubber particles often need to be quite small, and uniformly distributed. Another requirement for rubber toughened polymers is that the rubber phase morphology must not change during melt processes, i.e. rubber particle size and distribution should remain unaltered. This is usually assured by crosslinking the rubber phase, such as in the core-shell impact modifiers. The use of chemically modified gum rubber involves more variables for achieving a stable, controlled morphology. To achieve improved impact strength at low temperatures the glass transition temperature of the elastomer must be well below the desired usable temperature.

There are many types of impact modifiers for PVC which are in industrial use. These are usually broken down into the following two main categories [70]:

1. Pre-Determined Elastomer Particle Size (PDE):

   This group includes methyl methacrylate-butadiene-styrene (MBS), acrylate-methacrylate (all-acrylic), and acrylate-butadiene-methacrylate (modified acrylic) modifiers. These impact modifiers form a microparticulate disperse phase in the PVC matrix. The particle size and shape depend on the particular modifier. Modifiers of this kind have restricted compatibility with PVC. The rubber particle size in MBS type modifiers used commercially for PVC varies from an average of less than 0.08-2.0 microns .An optimum rubber particle size of 0.2 microns has been reported for MBS modifier in PVC [2].

2. Not Pre-Determined Elastomer Particle Size (PDE):

The modifiers in this group are chlorinated polyethylene (CPE) and ethylene-vinyl acetate (EVA). The dispersion of a modifier of this type ranges from a continuous network interpenetrating the PVC matrix, to virtually a complete molecular blend. The interpenetrating network is often referred to as a "honeycomb" structure. The particle size and shape of EVA and CPE are not predetermined (as in MBS) but are established during processing.

1.3 Background

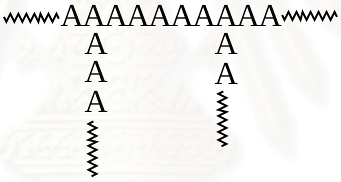
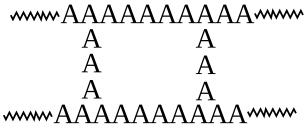
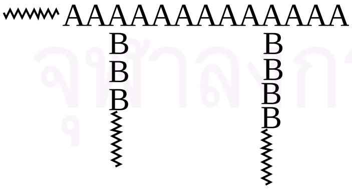
1.3.1 Graft Copolymerization

The type of polymerization process employed determines the structure of the resultant polymer. The structure of the macromolecule produced by homopolymerization is either linear, branched, or crosslinked. Copolymerization of two or more monomers yields four types of copolymer structure; graft, block, random, and alternating. The structures of various homo- and copolymers are depicted in Table 1.2.

Graft and block copolymers contain sequences of different monomeric units; a graft copolymer is branched with chains of monomer attached to a main chain based on another, while the block copolymer is linear. Usually, the synthesis of block and graft copolymers is a sequential process requiring a second or multiple step polymerization scheme.

A graft copolymer is a high polymer, the molecules of which consist of two or more polymeric parts, of different composition, chemically united together. A graft copolymer may be produced, for example, by polymerizing a given kind of monomer with subsequent polymerization of another kind of monomer onto the product of the first polymerization. The union of two different polymers by chemical reaction between their molecular end groups or by a reaction producing crosslinks between the different materials would also produce a graft copolymer.

Table 1.2 Structures of various homopolymers and copolymers [71].

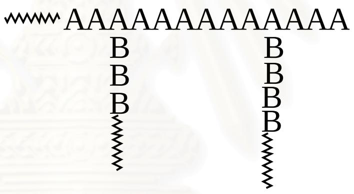
<table>
<tr><th colspan="3">Homopolymers</th></tr>
<tr><td><u>Linear</u></td><td><u>Branched</u></td><td><u>Crosslinked</u></td></tr>
<tr><td>∿∿∿ AAAAAAAAAAAA∿∿∿</td><td></td><td></td></tr>
<tr><th colspan="2">Copolymers</th></tr>
<tr><td><u>Graft</u></td><td><u>Block</u></td></tr>
<tr><td></td><td>∿∿∿AAAAAABBBBBB∿∿∿</td></tr>
<tr><td><u>Random</u></td><td><u>Alternating</u></td></tr>
<tr><td>∿∿∿ABAABABBBAABAA∿∿∿</td><td>∿∿∿ ABABABABABABAB∿∿∿</td></tr>
</table>

During a free radical graft copolymerization, monomer B is intended to be grafted onto backbone polymer A, but usually the final product of a graft copolymerization will contain the following three species [26]:

1. Homopolymer B which results from homopolymerization of monomer B.

2. Homopolymer A which is the original backbone polymer A not attacked by free radicals and therefore not involved in the graft copolymerization.

3. Graft copolymer which has graft of poly-B branching out from the backbone poly-A.



The graft efficiency was found depend on the following competing reaction:

1. Competition between monomer and backbone for the initiator radicals. When the benzoyl peroxide initiator radical attacks the rubber, it results in the formation of a rubber radical capable of initiating graft copolymerization.
2. Competition between monomer and backbone for the growing polymer radicals. The resulting rubber radical then needs to compete with polymer radicals for the monomer in order to form graft copolymers.
3. Competition between the various termination processes for the free polymer radicals.

The efficiency of the graft process will be effected by the mode of termination.

1.3.2 Mechanism of Grafting

The grafting of polymer in seed emulsion polymerization occurs on the entry of radicals from the aqueous phase into the polymer particle, where they add to a doudle bond or abstract hydrogen from the hydrocarbon chain.

If, in a system containing polymer P_r and growing chains of monomer M, chain transfer to P_r (i.e., abstraction of an atom such as H, or halogen, from P_r) occurs by the growing chains of M units, polymerization of the monomer can take please at these newly formed reactive sites. The product is a graft copolymer. The grafting mechanism is characterized by reaction (1.11)-(1.21) [25,30]:

Initiation:

Attacking monomer:

$$R^{\bullet} + M \dashrightarrow M^{\bullet}_{1} \tag{1.11}$$

Attacking rubber:

$$R^{\bullet} + P_r \dashrightarrow P_r^{\bullet} + RH \tag{1.12}$$

Re-initiation:

$$P_r^{\bullet} + M \dashrightarrow P_r\text{-}M^{\bullet}_{1} \tag{1.13}$$

Propagation:

Propagation of free polymerization:

$$M^{\bullet}_{1} + M \dashrightarrow M^{\bullet}_{2}$$

$$M^{\bullet}_{n} + M \dashrightarrow M^{\bullet}_{n+1} \tag{1.14}$$

Propagation of graft polymerization:

$$P_r\text{-}M^{\bullet}_{1} + M \dashrightarrow P_r\text{-}M^{\bullet}_{2}$$

$$P_r\text{-}M^{\bullet}_{n} + M \dashrightarrow P_r\text{-}M^{\bullet}_{n+1} \tag{1.15}$$

Chain-transfer:

Transfer to monomer:

$$M^{\bullet}_{n} + M \dashrightarrow M^{\bullet}_{1} + M_{n}$$

$$P_{r}\text{-}M^{\bullet}_{n} + M \dashrightarrow M^{\bullet}_{1} + P_{r}\text{-}M_{n} \tag{1.16}$$

Transfer to rubber:

$$M^{\bullet}_{n} + P_{r} \dashrightarrow P_{r}^{\bullet} + M_{n}$$

$$P_{r}\text{-}M^{\bullet}_{n} + P_{r} \dashrightarrow P_{r}^{\bullet} + P_{r}\text{-}M_{n} \tag{1.17}$$

Transfer to chain-transfer agent:

$$M^{\bullet}_{n} + RSH \dashrightarrow RS^{\bullet} + M_{n}$$

$$P_{r}\text{-}M^{\bullet}_{n} + RSH \dashrightarrow RS^{\bullet} + P_{r}\text{-}M_{n} \tag{1.18}$$

Termination:

Combination:

$$M^{\bullet}_{n} + M^{\bullet}_{m} \dashrightarrow M_{n+m}$$

$$P_{r}\text{-}M^{\bullet}_{n} + P_{r}\text{-}M^{\bullet}_{m} \dashrightarrow P_{r}\text{-}M_{n+m}\text{-}P_{r}$$

$$P_{r}\text{-}M^{\bullet}_{n} + M^{\bullet}_{m} \dashrightarrow P_{r}\text{-}M_{n+m} \tag{1.19}$$

Between rubber radicals:

$$P_{r}^{\bullet} + P_{r}^{\bullet} \dashrightarrow P_{r}P_{r} \tag{1.20}$$

Crossed termination:

$$P_{r}^{\bullet} + P_{r}\text{-}M^{\bullet}_{n} \dashrightarrow P_{r}\text{-}M_{n}\text{-}P_{r}$$

$$P_{r}^{\bullet} + M^{\bullet}_{n} \dashrightarrow P_{r}\text{-}M_{n} \tag{1.21}$$

where $R^{\bullet}$ is primary radical, M is vinyl monomer; $M^{\bullet}_{n}$ is vinyl polymer radical; P_{r} is rubber, $P_{r}^{\bullet}$ is macromolecule radical; and $P_{r}\text{-}M^{\bullet}_{n}$ is the growing graft copolymer radical chain; and RSH is the chain-transfer agent, mercaptan.

1.3.2.1 Radical Attack on Macromolecules by Transfer Mechanisms [19,72]

In general, during free-radical initiated polymerizations of ethylenic or vinyl monomers, (e.g. methyl methacrylate,) transfer reactions may take place between the growing polymer radical, monomer, dead polymer, or to a growing polymer radical, equation (1.16)-(1.18)

In each of these generalized mechanisms, the reaction proceeds by transfer of a hydrogen or halogen atom from the transfer molecule to the growing polymer chain. The growing chain is therefore terminated but the free-radical activity is transferred to the growing polymer chain. The growing chain is therefore terminated but the free-radical activity is transferred to the molecule donating the hydrogen or halogen atom. In this way a number of polymer chains form with each initiator fragment and each chain so formed has a reduced chain length compared to that which would have been formed in the absence of the chain-transfer reaction. During graft copolymerization with natural rubber, it is chain transfer to rubber, (equation (1.17),) which is of particular importance in the synthesis of graft copolymers by the transfer reaction.

A chain transfer reaction is characterized by a chain transfer constant, representing the ratio of the velocity constant for transfer of the chains to that for their growth. The role of chain transfer through the polymer is enhanced by a rise in temperature since the energy of activation of the chain transfer reaction is greater than that of growth reaction. The rate of chain transfer also depends on the polymer:monomer ratio, the lability of the atom being detached, the reactivity of the polymer radical, the type of initiator and the concentration used, as well as the chemical nature of the polymer and monomer (which determines their polarity and reactivity). The presence of steric hindrance is also an important factor, which influences the efficiency of the grafting reaction.

1.3.2.2 Radical Attack on Unsaturated Macromolecules [19,72]

Graft copolymers may be formed when vinyl monomers are polymerized in the presence of macromolecules containing double bonds. As natural and synthetic rubbers are the most typical representatives of polymers containing double bonds in the chain it is not surprising that the majority of the published literature on addition copolymerization techniques deals with “rubber” systems.

The initiator effect plays an important role for the successful grafting to rubber backbones. Allen et al. found that good yields of methyl methacrylate-rubber graft copolymers were obtained by the use of benzoyl peroxide initiator, while azobisisobutyronitrile (AIBN) produced only a mixture of homopolymer [20]. The cause of this specific initiator effect and the mechanism of the graft polymerization was determined by using ^{14}C-labeled initiators. It was found that benzoyl peroxide initiated grafting by prior reaction of the derived phenyl and benzoyloxy radicals with the poly(isoprene). This occurred by addition to double bond (equation 1.2) and by abstraction of the α-methylenic hydrogen atoms (equation 1.1) to give poly(isoprenic) alkyl and alkenyl radicals, respectively. The latter then act as loci for methyl methacrylate polymerization. The inability of AIBN to initiate graft polymerization was attributed to the markedly inferior capacity of the resonance stabilized $CN\text{-}\dot{C}\text{-}(CH_3)_2$ radicals, relative to $C_6H_5^{\bullet}$, and $C_6H_5COO^{\bullet}$’ to engage in double bond addition and hydrogen abstraction reactions.

Addition copolymerization of monomers with polymeric systems containing “residual” double bonds has also been employed as a method for graft copolymer synthesis. Although addition copolymerization reactions take place at lower temperatures and polymer concentrations than those needed for the chain transfer reaction, the process is often complicated by gel formation and chain transfer reactions. Except when the double bonds are in the terminal position (as, for example, with disproportionated polymers) this may arise as a result of the activation of hydrogen atoms in the α-position in double bonds in the main chain.

1.3.3 Macromolecular Free Radical Initiators Systems [73]

The initiators used in emulsion polymerization are water-soluble initiators such as potassium or ammonium persulfate, hydrogen peroxide, and 2,2′ -azobis(2-amidinopropane)dihydrochloride. Partially water-soluble peroxides such as succinic acid peroxide and t-butyl hydroperoxide and azo compounds such as 4,4′ -azobis(4-cyanopentanooic acid) have also been used. Redox systems are advantageous in yielding desirable initiation rates at temperatures below 50°C. Other useful redox systems include cumyl hydroperoxide or hydrogen peroxide with ferrous sulfite or bisulfite ion.

The redox activation hydroperoxide groups have a number of advantages over thermal activation. Redox polymerization is the basis of the majority of commercial processes for grafting monomers onto natural rubber. It is because of the general freedom from homopolymer formation from the copolymerizing monomer that this method is the one most widely used for grafting vinyl monomers to an extensive range of polymeric substrates.

1.3.3.1 Hydroperoxide-Iron Systems

Initiation systems comprising organic hydroperoxides and iron(II) salts have extensively been used for the low-temperature emulsion copolymerization. The radical-forming reaction is usually given as

$$\mathrm{ROOH} + \mathrm{Fe}^{2+} \text{ --------->} \quad \mathrm{RO}^{\bullet} + {}^{-}\mathrm{OH} + \mathrm{Fe}^{3+} \qquad (1.22)$$

Initiation occurring by way of the alkoxy radical. The system is capable of great diversification because of (a) the wide range of organic hydroperoxides which is available; (b) the possibility of controlling the availability of iron(II) ions by using preformed complexes or alternatively very insoluble iron(II) salts; (c) the possibility of adding other components to the system, such as reducing sugars, alcohols, thiols, glycols, aldehydes, and amines. It should be noted that the hydroperoxide will generally partition mainly in the non-aqueous phases of the system, whereas the iron compound will be confined to the aqueous phase. This feature provides additional control over the rate at which initiating radicals are produced through limitation of the rate at which the two components of the couple are brought together.

If a reducing agent is also added to the system, then the function of the iron(II) compound can be viewed as that of a catalyst which promotes interaction between hydroperoxide and the reducing agent. The hydroperoxide oxidises the iron(II) ions in accordance with reaction (1.22), thereby producing alkoxy radicals which initiate polymerization. The iron(III) ions thereby produced in turn oxidise the reducing agent, being themselves reduced to iron(II) ions once again.

1.3.3.2 Hydroperoxide-Polyamine Systems

The presence of appreciable quantities of iron in the eventual polymer is undesirable for at least two reasons: (a) it may cause discoloration and (b) it may catalyze oxidative degradation of the polymer. For these reasons, endeavors have been made to develop alternative activation system for hydroperoxides, which are nominally iron-free. Of the several systems, which have been investigated, the one which has received most attention is that which uses aliphatic polyamines as activator.

It appears that little is known regarding the precise chemistry of the hydroxide-polyamine system. However, it is possible to write a plausible radical-generating reaction as follows:

$$ROOH + R'NH_2 \text{ --------->} \quad RO^{\bullet} + R'NH^{\bullet} + H_2O \qquad (1.23)$$

1.3.4 Natural Rubber Latex

Depending on the origin and method of preparation, latex can be divided into three categories: natural latex, synthetic latex and artificial latex. The birth of natural rubber (NR) dates back to the fifteenth century when Columbus first reported that he had been intrigued on his journey through the New World. Raw NR, as supplied by plantations, always contains, in addition to rubber hydrocarbons, a certain amount of impurities, which also precipitate out in the coagulum of the latex. The amount of these impurities depends somewhat on the processing condition.

Natural rubber tree species of *Hevea brasiliensis* produces latex, which is a form of polymer in the colloid system. Fundamental characteristics of latex are usually found in the content of rubber, particle shape, size and particle size distribution. Kovuttikulrangsie and Tanaka found that the age of young Natural Rubber Hevea trees has an influence on the size of latex particles [74]. NR latex particles, obtained from trees which are 1 to 7 years old have an average particle size distribution of about 0.30 to 0.65 μm. The average molecular weight ($\overline{M}_w$) dramatically increased from 3.3×10^5 to 12.0×10^5. The polydispersity ($\overline{M}_w/\overline{M}_n$) or molecular weight distribution of rubber was remarkably wide, between 3 and 10. Different regular mature trees, 25-years-old, presented mode average particle sizes of about 1.0 μm. The average molecular weight ($\overline{M}_w$) was from about 6.7×10^5 to 3.0×10^6 and the polydispersity ($\overline{M}_w/\overline{M}_n$) was extremely extensive between 5 and 11.

It is well recognized that a proportion of any commercial unmilled *Hevea* rubber is insoluble in rubber solvents, this portion being termed the gel phase. Much work on the properties of this phase was done over several decades ago. The gel content varied with the source and type of rubber and depended on the nature of the solvent. If the gel phase is a simple crosslinked network, it should be insoluble in all the good solvents. The gel phase, which is partially soluble in some solvents, is also sometimes termed as soft-gel and recognized as one that cannot be a simple crosslinked network, but must have a more complex structure. The gel component in synthetic *cis*-1,4-polyisoprene is certainly a crosslinked rubber, arising from side-reactions during polymerization and does not possess a phase such as that which is present in NR.

Rubber from fresh field latex is normally completely soluble in rubber solvents, provided that the tree is regularly tapped. However, commercially available high-ammonia latex (HA-latex) contains a lot of the gel phase. This demonstrates that some degree of crosslinking might have occurred in HA-latex after or during storage. It has been hitherto believed that branching in NR originated from the abnormal groups such as aldehyde, epoxide and lactone group. However, it has been elucidated that these abnormal groups in NR are not major factors for branching and gel formations. The branch-points in NR are classified into two types: (1) branchings due to proteins, which are easily broken down by enzymatic deproteinisation; and (2) branchings originated from long-chain fatty acids and or phospholipids. Li, et al.

studied the dynamic variation of molecular structure and properties of natural rubber during accelerated storage [75]. The results showed that with prolonging of the storage time, the average molecular weight and the gel content increased, with the index of molecular weight distribution having decreased, the gel size increased gradually.

The main component of the natural rubber molecule is *cis* polyisoprene hydrocarbon. Structurally, this natural polymer is more complicated than its synthetic analogue due to the presence of a small quantity of non-rubber groups, normally referred to as abnormal groups, bonded to the main-chain molecule. These groups are believed to be of biological significance in the biosynthesis of rubber.

It is now generally accepted that crosslinking reactions of the normal groups are the major cause for the formation of branching in natural rubber. These branching entities eventually lead to the formation of gel and the occurrence of storage hardening of natural rubber, which distinguishes it from the synthetic *ci*s polyisoprene. The formation of gel during storage of dry rubber may involve a mechanism, which is different from that of microgel in latex, because the former is accelerated under low humidity conditions while the latter occurs in the aqueous medium.

Despite many years of investigation carried out by various workers, the mechanism for the gel formation has yet to be conclusively explained. Nevertheless, several abnormal groups have been reported to be present in the main-chain of the rubber polymer and these are summarized in Table 1.3

Recent advances have resulted in the production of NR-modified specialty rubbers as well as blends comprised of natural rubber and other polymers. Examples are Deproteinized Natural Rubber and Epoxidized Natural Rubber in addition to the more established specialty rubbers like Methacrylate grafted Natural Rubber (MG)

Table 1.3 Abnormal groups in natural rubber [76].

Groups	Fractions	Concentation mmol kg^{-1}
Fatty acids	Low Mw	10-12
Lactone	Gel	10-15
Aldehyde	Whole	10-35
		1.5-5.0
Amine	Whole	20-35
Epoxide	Whole	45-75
		10-15

and Superior Processing Natural Rubber (SP). New rubbers currently in the development pipeline are Liquid Natural Rubber and the Thermoplastic Natural Rubber. The new strategic thinking in the development and production of NR-based blends is to combine existing polymers to exploit their different, but complementary, properties rather than depend solely on discovering new or modified NR based polymer.

1.4 Scope of Thesis

The aim of this research work is to reveal the importance of the impact modification of core-shell latex particle for PVC blend, the graft copolymers of styrene and methyl methacrylate onto natural rubber, which can be expected to have better impact resistant properties. Before this work began, the graft copolymerization had been investigated for several years and several works had been carried out. In order to better understand the graft copolymerization of vinyl monomer onto diene-based polymers. The purpose of this research was to synthesize the graft copolymers of vinyl monomer onto of styrene and methyl methacrylate onto natural rubber, polybutadiene, and butadiene-styrene copolymers latex using redox initiator. A study of graft copolymerization is contained herein which investigates the process parameters affecting the grafting reaction in seeded emulsion polymerization. As mentioned in the Introduction, since numerous graft copolymers have been reported to be used effectively as a impact modifier for polymer blends; it was of interest to determine whether the graft copolymers synthesized here could offer improved impact resistance for PVC blends. The final phase of this thesis provides information on blends of graft copolymers with PVC and the impact resistance of such blends.

In this thesis the synthesis of graft copolymers, used as a impact modifier for PVC will be described. Chapter 1 of this thesis contains a review of relevant literature. The focus of grafting of vinyl monomers onto polydiene-based polymers synthesis, effects of process parameters, and mechanism were included.

In Chapter 2 the experimental methods used for synthesis of the graft copolymers of methyl methacrylate and styrene onto natural rubber by using cumene hydroperoxide/sodium formaldehyde sulfoxylate dihydrate/EDTA-chelated Fe^{2+} as a redox initiator are outlined. The effects of the process factors such as the amount of initiator, emulsifier and chain-transfer agent, monomer-to-rubber ratio, and temperature on the grafting efficiency (GE) are investigated.

In Chapter 3, the six reaction variables which were identified as important to graft copolymerization of methyl methacrylate and styrene onto natural rubber by using cumene hydroperoxide/tetraethylenepentamine as a redox initiator are considered and a detailed, experimental design is presented. The results of two fractional factorial designs of the effect of process parameters on the grafting presented in this chapter provides improved process understanding and establishes the basis for the experiments which were carried out to synthesize graft copolymers of methyl methacrylate and styrene onto polybutadiene, and poly(butadiene-*co*-styrene) latex reported in Chapter 4.

In Chapter 5, the results of mechanical properties of the blends of graft copolymers with PVC are presented. Four levels of selected graft copolymers loading in the PVC formulation were studied; 5, 8, 10, and 15 phr. The measurements of tensile strength and impact resistance for blend are also reported.

Important conclusion regarding the finding of this thesis and recommendation for future work are provided in Chapter 6.

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CHAPTER 2

GRAFT COPOLYMERS FROM NATURAL RUBBER USING CUMENE HYDROPEROXIDE/SODIUM FORMADEHYDE SULFOXYLATE/EDTA-CHELATED Fe^{2+} REDOX INITIATOR

2.1 Introduction

The chemical modification of natural rubber by grafting with vinyl monomers using various initiator systems has gained considerable importance in modifying the properties of natural rubber [1-4]. It is well known that the introduction of a small amount of compatibilizer can lead to major changes in mechanical properties. It has been reported that graft copolymers can be used effectively as a compatibilizer for polymer blends [5,6]. For natural rubber, research has confirmed that methyl methacrylate and styrene are the most suitable monomers when polymerized to give a high level of grafting [7]. Graft copolymers are produced when vinyl monomers are attached to the backbone unsaturation in natural rubber through carbon to carbon bonds. Enyiegbulum and Aloka reported that graft copolymers of natural rubber and methyl methacrylate were produced by polymerizing methyl methacrylate in a toluene solution using benzoyl peroxide initiator, whereby an increase in concentration of both methyl methacrylate and initiator resulted in a decrease of grafting efficiency (GE) [8]. Lenka et al. reported that the graft copolymerization of methyl methacrylate onto rubber using potassium peroxydisulfate catalyzed by silver ion was temperature-dependent [9]. A number of reports [10-13] have appeared on grafting of vinyl monomers such as methyl methacrylate, styrene, or styrene/methyl methacrylate onto natural rubber latex particles using a redox initiation system. The effect of grafting efficiency on the material morphology has been studied using transmission electron microscopy and dynamic mechanical analysis [14,15].

Synthesis of graft copolymers from natural rubber has been carried out in solution, solid rubber, and latex phases; however, the most economical and practical method is possibly latex modification [15]. Latex particles with a soft core and a hard shell are modified as impact modifiers, whereas particles with a hard core and a soft shell are usually used in the coating and adhesive fields [16]. The graft copolymer of vinyl monomers such as styrene and methyl methacrylate onto natural rubber, comprising an inner soft polymer sphere, the “core” and an outer hard polymer the “shell” can be expected to have better impact-resistance properties. Even though the formation of particles may be carried out in two continuous stages, a core-shell structure does not necessarily occur. The phase separation, during the course of a seeded emulsion polymerization, leads to a variety of particles of different phase structure, e.g., “raspberry-like”, “acorn-like”, “sandwich-like” and “inverted” structure [17].

The purpose of this work was to investigate the influence of the process factors on the graft copolymerization; such as initiator, amount used in the secondary polymerization, polymerization temperature, the amount of emulsifier and chain-transfer agent, and monomer-rubber ratio on the grafting level (GL) and grafting efficiency (GE). The grafting of styrene and methyl methacrylate onto natural rubber (NR) latex particles was carried out using the cumene hydroperoxide/ sodium formaldehyde sulfoxylate dihydrate/ EDTA-chelated Fe^{2+}, redox initiation system. The redox initiation system produces radicals that can be used to initiate polymerization, occurring either on the natural rubber backbone or on the monomer to be grafted. The radical formation on the monomer results in homopolymerization. However, initiators capable of creating radicals at various sites on the natural rubber backbone are preferred. The redox initiation system significantly favored grafting, limiting the scope for formation of ungrafted (or free) copolymers of the monomer mixture, thus providing improved grafting efficiency. Initiation systems comprising organic hydroperoxides, reducing agent and iron chelate of EDTA redox initiator have been extensively used at moderate temperature and gave high yields of grafting in the emulsion polymerization. The hydroperoxide oxidizes the iron (II) ions, thus introducing alkoxy radicals that initiate polymerization. The iron (III) ions also produced in turn oxidize the reducing agent, being themselves reduced to iron (II) ions once again [18].

2.2 Experimental

2.2.1 Materials

Natural rubber latex used was 60% dry rubber content (DRC), commercial high-ammonia natural rubber latex. Reagent grade styrene (Aldrich, purity ~99%) and methyl methacrylate (Aldrich, purity ~99%) monomer were purified by washing with 10% sodium hydroxide solution to remove inhibitor, followed by deionized water and by distillation under reduced pressure. The chain-transfer agent n-dodecyl mercaptan (nDM, Aldrich), the emulsifier sodium dodecyl sulfate (SDS, Aldrich, purity ~98%), the stabilizer isopropanol, the buffer potassium hydroxide (KOH, Aldrich), the initiators, the water soluble initiator; potassium persulfate ($K_2S_2O_8$, KPS, Fluka, p.a.) or the oil soluble initiator, cumene hydroperoxide ($C_9H_{12}O_2$, CHPO, Aldrich, purity ~80%) in combination with a redox system, the reducing agent sodium formaldehyde sulfoxylate ($CH_3NaO_3S\cdot2H_2O$, SFS, Aldrich), iron (II) sulfate heptahydrate ($FeSO_4\cdot7H_2O$ Fluka, purity ~98%) and ethylenediamine tetraacetic acid (EDTA, Aldrich) were used as received. Deionized water was used throughout the work. A solution was made of SFS, $FeSO_4$, and EDTA as well, all in oxygen free water at pH 4, as described by Prince and Spitz [19]. The ratio of the components in the redox system added, CHPO/SFS/EDTA-chelated Fe^{2+}, was 1.0/1.0/0.08 (w/w/w), giving reasonable polymerization rates at low temperature [20].

2.2.2 Preparation of Grafted Natural Rubber

The graft polymerization was conducted in a 1-L, four-necked glass reactor, equipped with a four-curved blade impeller, condenser, and thermometer. NR latex and an aqueous solution of additives were charged to the reactor and the dissolved oxygen in the ingredients was removed by purging nitrogen gas for at least 30 min through the mixture, providing still a stable latex. If necessary, buffer was added to maintain the pH of the system at 10. The monomer mixture with mercaptan was fed to the reactor. The solution of SFS and EDTA-chelated Fe^{2+} were added. The NR seed latex was swollen with the monomer mixture for 1 h at reaction temperature before adding the initiator. The polymerization reaction condition used the stirring speed of 200 rpm and the reaction time of 8 h with reflux. The polymerization temperature was maintained using a constant-temperature water bath and for polymerization runs, the 50:50 (w/w) monomer mixture of styrene and methyl methacrylate was kept constant. The product latex was discharged into boiling water containing 5% formic acid and the polymer product precipitated. The product was washed with deionized water. The gross polymer was recovered and dried to constant mass in a vacuum oven at 40^{o}C.

The recipes and variable factors for the graft copolymerization are shown in Table 2.1 and Table 2.2.

Table 2.1 Graft copolymerization recipes (in parts by weight).

Ingredients	Weight (g)
Water	100
Natural rubber latex	50
Potassium hydroxide	0.12
Isopropanol	3

2.2.3 Product Characterization

2.2.3.1 Soxhlet Extraction

Ungrafted natural rubber was washed out in a soxhlet extractor using 60-80^{o}C boiling point petroleum ether for 24 h. The residue was dried to constant weight in an oven at 40^{o}C under vacuum for 24 h. To remove free copolymers, the residue was extracted in a methyl ethyl ketone (MEK)/acetone (50:50 v/v) mixture just as described when petroleum ether was used. The weight difference between the initial sample and extracted samples are the measure of free rubber, free copolymers, grafting efficiency, and grafting level.

In this system, there are many components in the gross polymer sample. Ungrafted poly(methyl methacrylate) (PMMA), polystyrene (PST), and poly(styrene-*co*-methyl methacrylate) (P(ST/MMA)) and ungrafted natural rubber is referred to as free copolymers and free rubber, respectively. Grafted copolymers are referred to as NR-g-PMMA, NR-g-PST, and as NR-g-P(ST/MMA).

Table 2.2 Parameters of various experiments.

Experiment	Type of initiator	Initiator (phr)	Temperature (°C)	nDM (phr)	Emulsifier (phr)	Monomer/ Rubber
GNR01	CHPO/EDTA-Fe^{2+}/SFS	1.5	70	0	1.5	1:1
GNR02	CHPO/EDTA-Fe^{2+}/SFS	0.5	70	0	1.5	1:1
GNR03	CHPO/EDTA-Fe^{2+}/SFS	1.0	70	0	1.5	1:1
GNR04	CHPO/EDTA-Fe^{2+}/SFS	2.0	70	0	1.5	1:1
GNR05	CHPO/EDTA-Fe^{2+}/SFS	2.5	70	0	1.5	1:1
GNR06	CHPO/EDTA-Fe^{2+}/SFS	1.5	50	0	1.5	1:1
GNR07	CHPO/EDTA-Fe^{2+}/SFS	1.5	60	0	1.5	1:1
GNR08	CHPO/EDTA-Fe^{2+}/SFS	1.5	80	0	1.5	1:1
GNR09	CHPO/EDTA-Fe^{2+}/SFS	1.5	70	0.5	1.5	1:1
GNR10	CHPO/EDTA-Fe^{2+}/SFS	1.5	70	1.0	1.5	1:1
GNR11	CHPO/EDTA-Fe^{2+}/SFS	1.5	70	1.5	1.5	1:1
GNR12	CHPO/EDTA-Fe^{2+}/SFS	1.5	70	0	0.5	1:1
GNR13	CHPO/EDTA-Fe^{2+}/SFS	1.5	70	0	1.0	1:1
GNR14	CHPO/EDTA-Fe^{2+}/SFS	1.5	70	0	2.0	1:1
GNR15	CHPO/EDTA-Fe^{2+}/SFS	1.5	70	0	1.5	0.75:1
GNR16	CHPO/EDTA-Fe^{2+}/SFS	1.5	70	0	1.5	1.25:1
GNR17	CHPO/EDTA-Fe^{2+}/SFS	1.5	70	0	1.5	1.50:1
GNR18	KPS	1.5	70	0	1.5	1:1
GNR19	KPS	1.5	70	0.5	1.5	1:1
GNR20	KPS	1.5	70	1.0	1.5	1:1

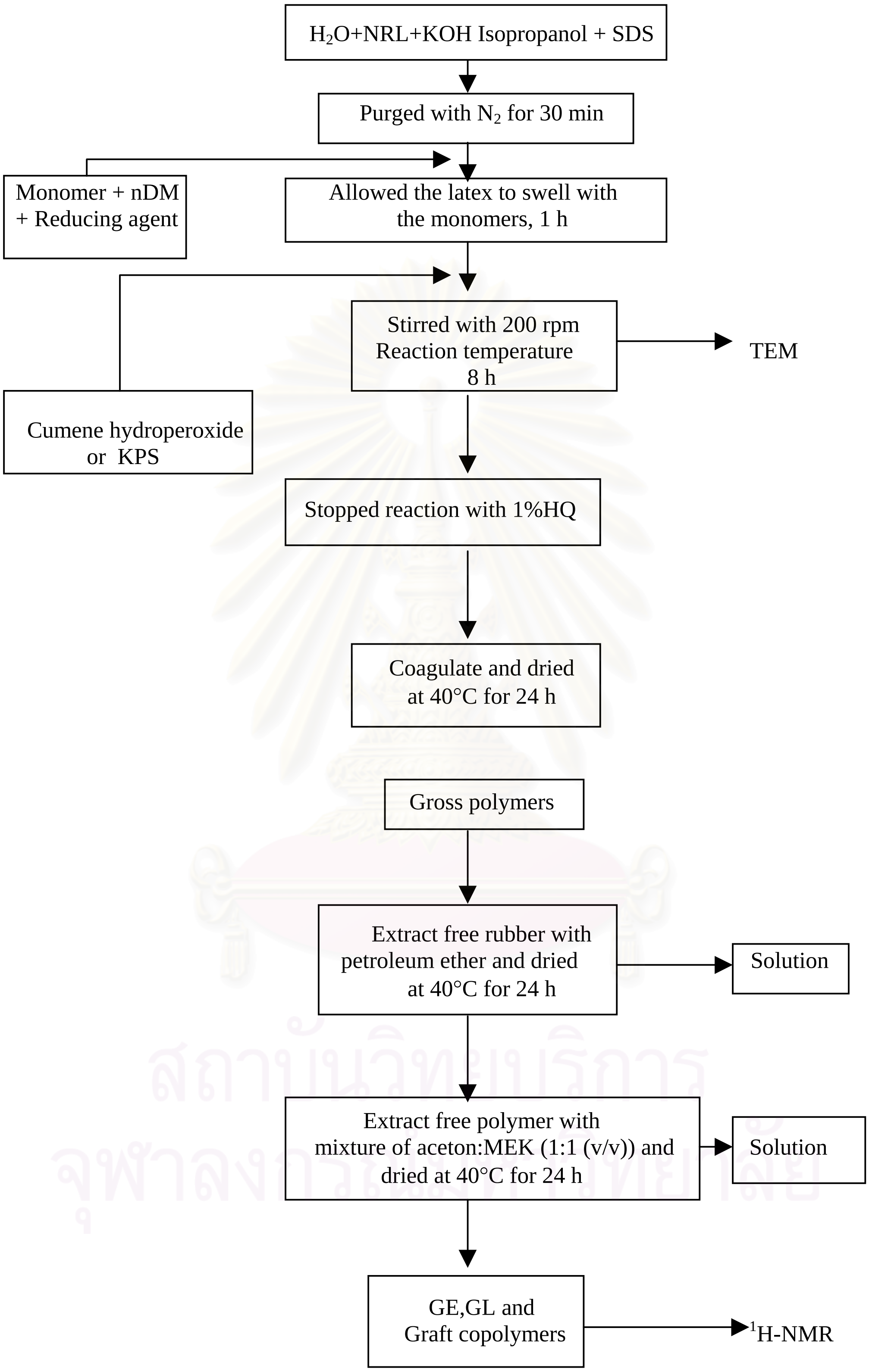


Figure 2.1 The complete experimental procedure.

$$\text{Grafting efficiency (GE, \%)} = \frac{\text{total weight of monomers grafted}}{\text{total weight of monomers polymerized}} \times 100 \quad (2.1)$$

$$\text{Grafting level (GL, \%)} = \frac{\text{total weight of graft copolymers}}{\text{total weight of rubber grafted}} \times 100 \quad (2.2)$$

$$\text{Graft copolymer (GNR, \%)} = \frac{\text{total weight of graft copolymers}}{\text{total weight of the gross polymers}} \times 100 \quad (2.3)$$

$$\text{Free copolymers (FP, \%)} = \frac{\text{total weight of free copolymers}}{\text{total weight of the gross polymers}} \times 100 \quad (2.4)$$

2.2.3.2 Polymer Characterization

Nuclear magnetic resonance spectroscopy has become a very powerful tool for characterizing the structures of polymers, providing qualitative and quantitative information about their compositions and the arrangements of their repeating unit along their chains. In the present investigation, the ^{1}H-NMR spectra of all the polymers were recorded using Bruker 250 MHz instrument using 5-10% (w/v) solution in deuterated chloroform ($CDCl_3$).

2.2.3.3 Electron Microscopy

The latex was diluted 400 times with deionized water to a concentration of 0.025 %wt. To this solution 1 ml of a 2% aqueous OsO_4 solution was added and allowed to stain the NR in the graft copolymers overnight. The morphology was examined by using a JEM-200CX transmission electron microscope (TEM) at 120 kV.

2.3 Results and Discussion

The effect of process parameters on the total conversion, the contents of component of gross polymer such as free rubber, free polymer, and graft copolymers, grafting level, and grafting efficiency was investigated. The experimental results (20 experiments) are listed in Table 2.3.

2.3.1 Mechanism of Grafting

The cumene hydroperoxides in the dilute aqueous solution induced by the iron (II) ions decompose to yield alkoxy radicals ($RO^{\bullet}$). If a reducing agent is also added to the system, then the function of the iron (II) ions can be viewed as that of a catalyst, promoting interaction between hydroperoxide and the reducing agent. The alkoxy radical might interact with the monomer or the rubber molecule producing macroradical which initiates grafting. During the formation of the graft copolymers, the surface of latex particles became the loci of polymerization. It is possible for the α- methylenenic hydrogen atoms in the natural rubber, being more active, to become the sites of graft copolymerization. The alkoxy radicals can not only attack the α-methylenenic hydrogen atoms to produce polyisoprene radicals, which initiate monomers to form the graft copolymers, but initiate monomers to form free polymer radicals, which combine with polyisoprene radicals to terminate or transfer to natural rubber to form graft copolymers. And some of the free polymer radicals still terminate to form free copolymers on the surfaces of the latex particles.

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

Initiation:

Attacking monomer:

$$RO^{\bullet} + M \dashrightarrow M^{\bullet}_1 \qquad (2.5)$$

Attacking rubber:

$$RO^{\bullet} + NR\text{-}H \dashrightarrow NR^{\bullet} + ROH \qquad (2.6)$$

Table 2.3 The experimental results of graft copolymerization.

Experiment	Total conversion (%)	Free rubber (%)	Free polymer (%)	Graft copolymer (%)	Graft level (%)	Grafting efficiency (%)
GNR01	92.5	16.7	13.4	70.0	83.9	72.1
GNR02	86.3	27.2	24.8	48.0	65.9	46.4
GNR03	91.1	22.3	20.4	57.3	73.8	57.3
GNR04	95.6	16.8	9.5	73.7	88.6	80.6
GNR05	97.6	24.2	35.8	40.0	52.7	27.5
GNR06	85.9	50.9	28.9	20.3	41.2	37.5
GNR07	85.4	37.4	16.2	46.5	74.2	64.9
GNR08	97.2	22.9	19.2	57.9	75.1	61.1
GNR09	90.5	36.5	30.9	32.6	51.4	35.0
GNR10	75.3	53.2	35.0	11.8	25.3	18.6
GNR11	77.9	53.0	37.1	9.8	21.0	15.2
GNR12	85.1	23.5	13.1	63.4	82.9	71.5
GNR13	86.6	13.2	14.9	72.0	82.9	68.0
GNR14	96.2	16.9	35.9	47.2	56.8	26.8
GNR15	90.1	20.9	10.2	68.9	87.1	74.6
GNR16	93.4	16.7	20.0	63.4	76.0	62.9
GNR17	96.1	12.1	25.6	62.3	70.9	56.6
GNR18	78.3	44.4	24.0	31.6	56.8	45.3
GNR19	79.8	38.3	34.5	27.2	44.0	22.2
GNR20	70.7	50.9	40.4	8.8	17.9	9.6

Re-initiation:

$$\mathrm{NR}^{\bullet} + \mathrm{M} \dashrightarrow \mathrm{NR\text{-}M}^{\bullet}_{1} \qquad (2.7)$$

Propagation:

Propagation of free polymerization:

$$\mathrm{M}^{\bullet}_{1} + \mathrm{M} \dashrightarrow \mathrm{M}^{\bullet}_{2}$$

$$\mathrm{M}^{\bullet}_{n} + \mathrm{M} \dashrightarrow \mathrm{M}^{\bullet}_{n+1} \qquad (2.8)$$

Propagation of graft polymerization:

$$\mathrm{NR\text{-}M}^{\bullet}_{1} + \mathrm{M} \dashrightarrow \mathrm{NR\text{-}M}^{\bullet}_{2}$$

$$\mathrm{NR\text{-}M}^{\bullet}_{n} + \mathrm{M} \dashrightarrow \mathrm{NR\text{-}M}^{\bullet}_{n+1} \qquad (2.9)$$

Chain-transfer to macromolecules:

Transfer to monomer:

$$\mathrm{M}^{\bullet}_{n} + \mathrm{M} \dashrightarrow \mathrm{M}^{\bullet}_{1} + \mathrm{M}_{n}$$

$$\mathrm{NR\text{-}M}^{\bullet}_{n} + \mathrm{M} \dashrightarrow \mathrm{M}^{\bullet}_{1} + \mathrm{NR\text{-}M}_{n} \qquad (2.10)$$

Transfer to rubber:

$$\mathrm{M}^{\bullet}_{n} + \mathrm{NR\text{-}H} \dashrightarrow \mathrm{NR}^{\bullet} + \mathrm{M}_{n}\mathrm{H}$$

$$\mathrm{NR\text{-}M}^{\bullet}_{n} + \mathrm{NR\text{-}H} \dashrightarrow \mathrm{NR}^{\bullet} + \mathrm{NR\text{-}M}_{n}\mathrm{H} \qquad (2.11)$$

Transfer to chain-transfer agent:

$$\mathrm{M}^{\bullet}_{n} + \mathrm{A} \dashrightarrow \mathrm{A}^{\bullet} + \mathrm{M}_{n}$$

$$\mathrm{NR\text{-}M}^{\bullet}_{n} + \mathrm{A} \dashrightarrow \mathrm{A}^{\bullet} + \mathrm{NR\text{-}M}_{n}\mathrm{H} \qquad (2.12)$$

Termination by combination:

$$\mathrm{M}^{\bullet}_{n} + \mathrm{M}^{\bullet}_{m} \dashrightarrow \mathrm{M}_{n+m}$$

$$\mathrm{NR\text{-}M}^{\bullet}_{n} + \mathrm{NR\text{-}M}^{\bullet}_{m} \dashrightarrow \mathrm{NR\text{-}M}_{n+m}\text{-}\mathrm{NR}$$

$$\mathrm{NR\text{-}M}^{\bullet}_{n} + \mathrm{M}^{\bullet}_{m} \dashrightarrow \mathrm{NR\text{-}M}_{n+m} \qquad (2.13)$$

where $RO^\bullet$ is alkoxy radical, M is vinyl monomer; $M^\bullet_n$ is vinyl polymer radical; NR-H is natural rubber; H is α-methylenic hydrogen atom; $NR^\bullet$ is polyisoprene radical; and $NR\text{-}M^\bullet_n$ is the growing graft polymer radical chain; and A is the chain-transfer agent.

To determine the presence of the graft copolymers, the products were extracted by petroleum ether and the mixture of acetone and MEK, respectively. After the solvent extraction, the graft copolymers were swollen with $CDCl_3$ and analyzed by ^{1}H-NMR. Figure 2.2 illustrates the ^{1}H-NMR spectrum of the polymers. The peaks at 5.15 ppm are assigned to the olefinic protons content in the natural rubber. The signals at 6.5-7.5 ppm are attributed to the phenyl group of PST. The peaks observed at 3.7 ppm are attributed to the methoxy group of PMMA. These ^{1}H-NMR analyses confirm that the latex prepared in this emulsion polymerization contained graft copolymers.

It is feasible that grafting occurs by initiator radical attack on natural rubber, however a considerable amount of previous work suggests that chain-transfer processes can not be neglected. Allen et al studied the mechanism of the graft copolymerization of methyl methacrylate in the presence of polyisoprene and suggested that the formation of graft copolymers involved the chain-transfer reaction when benzoyl peroxide was used as initiator [21]. A similar observation has been made by Merkel et al. in the case of grafting of methyl methacrylate onto polybutadiene [22].

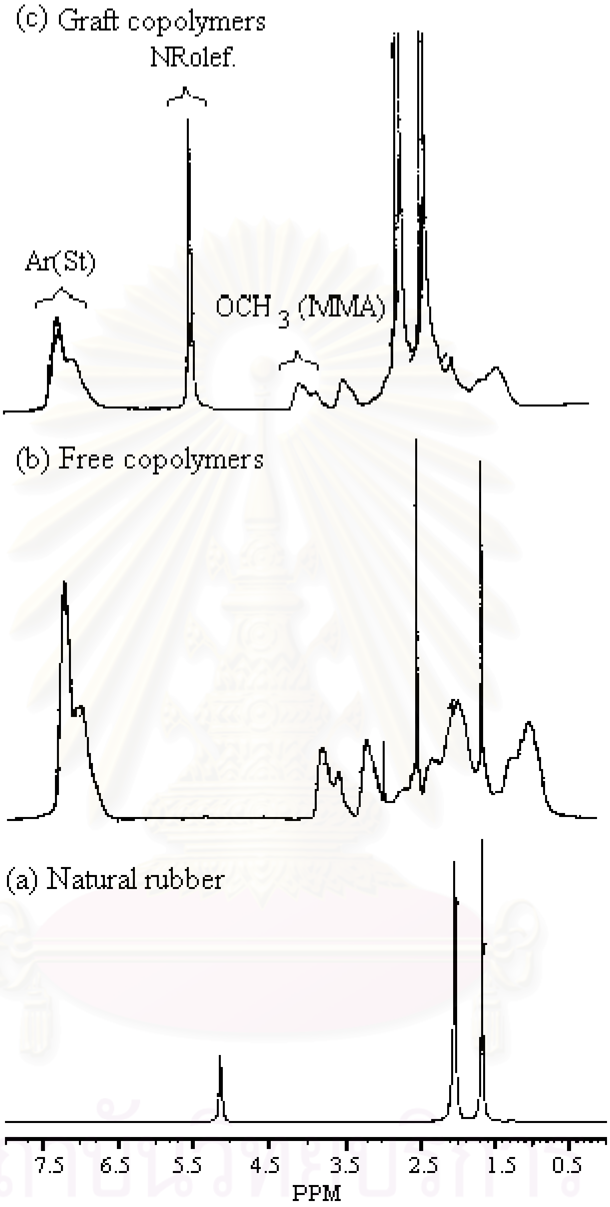


Figure 2.2 250-MHz ^{1}H-NMR spectra of polymers. (a) Natural rubber, (b) Free copolymers, and (c) Graft copolymers. Ar(St) represents the resonance of the aromatic protons of the styrene unit, NRolef. represents the resonance of the olefinic protons of the natural rubber unit, and OCH_3(MMA) represents the resonance of the methoxy protons.

2.3.2 Effect of Type of Initiator

Water soluble initiators are most often used in emulsion polymerization and initiators based on persulfate are common. The initiator dissociation reaction is the symmetrical O-O bond scission of the persulfate anion:

$$\left[O_3S - O - O - SO_3 \right]^{2-} \longrightarrow 2\left[\cdot O - SO_3^{-} \right] \qquad (2.14)$$

Combinations of organic hydroperoxides with reducing agents and ferrous iron have been used in the emulsion polymerization of cold GR-S rubber. Traditionally, ferrous sulfate has been used as the source of Fe^{2+} and various sugars as the reducing agents; however, it was found that Fe^{2+} chelated by ethylenediaminetetraacetic acid (EDTA) activated the hydroperoxide-initiator when combined with sulfoxylate reducing agents such as sodium formadehyde sulfoxylate . The EDTA-Fe^{2+} chelate acted as a reservoir, which regulated the Fe^{2+} concentration in the polymerization system and prevented premature precipitation of the iron, in which an iron source in minute quantity was required which then followed a redox catalytic cycle (Figure 2.3).

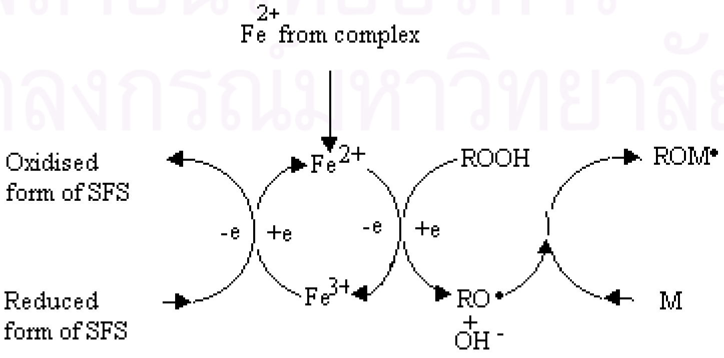
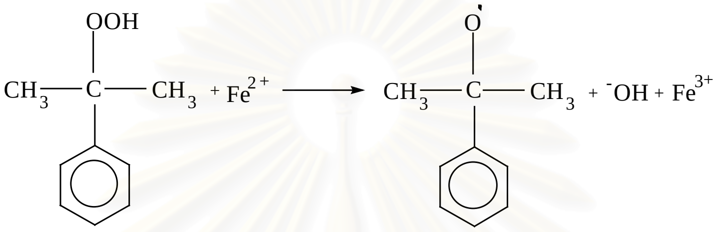


Figure 2.3 The interactions between the various components of a hydroperoxide-iron-reducing agent initiation system [18].

Traditionally, cumene hydroperoxide has been used as the oxidizing agent in these systems because the hydroperoxides which were the most effective in grafting reactions were those with the lowest solubility in water. Nevertheless, it is found in the literature that oil soluble initiators of different water solubility do not show much variety in their GE values [20]. The radical reaction is shown below:



(2.15)

Figure 2.4 shows the grafting efficiency of graft copolymerization, using both types of initiators, KPS or CHPO, over a range of chain-transfer agent concentration. The redox initiator system was found to be very effective and high GE was observed. This can be explained by the rate high of radical generation (i. e., the rate of the redox reaction). The CHPO/EDTA-Fe^{2+}/SFS initiated polymerization performed at rate faster compared to those initiated by the persulfate reaction. Consequently, for the persulfate system the concentration of radicals was lower, fewer monomers were polymerized and hence the rate of graft reaction was slower. Therefore, using CHPO/EDTA-Fe^{2+}/SFS redox initiator, caused an effective increase in radical concentration in the system, then produced a graft copolymer with high radical content. Normally in emulsion polymerization, a water soluble initiator like KPS is used. In emulsion graft polymerizations, however, oil soluble initiators are more widely used because these tend to give higher GE values. The organic hydroperoxide/sodium formaldehyde sulfoxylate/EDTA-Fe^{2+} redox initiator gave high conversion and grafting efficiency. (see experiment GNR01 compared to

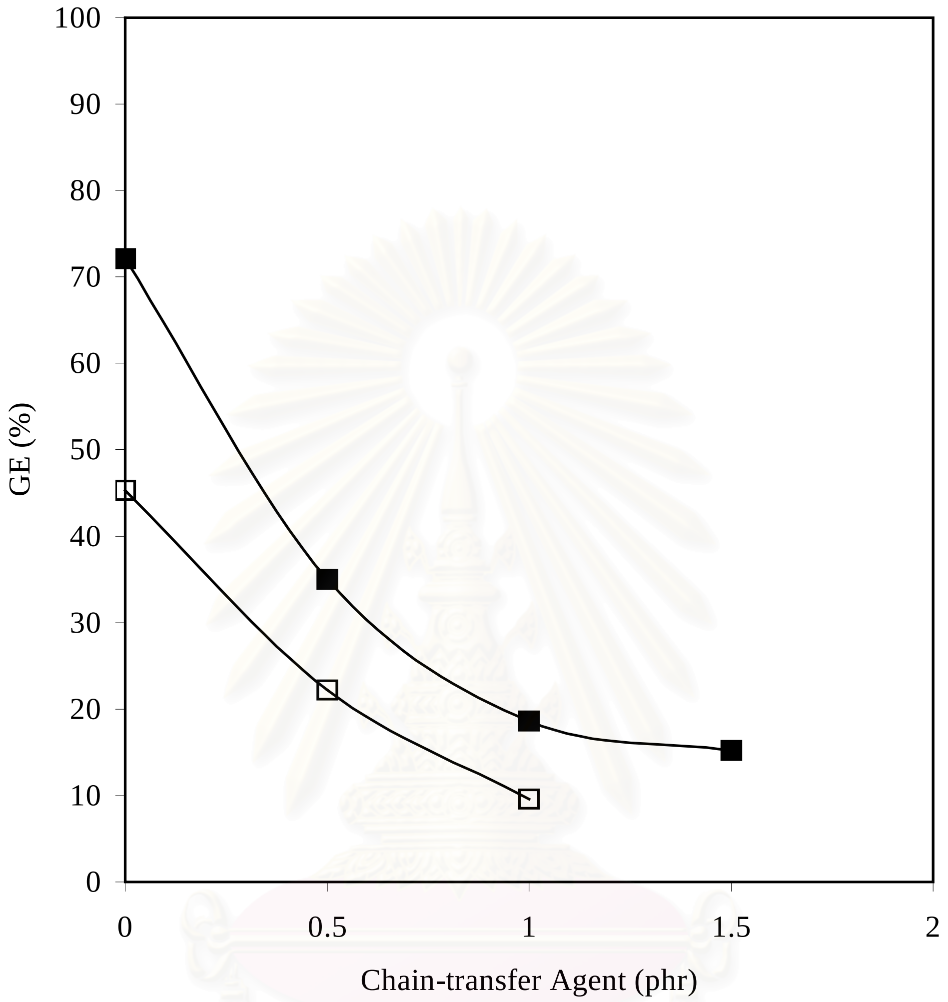


Figure 2.4 Effect of the type of initiator on grafting efficiency

CHPO/SFS/EDTA-chelated Fe^{2+} (■), KPS (□).

<u>Experimental Condition</u>

The amount of initiator = 1.5 phr

The amount of emulsifier = 1.5 phr

The monomer-to-rubber ratio = 1:1

The polymerization temperature = 70°C

GNR18, experiment GNR09 compared to GNR19, and experiment GNR10 compared to GNR20 in Table 2.3).

2.3.3 Effect of Initiator

The effect of the amount of initiator on the GE and GL was studied over the range of approximately 0.5 to 2.5 phr while keeping the concentration of all other reagents constant. The GE and GL were seen to increase with an increase in amount of initiator from 0.5 to 2.0 phr (Figure 2.5). This trend can be explained by the fact that the radicals transfer to either rubber or monomer, producing macroradicals, which is enhanced on increasing the initiator, thus resulting in an increase in grafting. However, beyond the amount of 2.0 phr, the GE and GL decrease. This is due to the conversion of free copolymers increasing again over 2.0 phr. Under this condition, the chain length of grafts has hardly anything to do with the free polymer radicals. The excessive free polymer radicals react with each other to form free copolymers more than to graft on the natural rubber and decrease the chain length of the grafts. Therefore, the production of free polymer is promoted more at high initiator content (Figure 2.5). On the other hand, the probability for the rate of chain-transfer for the free polymer radicals to the natural rubber backbone is less than the rate of termination of free polymer radicals, favoring the termination process of copolymers over the chain-transfer process. Similar results were also reported by Lenka at al. [9-11] in the case of grafting methyl methacrylate onto natural rubber.

2.3.4 Effect of Polymerization Temperature

The rate of decomposition of the initiator depends on the reaction temperature. With increase in reaction temperature, more alkoxy radicals are produced. It is also

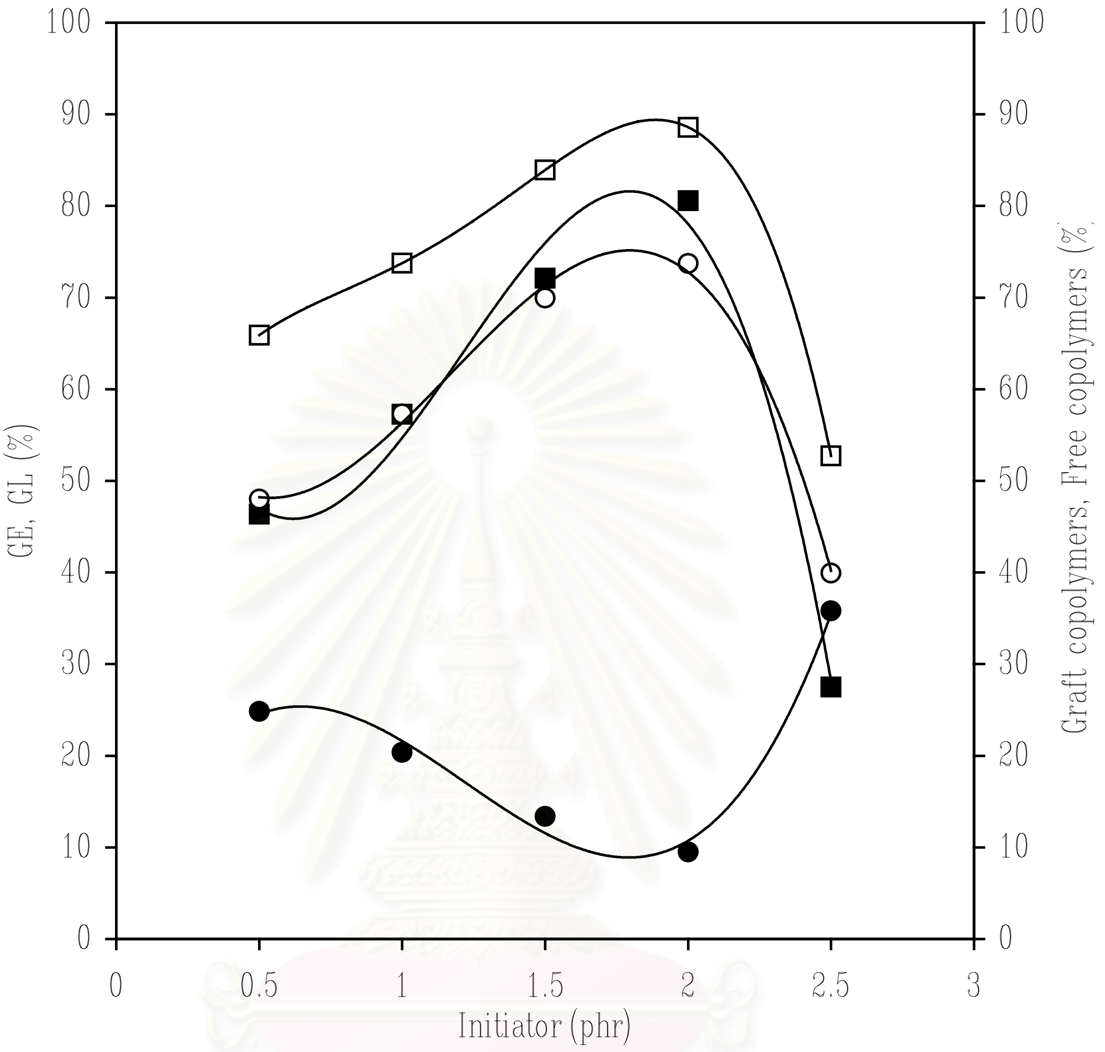


Figure 2.5 Effect of the amount of initiator on grafting efficiency (■), grafting level (□), free copolymers (●), and graft copolymers (○).

Experimental Condition

The type of initiator	= CHPO/SFS/EDTA-chelated Fe^{2+}
The amount of emulsifier	= 1.5 phr
The amount of chain-transfer agent	= 0.0 phr
The monomer-to-rubber ratio	= 1:1
The polymerization temperature	= 70°C

known that the transfer of alkoxy radicals to the rubber chain produces the graft copolymers. So, the perusal of the results indicates that the GE and GL increase as the polymerization temperature is increased up to 70^{o}C (Figure 2.6). And then both GE and GL decrease with further increase in the reaction temperature. This may be due to the very rapid decomposition of the initiator yielding a high instantaneous radical concentration and the radicals then might be acting as radical scavengers, which results in decreasing the initiator amount. The result is a lower initiator efficiency which, however, fails to produce both the corresponding ungrafted and graft copolymers.

2.3.5 Effect of Emulsifier

For the variation of the amount of emulsifier from 0.5 to 1.5 phr, the curve runs almost parallel to the X axis (Figure 2.7). The results indicate that the amount of emulsifier has little effect on GE and GL due to no occurrence of coagulation of particles when the emulsifier amount is just adequate to keep colloidal stability of the particles. However, GE and GL decrease when more is charged. Zhao et al observed similar results for the graft copolymerization of styrene and methyl methacrylate onto styrene-butadiene rubber [16]. The possibility of polymerization is that there will be more free micelles existing in the water phase, resulting in the increasing formation of free copolymers. So, there will be less monomer for grafting onto the NR latex backbone and free copolymerization is preferred to graft copolymerization.

The morphology of natural rubber core (darker areas) with PST/MMA shell (lighter areas) prepared at different emulsifier concentration is shown in Figure 2.8. From this figure, at emulsifier concentration below 1.5 phr, neither coagulation nor secondary nucleation of any importance takes place (Figure 2.8a) and at emulsifier

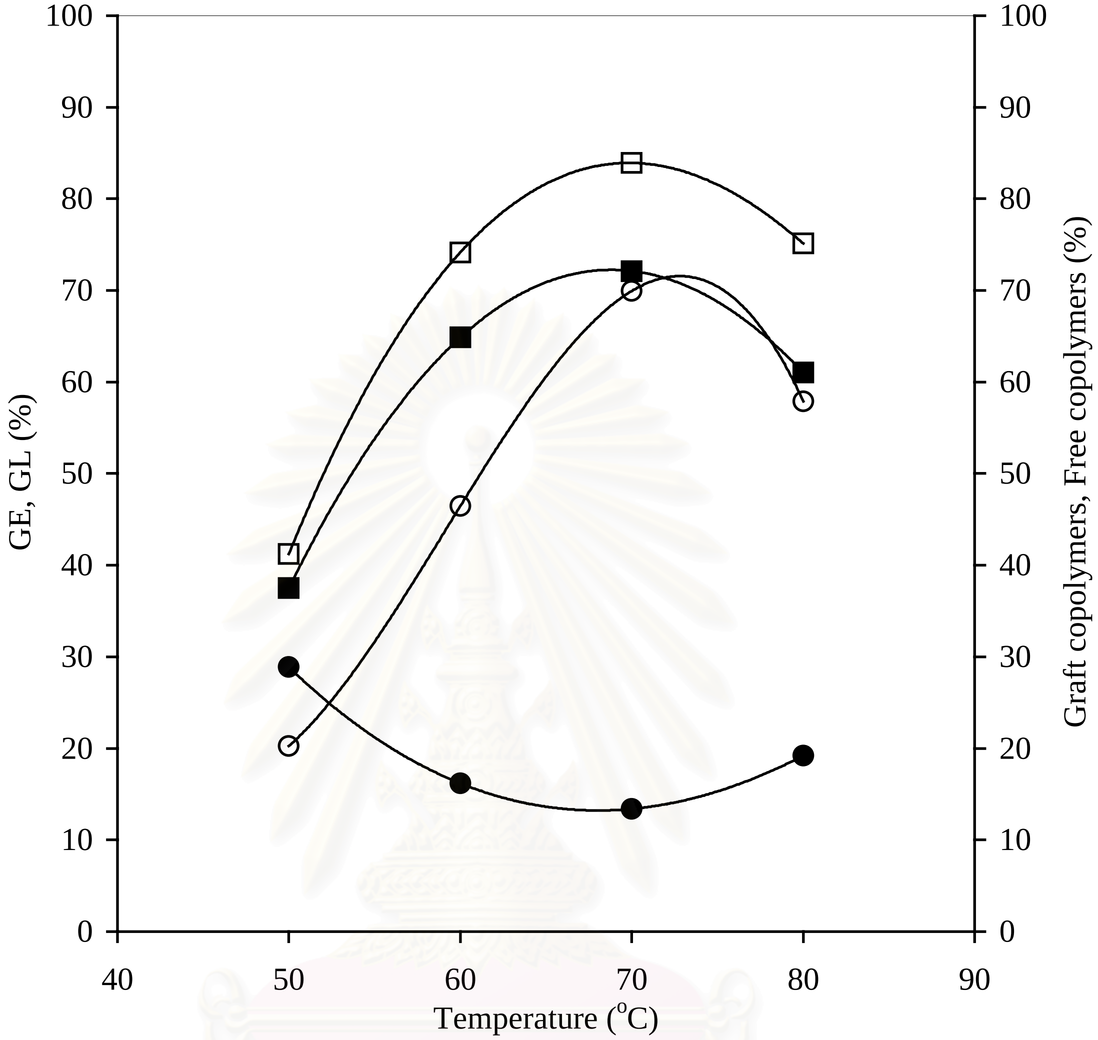


Figure 2.6 Effect of polymerization temperature on grafting efficiency (■), grafting level (□), free copolymers (●), and graft copolymers (○).

<u>Experimental Condition</u>

The type of initiator = CHPO/SFS/EDTA-chelated Fe^{2+}

The amount of initiator = 1.5 phr

The amount of emulsifier = 1.5 phr

The amount of chain-transfer agent = 0.0 phr

The monomer-to-rubber ratio = 1:1

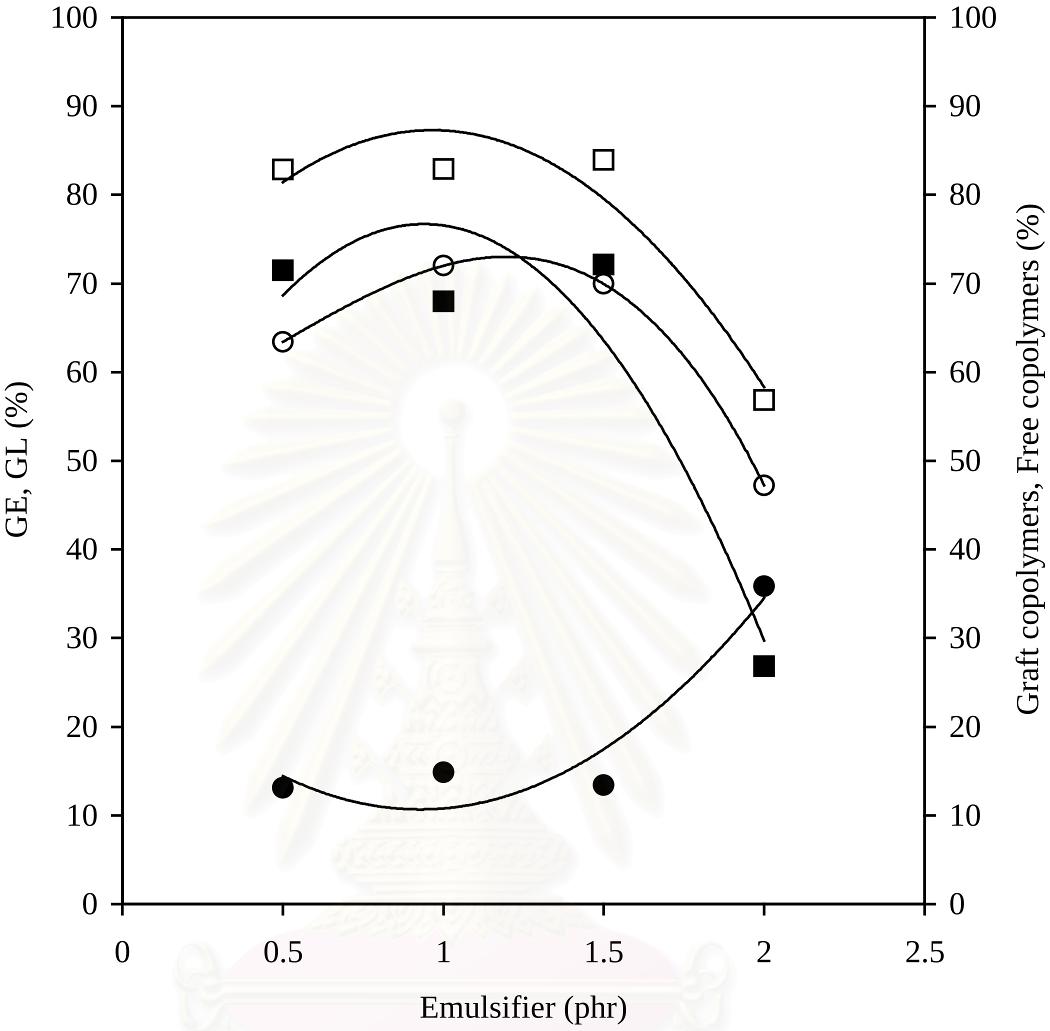


Figure 2.7 Effect of the amount of emulsifier on grafting efficiency (■), grafting level (□), free copolymers (●), and graft copolymers (○).

<u>Experimental Condition</u>

The type of initiator = CHPO/SFS/EDTA-chelated Fe^{2+}

The amount of initiator = 1.5 phr

The amount of chain-transfer agent = 0.0 phr

The monomer-to-rubber ratio = 1:1

The polymerization temperature = 70°C

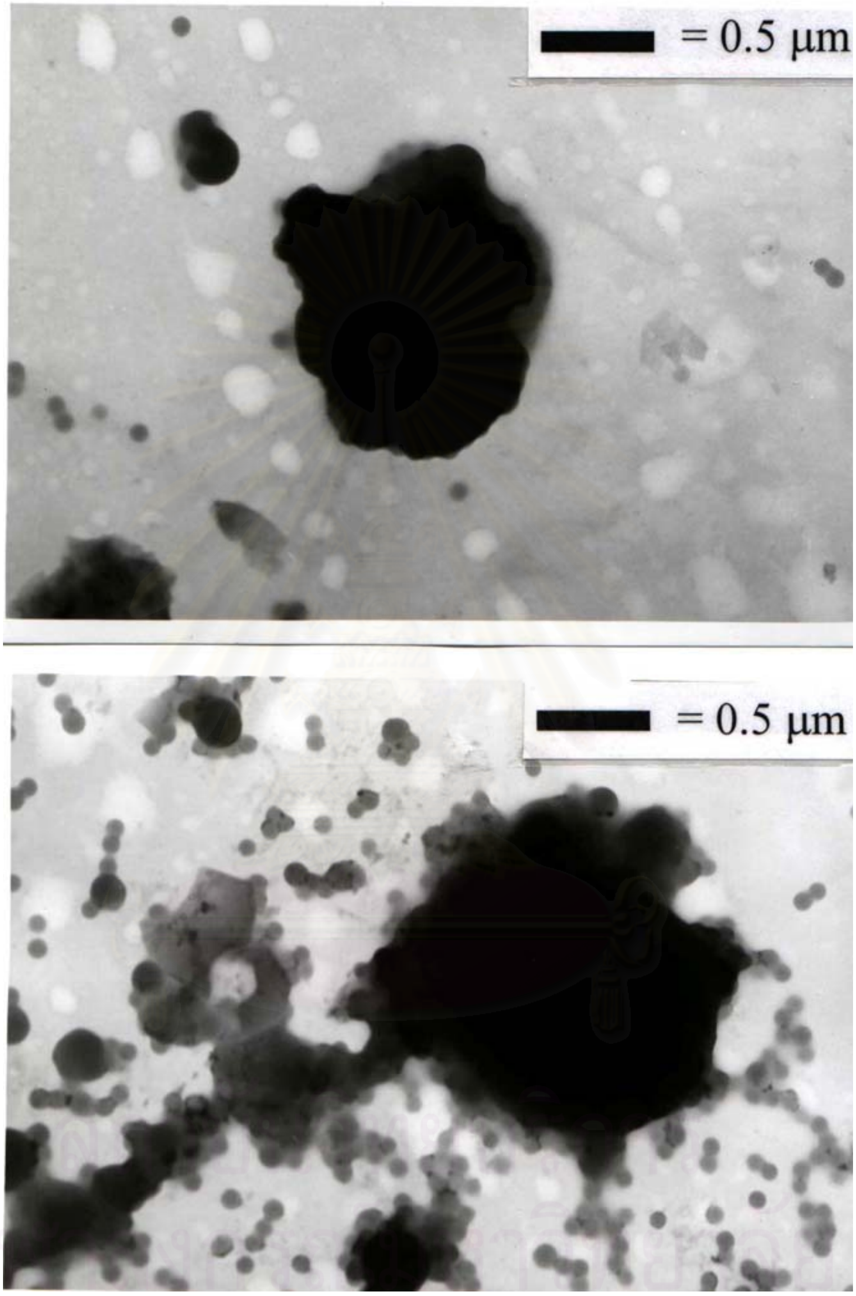


Figure 2.8 Transmission electron micrographs of the particle morphologies of graft copolymers prepared using redox initiator: (a) 1% SDS, (b) 2% SDS at CHPO = 1.5 phr, nDM = 0.0 phr, the monomer-to-rubber ratio = 1:1, and the temperature = 70°C.

concentration above 1.5 phr, the GE is lower due to the occurrence of secondary nucleation (Figure 2.8b).

2.3.6 Effect of Monomer-to-Rubber Ratio

Figure 2.9 shows the relationship between GE and GL and monomer-to-rubber ratio in the two-stage emulsion polymerization. The grafting decreases with increasing monomer-to-rubber ratio. This result may be explained by a mechanism involving a surface-controlled process, which has previously been reported [16,22]. 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 through diffusion of the monomer to the rubber chain, compared to the copolymerization of monomers. As a result, the grafting efficiency decreases with increasing monomer-to-rubber ratio.

2.3.7 Effect of Chain-Transfer Agent

Aliphatic mercaptans are widely used in polymerization in order to reduce the polymer chain length for the range required for the growth rate of polymer particles in the emulsion polymerization. The graft chains could be controlled by use of chain-transfer agents. The effect of the amount of chain-transfer agent, n-dodecyl mercaptan on GE and GL, is shown in Figure 2.10. It seems that the mercaptan amount has a significant effect on the grafting. Both GE and GL decrease with an increase of the mercaptan amount up to 1.0 phr and then GE and GL decrease marginally. As the

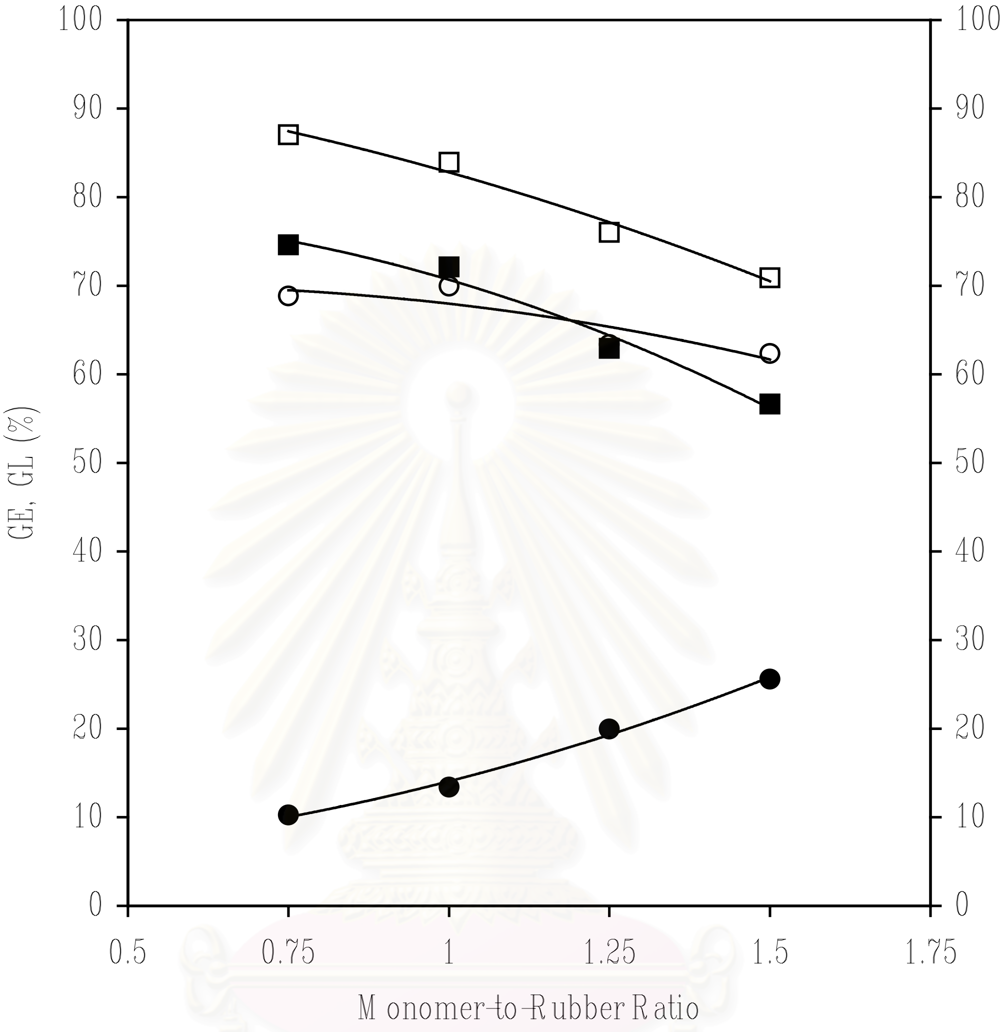


Figure 2.9 Effect of monomer-to-rubber ratio on grafting efficiency (■), grafting level (☐), free copolymers (●), and graft copolymers (○).

Experimental Condition

The type of initiator = CHPO/SFS/EDTA-chelated Fe^{2+}

The amount of initiator = 1.5 phr

The amount of emulsifier = 1.5 phr

The amount of chain-transfer agent = 0.0 phr

The polymerization temperature = 70°C

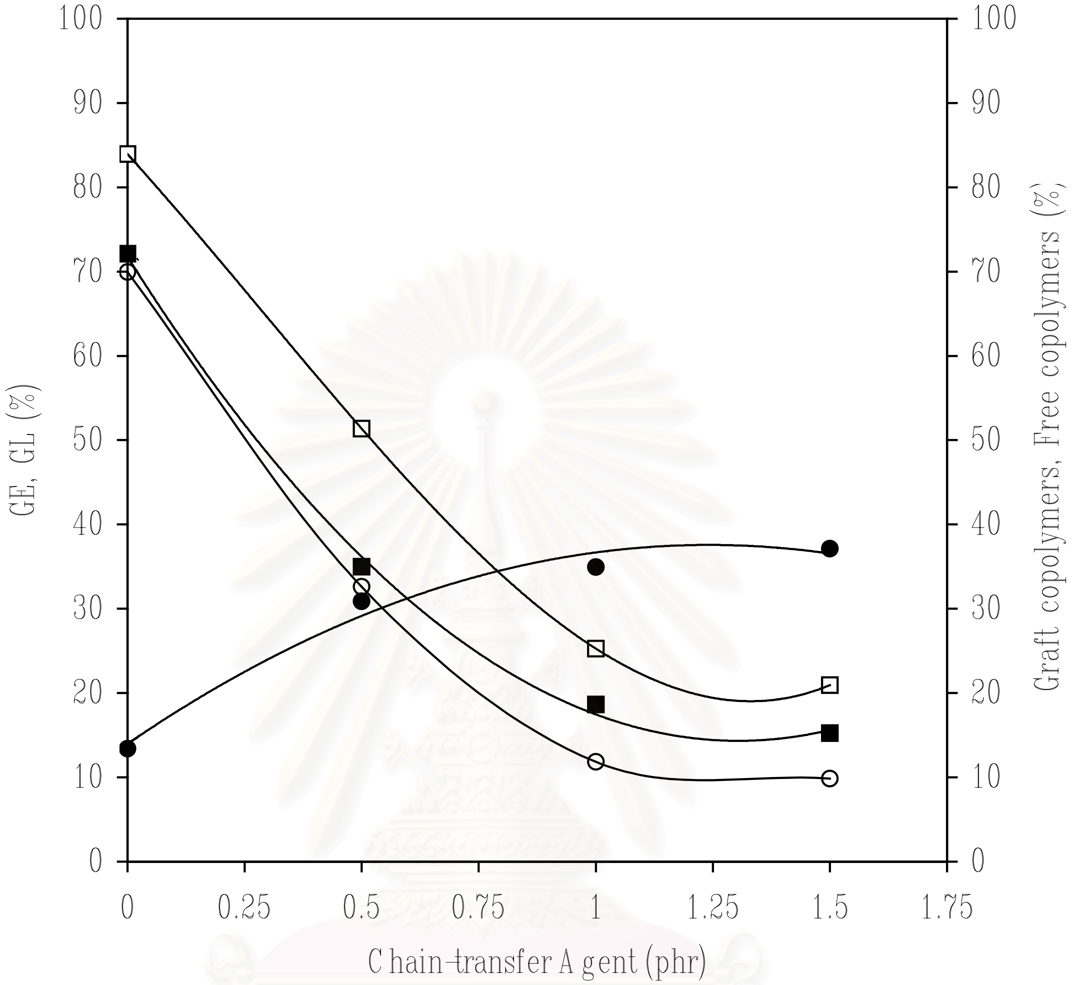


Figure 2.10 Effect of the amount of chain-transfer agent on grafting efficiency (■), grafting level (□), free copolymers (●), and graft copolymers (○).

Experimental Condition

The type of initiator = CHPO/SFS/EDTA-chelated Fe^{2+}

The amount of initiator = 1.5 phr

The amount of emulsifier = 1.5 phr

The monomer-to-rubber ratio = 1:1

The polymerization temperature = 70°C

mercaptan content increases, the rate of chain-transfer reaction of free radicals to mercaptan increases, which results in a decrease of macroradical formation, thereby decreasing the grafting and free copolymerization. Increasing the loading of chain transfer agents can progressively decrease the chain length per particle. On the other hand, when the chain transfer agent increases, one can notice that the percentage of graft copolymers and free copolymers is shifted to a lower level (Figure 2.10), thus enhancing the transfer reaction of radicals to chain-transfer agent. Aerdts et al. [23] has observed a similar retardation effect in the graft copolymerization of styrene or methyl methacrylate onto polybutadiene. The grafting efficiency was found to be detrimentally affected by use of chain-transfer agents. This was indeed expected, as the presence of mercaptans in the reaction mixture provides no ability to continue the propagation of the chains.

2.3.8 Effect of Grafting Efficiency on Particle Morphology

The grafting of styrene and methyl methacrylate onto the natural rubber is a core-shell type, emulsion copolymerization. The grafted natural rubber particles consist of the natural rubber core and the compatibilized PST/MMA shell. The morphology of natural rubber and the grafted natural rubber with different grafting efficiency is shown in Figure 2.11. The darker areas represent the natural rubber core regions, while the lighter areas are PST/MMA film as shell. The surface of the natural rubber latex particle is smooth (Figure 2.11a). The presence of nodules on the surface of the graft copolymers may be due to the growing macroradical chains, which are grafted onto the surface of the natural rubber particle and continue to propagate to form the shell layer. Furthermore, it has been demonstated that grafting of the second stage polymer onto the core particle produces heterogeneous structures (core-shell structures), which are formed by phase saperation of incompatible polymers during polymerization. Most of the methyl methacrylate and styrene polymerized in the aqueous phase to form secondary particles, which then flocculated with the natural rubber seed particles. At the low grafting efficiency (Figure 2.11b), the natural rubber seed particle was a compact packing of PST/MMA particles. When the grafting efficiency increased, the PST/MMA particles enhanced the encapsulation of the core and then fused to give a shell layer with smooth surface (Figure 2.11c, 2.11d). Figure 2.11 clearly shows that increasing the grafting efficiency gave thicker poly(styrene-*co*-methyl methacrylate) shells around the natural rubber cores. The natural rubber seed particles have the complete closed shell at high level of grafting efficiency.

On the other hand, polymer molecules are considered to be incapable of moving freely inside the latex particle because of long chain characteristics and chain entanglements. Hence, a polymer chain is unlikely to translate without restriction. The growing polymer molecule (free radical) can move by molecular motion or by a propagation event. Base on this concept, and taking into account that the end of the oligomeric free radical will preferentially remain in the surface layer of the polymer particle, the movement of a growing polymer molecule (free radical) is likely to be confined near the surface layer of the polymer particle.

According to the above discussion, the nonuniform particle morphology now can be interpreted as resulting from an “encapsulation” process [24]. This heterogeneous morphology can be view as the result of “old” polymer molecules being encapsulated with “new” polymer molecules during the course of polymerization. If the old polymer molecules possess different physical properties from those of new polymer molecules, then the core-shell structure would be expected. Vanderhoff et al. implied that during the course of polymerization, old

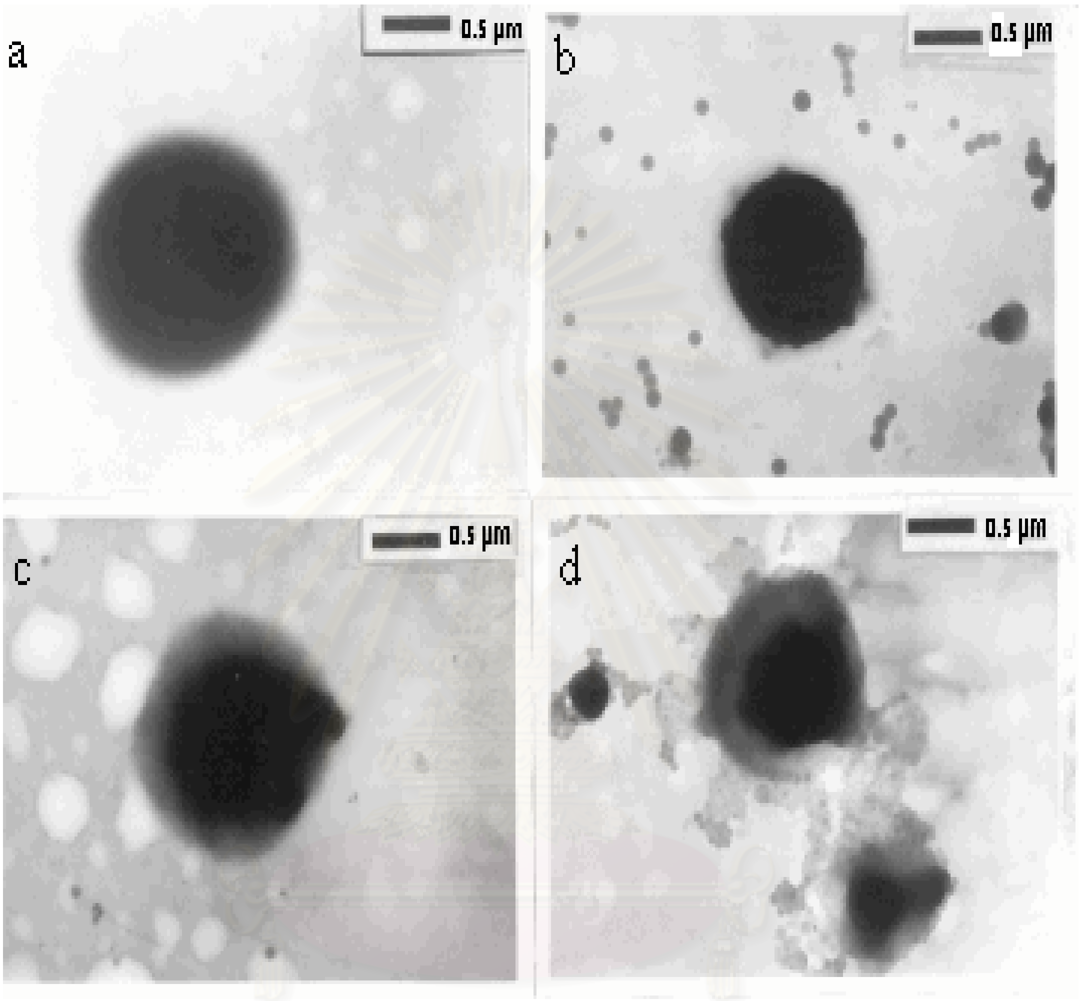


Figure 2.11 Transmission electron micrographs of polymers: (a) natural rubber; (b) 15% GE; (c) 61% GE; (d) 72% GE (×30,000).

polymer molecules would be encapsulated with new polymer molecules and gave the pathway (Figure 2.12) to the postulate encapsulation mechanism [25].

Figure 2.12 shows one hypothetical pathway to prepare core-shell particles based on the heterocoagulation of newly formed oligomers onto the seed particles, which grow until they merge with one another and form a fused shell. A series of micrographs as shown in Figure 2.13 depicted that the growth pattern of the composite latex particles closely resembled the pathway of Figure 2.13. Most of the vinyl monomer was polymerized in the aqueous phase to form secondary particles, which then flocculated with the seed particles (Figure 2.13a). This heterocoagulation was followed by further polymerization of monomers in localized domains near the particle surface (Figure 2.13b). The uneven surfaces of the larger composite particles also showed this unique pattern of particle growth (Figure 2.13c) and the fusion of the shell layer to give a smooth surface (Figure 2.13d).

2.4 Conclusion

The cumene hydroperoxide redox initiator was found to be very effective and resulted in high grafting efficiency due to high rate of radical generation. The hydroperoxide initiator, being partially water soluble, is believed to produce initiating radicals at or near the particle interface and thus causes preferential copolymerization of the monomer in the region of the particle surface. The graft copolymerization of styrene and methyl methacrylate mixtures onto natural rubber seed latex using the redox initiator system is dependent on the main process factors such as the amount of initiator, emulsifier and chain-transfer agent, monomer-to-rubber ratio, and temperature.

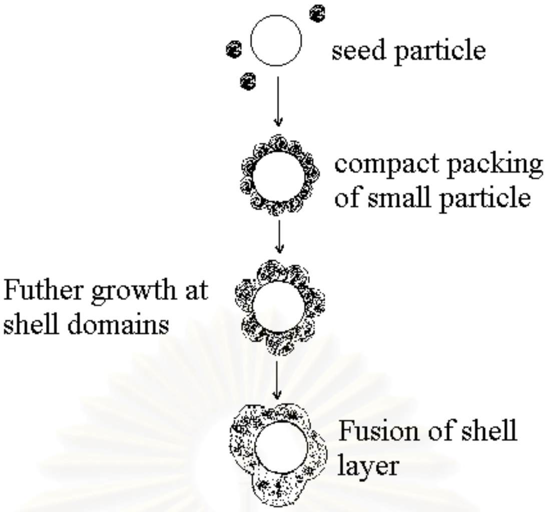


Figure 2.12 Pathway to prepare core/shell particle [25].

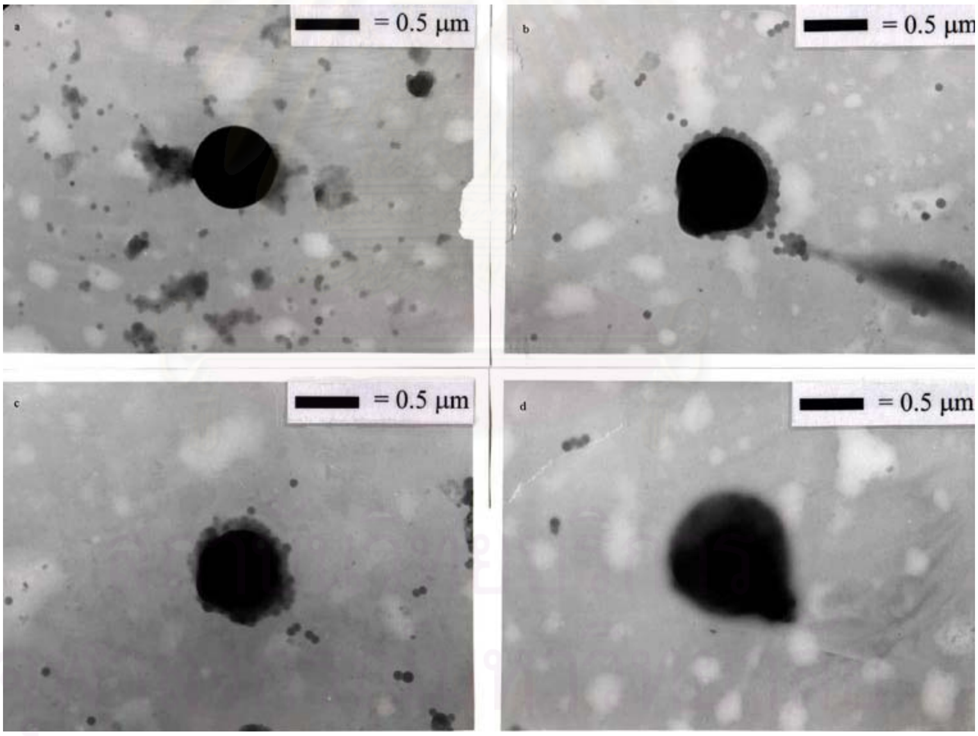


Figure 2.13 Transmission electron micrographs of the particle morphologies of GNR06 during the graft copolymerization: (a) 2 h, (b) 4 h, (c) 6 h, and (d) 8 h (×30,000).

An increase in the concentration of initiator up to 2 phr increased both the grafting efficiency and grafting level. The grafting yield increased with increasing temperature up to 70°C and then decreased, suggesting that a large amount of free radicals, produced at higher temperature, may combine by themselves reducing the amount of initiator. The emulsifier amount has a small effect on grafting styrene and methyl methacrylate onto natural rubber. The grafting efficiency decreased as monomer-to-rubber ratio increased, indicating that the graft copolymerization occurs on the surface of the latex particles. The grafting decreased as the amount of chain-transfer agent increased due to the decrease of macroradical formation.

Characterization of the graft copolymers by ^{1}H-NMR and TEM indicates the occurrence of grafting on the natural rubber backbone in the core-shell latex particles. The graft reaction mainly occurs by removal of hydrogen from the natural rubber followed by addition of macroradical units to that site. The mechanism of core-shell particle formation should be considered. The growing polymeric chain produced in water might precipitate onto the surface of the latex particle an continue to propagate to form the shell layer. Furthermore, it was confirmed that the graft copolymerization is a surface-controlled process.

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CHAPTER 3

GRAFT COPOLYMERS FROM NATURAL RUBBER USING AMINE ACTIVATED HYDROPEROXIDE

3.1 Introduction

Graft copolymerization onto an existing polymer backbone has proved to be one of the major interests with redox polymerization system. The successful grafting of vinyl monomers onto NR involves the creation of free radical on the backbone of rubber, thus having gained bountiful importance in modifying properties of natural rubber. Such a novel material, becoming available by combining rubber material with non-rubber polymers, could lead to many technical applications, depending for example on the glass transition temperature of the second polymer. The graft copolymers of vinyl monomers such as styrene and methyl methacrylate onto natural rubber, comprising an inner soft polymer sphere, the "core," and an outer hard polymer the "shell," can be expected to have better impact-resistant properties. The properties balance of the graft copolymers of styrene and methyl methacrylate onto natural rubber allows targeting this material as potential MBS (Poly(styrene-*co*-butadiene-*co*-methyl methacrylate), impact modified copolymers) replacement. In order to promote a core-shell structure, we used the redox initiator couple, cumene hydroperoxide/tetraethylenepentamine. Many aliphatic and alicyclic amines have the ability to decompose organic peroxides vigorously, but in peroxide-catalyzed emulsion polymerization only a limited number of amines have an activating effect so powerful that it is possible by adding them to the system to bring about rapid polymerization at a low temperature. The polyalkylenepolyamines were, however, observed to have a powerful activating effect in the emulsion polymerization of styrene although only a mild effect in the bulk polymerization of this monomer. Hydroperoxides of the type of cumene hydroperoxide were found to be particularly susceptible to activation by polyalkylenepolyamines. Two structural requirements are believed necessary if successful activation is to occur. First, the amine must contain within the amine groups different substitution, either primary and secondary or primary and tertiary within the same molecule. Second, the amine groups must be separated by no more than two carbons. Whitby et al. [1] have given extensive information on the comparative effectiveness of a wide range of polyalkylenepolyamines. The polyethylenepolyamines from diethylenetriamine to nonaethylenedecamine were investigated, and the conclusion reached that the effectiveness reaches a maximum in tetraethylenepentaamine and pentaethylenehexamine, and then gradually decreases as the molecular size is further increased. As examples of the effectiveness of the polyamines in activating low-temperature polymerization, the following may be cited: (a) in a soap emulsion at 10° C with 0.21 pphm of cumene hydroperoxide and 0.2 pphm of tetraethylenepentamine as initiator, styrene was polymerized to 73% conversion in 1 h; (b) a 30:70 styrene-butadiene mixture in the same system gave 70% of polymer in 6 h.

Investigation into supposedly iron-free activated peroxide systems resulted in the development of polyamine activators. The redox initiator couple, cumene hydroperoxide/tetraethylenepentamine was used in this work. This system was chosen because it operates very efficiently at the high pH values normally encountered in natural rubber latex [2]. In this case, 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 tetraethylenepentamine (TEPA) is water-soluble. The cumene hydroperoxides in the dilute aqueous solution decomposed to yield alkoxy radicals. The alkoxy radical might interact with the monomer or the rubber molecule producing macroradical which initiates grafting. During the formation of the graft copolymers, the surface of latex particles became the loci of polymerization. It is possible for the backbone in the natural rubber, being more active, to become the sites of graft copolymerization. The alkoxy radicals can not only attack the backbone to produce polyisoprene radicals, which initiate monomers to form the graft copolymers, but initiate monomers to form free polymer radicals, which combine with polyisoprene radicals to terminate or transfer to natural rubber to form graft copolymers. And some of the free polymer radicals still terminate to form free copolymers on the surfaces of the latex particles. The growing polymer chains, graft or ungrafted, will terminate by recombination with another macroradical, chain transfer or disproportionation.

It is feasible that grafting occurs by initiator radical attack on natural rubber, however a considerable amount of previous work suggests that chain-transfer processes can not be neglected. Allen et al. [3] studied the mechanism of the graft copolymerization of methyl methacrylate in the presence of polyisoprene and suggested that the formation of graft copolymers involved the chain-transfer reaction when benzoyl peroxide was used as initiator. A similar observation has been made by Merkel et al. [4] in the case of grafting of methyl methacrylate onto polybutadiene.

However, literature describing the effects of process conditions on the characteristics of the graft copolymers obtained is scarce. Effects of process variables have been described by several researches. Gasperowicz et al. [5] has investigated the grafting of styrene onto poly(butyl acrylate) in emulsion form. The parameters investigated in relation to the degree of monomer conversion and the grafting efficiency of polystyrene were: time, temperature, concentration of initiator and emulsifier and the monomer/polymer ratio. The grafting efficiency, which decreases increasing the time of reaction, is weakly affected by the temperature of polymerization, and decreases with an increase in the monomer/polymer ratio. The grafting efficiency decreases with increasing initiator concentration, although, within the concentration range studied, a maximum grafting efficiency was observed. Sundberg et al. [6] described the grafting mechanism for seeded polymerization. They have shown that the grafting mechanism is substantially affected by several factors: temperature, concentration of initiator (peroxodisulfate), concentration of transfer agent (CCl_4), the mode of seeded polymerization and monomer/polymer (M/P) ratio. The rate of polymerization rapidly increased with temperature in batch polymerization; by contrast, in the case of semicontinuous polymerization, only a slight increase was observed under the same conditions. The dependence of the grafting efficiency on temperature and the mode of polymerization was the reverse. The authors explained the increase in the fraction of graft copolymer with temperature by the more frequent entry of initiating radicals into the particles, where they attacked more vigorously the unsaturated double bonds to increase the initiation rate of grafting. The temperature enhancement was accompanied by a decrease in the equilibrium monomer concentration in the particles and an increase in the polymer/monomer ratio, which also led to an increase in grafting efficiency. The grafting efficiency increased with peroxodisulfate concentration and, conversely, it decreased with increase in concentration of a transfer agent.

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 provide a more efficient approach to deal with a large number of variables. Moreover, if there are statistical interactions between factors, that is where the effect of one factor is dependent on the value of another factor; such information will not be obtained using the one-factor-at-a-time technique. Within this framework the influence of process variables including the concentrations of initiator, emulsifier, and chain-transfer agent, the reaction temperature, the ratio of monomer mixture, and monomer to rubber ratio was investigated. Statistical analysis was used to study the influence of each process variable irrespective of and in combination with the other process variable on the grafting efficiency.

The large number of independent variables involved in graft copolymerization processes lead to thorough experimental study. In this chapter, six process variables, which are expected to have an effect on the grafting efficiency, are considered. These variables include the concentrations of initiator, emulsifier, and chain-transfer agent, the reaction temperature, the ratio of monomer mixture, and monomer to rubber ratio. The effects are complex and may include many interactions. The purpose of the work is to investigate the effects, of each process variable identified, on the grafting efficiency. The factorial experimental design is one of the most commonly used methods to realize the effects of some independent variables that significantly affect the final experimental results. The analysis of the data collected during the factorial designs is discussed. Results from two fractional factorial designs are presented.

3.2 Experimental

3.2.1 Materials

Most of chemicals used were described in a previous section (Section 2.2.1). A different activator agent, tetraethylenepentamine, ($HN(CH_2CH_2NHCH_2CH_2NH_2)_2$, TEPA, Aldrich), was used as received.

3.2.2 Preparation of Grafted Natural Rubber

The graft polymerizations were carried out using a 300 ml Parr reactor, equipped with a condenser. Natural rubber latex and an aqueous solution of additives were charged to the reactor and the dissolved oxygen in the ingredients was removed by purging nitrogen gas for at least 30 min through the mixture, providing still stable latex. If necessary, buffer was added to maintain the pH of the system at 10. The monomer mixture with mercaptan was fed to the reactor, then tetraethylenepentamine (TEPA), was used to activate the cumene hydroperoxide; (CHPO : TEPA = 1:1 w/w) were added. The NR seed latex was swollen with the monomer mixture for 1 h at reaction temperature before adding the initiator. The polymerization reaction condition was the stirring speed of 200 rpm and the reaction time of 8 h under reflux at the reaction temperature. The polymerization temperature was maintained constant for polymerization runs. Samples were taken at intervals to determine the monomer conversion on a weight basis. The post treatment included the coagulation of polymer latex and washing by deionized water. The gross polymer was recovered and dried to a constant weight in a vacuum oven at 40°C for 24 h. The complete experimental procedure is summarized in Figure 3.1. The standard recipes used for the graft copolymerization is shown in Table 3.1.

Table 3.1 Standard recipes used for graft copolymerization.

Ingredients	Quantities
Natural rubber (60% DRC)	50 g
Water	70 g
Stabilizer amount	3 g
Buffer amount	0.12 g
Redox initiator amount	
CHPO:TEPA = 1:1	Variable
Surfactant amount	Variable
Chain-transfer agent	Variable
Styrene amount	Variable
Methyl methacrylate amount	Variable

3.2.3 Determination of Monomer Conversion

The gravimetric analysis was based on total polymer. To determine the monomer conversion, latex samples (ca. 5 ml) were pipetted from the polymerization vessel into a tared weighing aluminum dish at predetermined times during the polymerization, and three drops of 1% hydroquinone solution were added to each dish to quench the polymerization. The dishes were dried to a constant weight in a vacuum oven (~ 40°C). The % solid was determined.

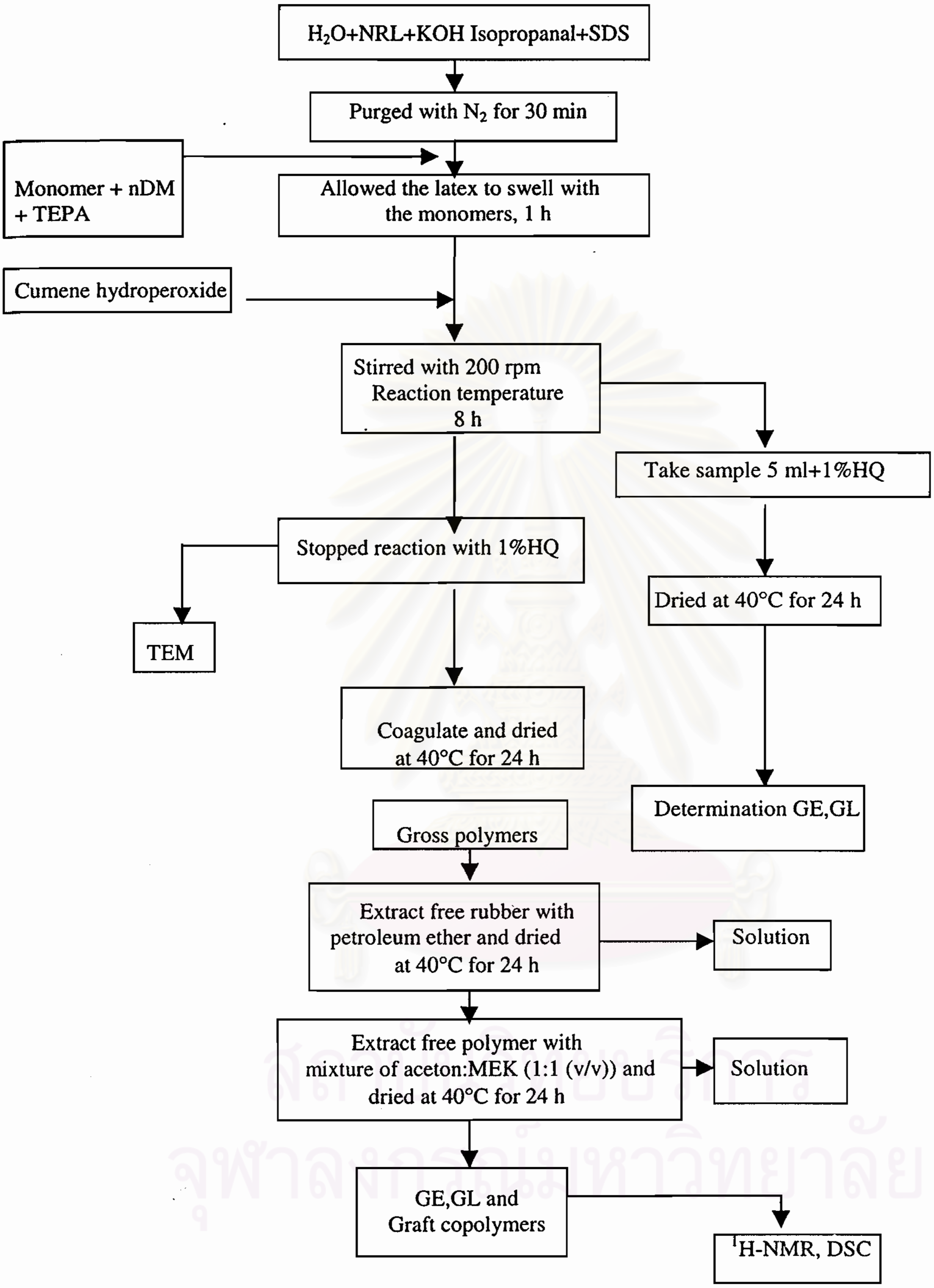


Figure 3.1 The complete experimental procedure.

The sample also included solid residues other than polymer, so these residues (emulsifier, initiator, etc.) were taken into account to calculate the conversion. The samples were corrected for the non-polymeric solid content by knowledge of the initial charge to the reactor. The conversion, a measure of how much monomer is converted into polymer, was calculated::

$$x = \frac{\left[\left(\frac{\%\ \text{solids}}{100}\right) - \text{weight fraction initiator - weight fraction emulsifier}\right]}{(\text{weight fraction monomer initially})} \qquad (3.1)$$

3.2.4 Product Characterization

The free rubber, free copolymers, graft copolymer, grafting efficiency, and grafting level were determined by soxhlet extraction, as mentioned in the previous section (Section 2.2.3.1).

3.2.5 Graft Copolymer Composition

The characterization of graft copolymers is much more complex than the characterization of low –molecular- weight polymer. Spectroscopy is among the most useful tools because it provides direct information on the polymer; for a graft copolymer, one can hope to identify the composition. Graft copolymer composition was determined using proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy, which was found to combine accuracy and reproducibility (± 2 weight per cent) with ease of analysis. A Bruker AC 250 MHz NMR spectrometer was used. Analysis was carried out in deuterated choloform (MSD Isotopes - approximately 2 per cent (w/v) at room temperature). The ^{1}H-NMR signal assignments for graft copolymers is presented in Table 3.2.

Table 3.2 ^{1}H-NMR signal assignments for graft copolymers.

Unit	Type of proton	ppm
Isoprene	Olefinic protons	5.1
Styrene	Aromatic protons	7.5-6.5
Methyl methacrylate	Methoxy protons	3.7
Isoprene Styrene Methyl methacrylate	All aliphatic protons	3.7-0.2

The GE and graft copolymer composition can be determined using NMR spectroscopy. From the different signal areas, the amount of styrene per proton (ST), the amount of isoprene per proton (NR), and the amount of MMA per proton (MMA) were calculated by the following equation:

$$ST = \frac{A_{\delta=7.5-6.5}}{5} \qquad (3.2)$$

$$MMA = \frac{A_{\delta=3.7}}{3} \qquad (3.3)$$

$$NR = \frac{A_{\delta=5.1}}{1} \qquad (3.4)$$

Then, the fraction of styrene (F_{ST}-g) and methyl methacrylate (F_{MMA}-g) in the graft copolymers were calculated by following equation:

$$F_{ST}\text{-g} = ST/(ST+MMA) \qquad (3.5)$$

$$F_{MMA}\text{-g} = MMA/(ST+MMA) \qquad (3.6)$$

3.2.6 Glass Transition Temperatures

The DSC thermograms of graft copolymers were obtained using a Perkin-Elmer DSC-4 differential scanning calorimeter with a Perkin-Elmer thermal analysis data station Model TADS-101. A 10 mg sample was placed in DSC sample pan, and the heating rate was 10°C • min $^{-1}$. The sample was quenched to -150°C, heated to 200°C, and kept at this temperature for 2 min, quenched again to -150°C, followed by heating to 200°C to remove the heat history and the second heating scan was recorded. The temperature at the inflection point was the glass transition temperature (T_g).

3.3 Experimental Design

Factorial designs can be extremely useful for a process about which little is known. A large number of variables are screened to determine the relationship which has a desired response, thus the factorial design is the most efficient approach to adopt [7]. These designs allow one to study a large number of variables simultaneously, while a large amount of information is obtained with a reduced experimental effort. When using screening design (two level fractional factorials), there is often confounding presented between the main effects and higher order interactions. With a judicious choice of the design however, the degree of confounding can be suitably reduced.

The clarification of experimental kinetics is an iterative process involving four steps as described by Box and Draper [8]. These steps are Conjecture, Design, Experimentation and Analysis. After the preliminary analysis step, one can return to the conjecture and design steps and start the iterative procedure again.

All four steps are necessary in a thorough experimental program. Experimentation usually results from conjecture about a process or the desire to learn more about a given process. Usually, as much emphasis must be placed on the design of experiments as on experimentation itself. Analysis of the results becomes equally important since proper analysis will ultimately lead to the best design for the next experimental phase. Neglecting the design of experiments will likely increase the experimental effort and perhaps invalidate the results.

3.3.1 Terminology [9]

Before discussing the results, it will be beneficial to review some terminology specific to experimental design. The definitions given below are adapted from Box, Hunter, and Hunter [7].

Factor: an independent variable, which is to be studied.

Level: amount or type of an independent variable used for a given experiment.

Generator: defining or type of an independent variable used for a given experiment.

Resolution: defines the confounding patterns present in a given design.

Confounding: when a given effect is assigned to more than one factor it is said to be confounded (confused).

Effects: the average change in response on moving from the low level to the high level of a given factor.

Interaction: if a two-factor interaction exists it means that the observed effects do not behave in an additive manner.

Factorial designs, one class of experimental designs, are very useful in identifying the main effects and interactions between two ore more effects 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 provide a more efficient approach to deal with a large number of variables.

3.4 Results and Discussion

Factorial designs require 2^N experiments if N factors have to be investigated. In this work, with six variables, this would lead to 64 experiments, which is still a large number. The number of experiments can be reduced by using only part of the factorial design (fractional factorial design) without loss of information about the main effects. However, some information about interaction effects will be lost. In this case, a fractional factorial was chosen since the higher-order interactions were expected to be negligible. One quarter of the 64 experiments, are chosen giving 16 experiments.

Statistical analysis was used to study the influence of each process variable irrespective of and in combination with the other process variables on the grafting efficiency, graft copolymers and free copolymers which are the responses or dependent variables to be measured for each run. Process variables were varied according to a 2^{6-2} design, Resolution R = (IV). A 2_{IV}^{6-2} fractional factorial design was chosen to estimate the main effects of the six variables studied. The design was of resolution IV, which means that the main effects were confounded with three-factor and greater interactions. Three-factor interactions in chemical processes are generally assumed to be negligible, although they cannot be completely neglected. Confounding was present among two-factor interactions but some knowledge of graft copolymerization kinetics allowed for interpretation of these results. For each process variable a "- level" and "+ level" was 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 3.3 are initiator concentration (INT), emulsifier concentration (EMUL), chain-transfer agent concentration (CTA), methyl methacrylate to styrene ratio (ST/MMA), monomer to rubber ratio (M/R) and reaction temperature (TEMP). The coding scheme and design factors of 16 experiments are shown in Table 3.4. Each combination of – and + levels represented an experiment. The results of graft copolymerization are shown in Table 3.5.

Table 3.3 Graft copolymerization runs: low and high level of design factors.

Ingredient	Name	Amount (Low = -1)	Amount (High = +1)
[INI]	cumene hydroperoxide	1 phr	2 phr
TEMP	reaction temperature	50°C	70°C
[EMUL]	SDS	1 phr	2 phr
[CTA]	n-dodecyl mercaptan	0 phr	0.5 phr
ST/MMA	styrene/methyl methacrylate	0.75	1.0
M/R	monomer/rubber ratio	1.0	1.25

Table 3.4. Design factor levels for factorial designed experiments.

Experiment	Design factor					
	INI	TEMP	EMUL	CTA	ST/MMA	M/R
GNR21	-1	-1	-1	-1	-1	-1
GNR22	+1	-1	-1	-1	+1	-1
GNR23	-1	+1	-1	-1	+1	+1
GNR24	+1	+1	-1	-1	-1	+1
GNR25	-1	-1	+1	-1	+1	+1
GNR26	+1	-1	+1	-1	-1	+1
GNR27	-1	+1	+1	-1	-1	-1
GNR28	+1	+1	+1	-1	+1	-1
GNR29	-1	-1	-1	+1	-1	+1
GNR30	+1	-1	-1	+1	+1	+1
GNR31	-1	+1	-1	+1	+1	-1
GNR32	+1	+1	-1	+1	-1	-1
GNR33	-1	-1	+1	+1	+1	-1
GNR34	+1	-1	+1	+1	-1	-1
GNR35	-1	+1	+1	+1	-1	+1
GNR36	+1	+1	+1	+1	+1	+1

Table 3.5 The experimental results of graft copolymerization for NR.

Experiment	Total conversion (%)	Free rubber (%)	Free polymer (%)	Graft copolymers (%)	Grafting efficiency (%)
GNR21	90.0	26.1	18.8	55.1	53.5
GNR22	92.6	22.1	12.1	65.8	70.5
GNR23	92.2	13.1	17.9	69.1	62.8
GNR24	93.5	13.6	9.9	76.5	79.5
GNR25	91.6	14.7	24.0	61.3	49.8
GNR26	93.5	15.1	26.7	58.2	44.7
GNR27	91.5	24.1	14.6	61.3	64.0
GNR28	93.3	20.1	6.0	73.9	85.4
GNR29	92.8	13.4	27.1	59.5	43.6
GNR30	93.9	10.0	25.7	64.2	46.9
GNR31	91.9	18.2	17.1	64.7	58.1
GNR32	92.8	18.8	18.7	62.5	54.5
GNR33	91.5	20.0	17.5	62.5	56.9
GNR34	93.1	20.5	21.8	57.7	47.0
GNR35	91.7	11.8	26.2	62.1	45.3
GNR36	93.6	8.4	23.3	68.4	51.9

3.4.1 Rate of Polymerization

For graft copolymerization of styrene and methyl methacrylate on NR, monomer conversion as a function of reaction time was investigated. Figure 3.2 show the monomers conversion vs. time profiles for all 16 experiments from 2^{6-2}_{IV} fractional factorial design. When using fractional designs, more than one variable is changed per experiment and the conversion vs. time profiles for 2^{6-2}_{IV} design are grouped according to chain transfer agent amount at each of the two temperature levels.

For all sixteen experiments, the shape of conversion *vs* time curves was identical and the rate of polymerization was similar. The polymerization rates were extremely rapid at initial period (<180 sec) before reaching a plateau level. From Figure 3.2, the cumene hydroperoxide/tetraethylenepentamine, redox initiator, was effective for graft copolymerization under a wide variety of conditions. This is shown by the rapid increase of monomer conversion. After the first 2-3 hours, conversion of vinyl monomer in the reactor was high and remained constant. Although a slight difference among the limiting conversions reached was observed (probably within experimental error), under no circumstance, did the conversion levels approach 100 percent.

Figure 3.2a and 3.2b show the conversion *vs* time profiles at low level temperature and high level temperature, respectively. It can be seen that it takes a much longer time to reach a limiting conversion using the low level temperature when compared with the high level temperature. Because the rate of redox reaction usually follows Arrhenius type relationships and consequently, the decomposition rates increase. Therefore, at higher temperatures, more primary radicals were produced initially and the rates of polymerization were faster than those at lower temperatures.

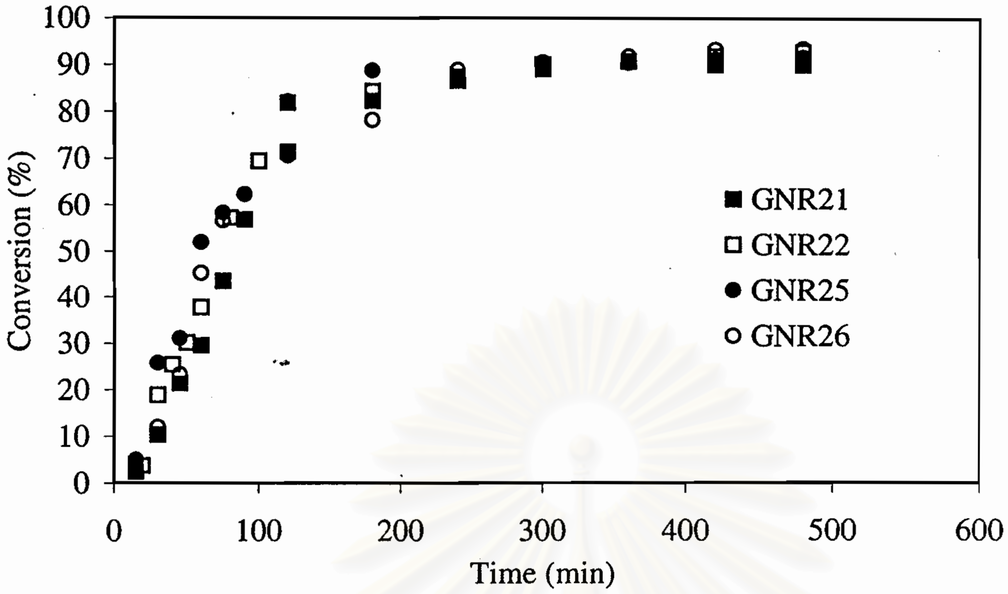


Figure 3.2a Conversion *vs* time profiles for GNR21, GNR22, GNR25, and GNR26 (low level TEMP and low level CTA).

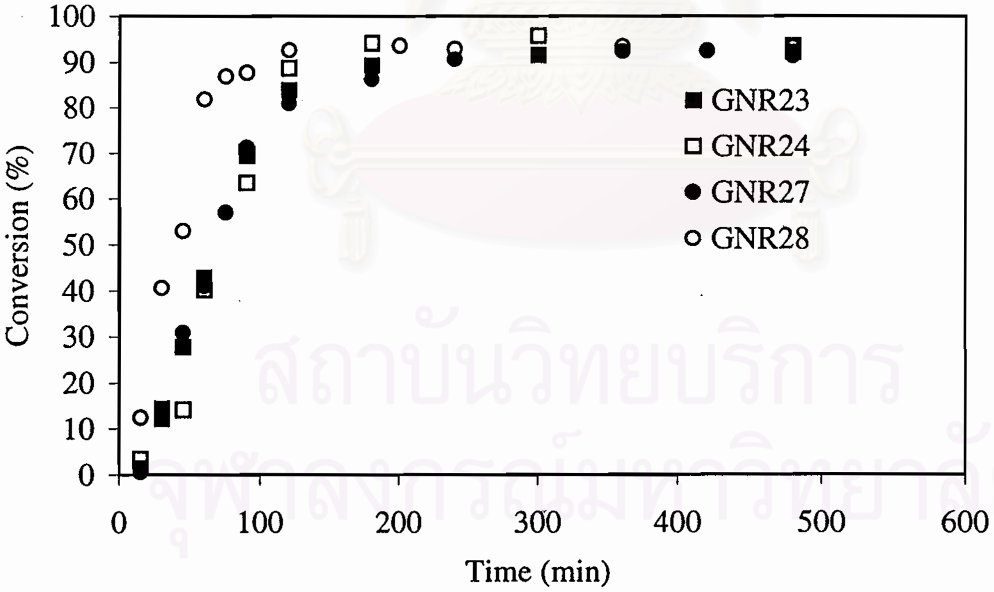


Figure 3.2b Conversion *vs* time profiles for GNR23, GNR24, GNR27, and GNR28 (high level TEMP and low level CTA).

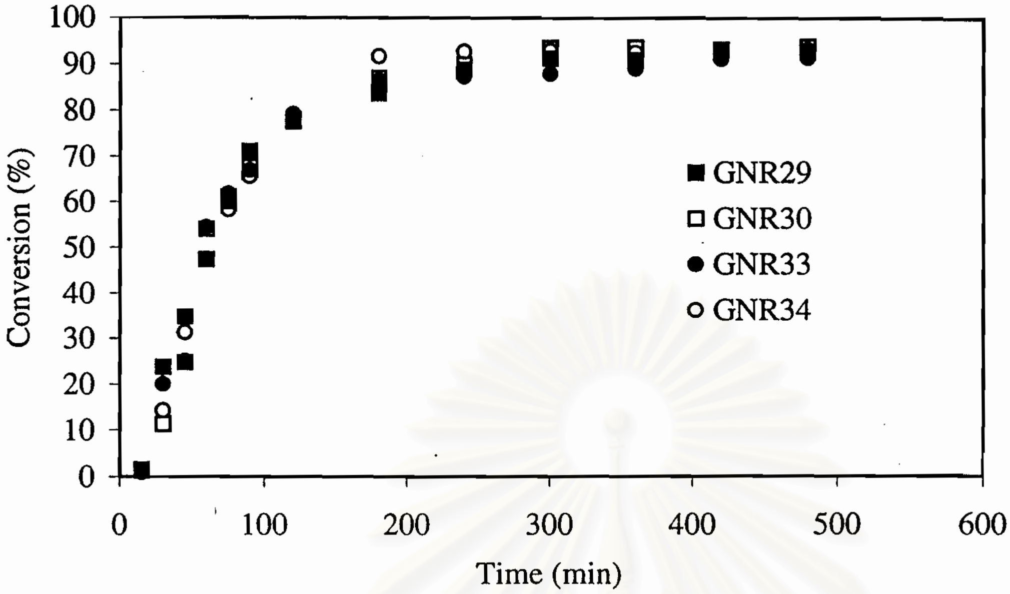


Figure 3.2c Conversion *vs* time profiles for GNR29, GNR30, GNR33,

and GNR34 (low level TEMP and high level CTA).

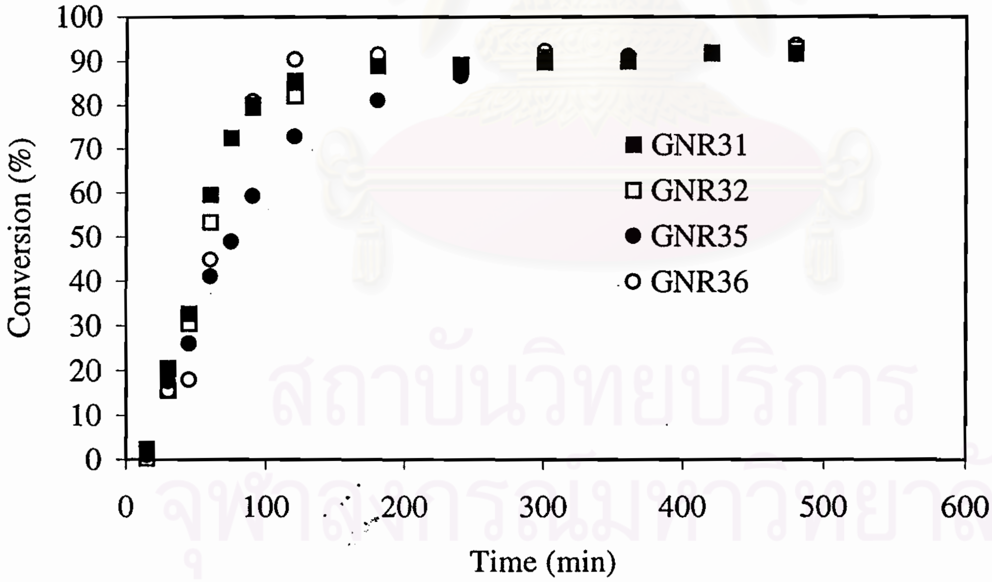


Figure 3.2d Conversion *vs* time profiles for GNR31, GNR32, GNR35,

and GNR36 (high level TEMP and high level CTA).

Figure 3.2a and 3.2c show the conversion *vs* time profiles for the experiments using the low level and high level amount of chain transfer agent, respectively. There were no significant differences in polymerization rate between the low level and high level amount of chain transfer agent. It is possible that only free copolymerization occurred and the free copolymers were entangled with the seed particles. When the chain transfer agent was added, the amount of chain transfer agent did not further influence the rate of polymerization.

Figure 3.3 shows the plots of grafting efficiency versus conversion which had the similar trend for all sixteen experiments. At the beginning (conversion <10%), no graft copolymerization was observed. As the polymerization proceeds, the grafting efficiency, increased gradually over the range of conversion of 10 to 85% and then steeply increased at high conversion (>85%). The results can be explained by an " encapsulation" process as discussed in Section 2.3.7. At the beginning, the conversion increased rapidly since most of the styrene and methyl methacrylate was polymerized in the aqueous phase to form new particles which became bound to the swollen particle surface and then encapsulated the seed

Therefore, at low monomer concentration, the probability for chain transfer to NR would increase, so more graft sites were initiated, leading to a sudden increase in GE at high conversion (>85%). A sudden increase in GE with high conversion 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 particle. 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. On the other hand, polymer molecules are considered to be incapable of moving freely inside the

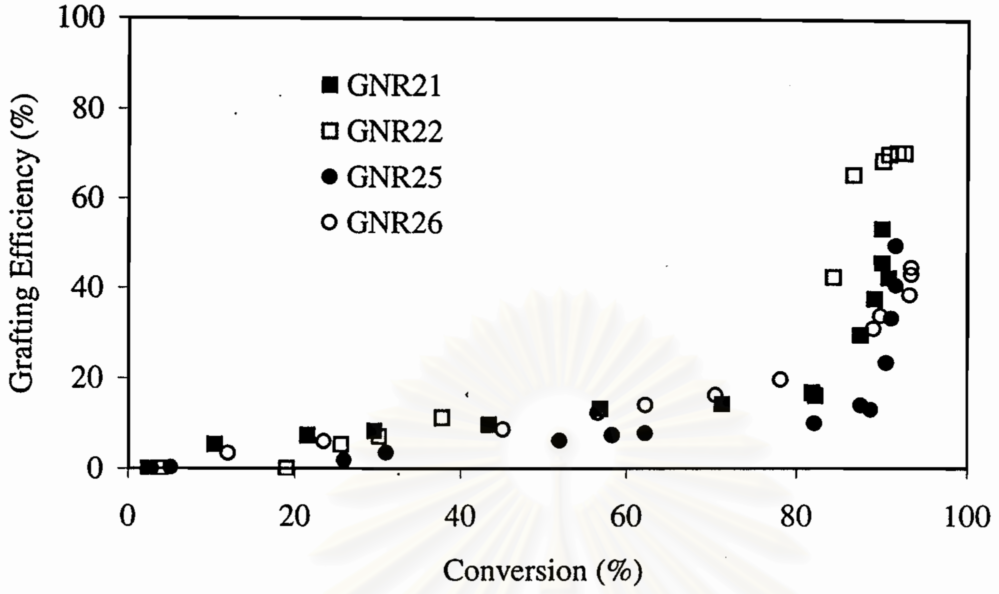


Figure 3.3a Grafting efficiency as a function of conversions for GNR21, GNR22, GNR25, and GNR26 (low level TEMP and low level CTA).

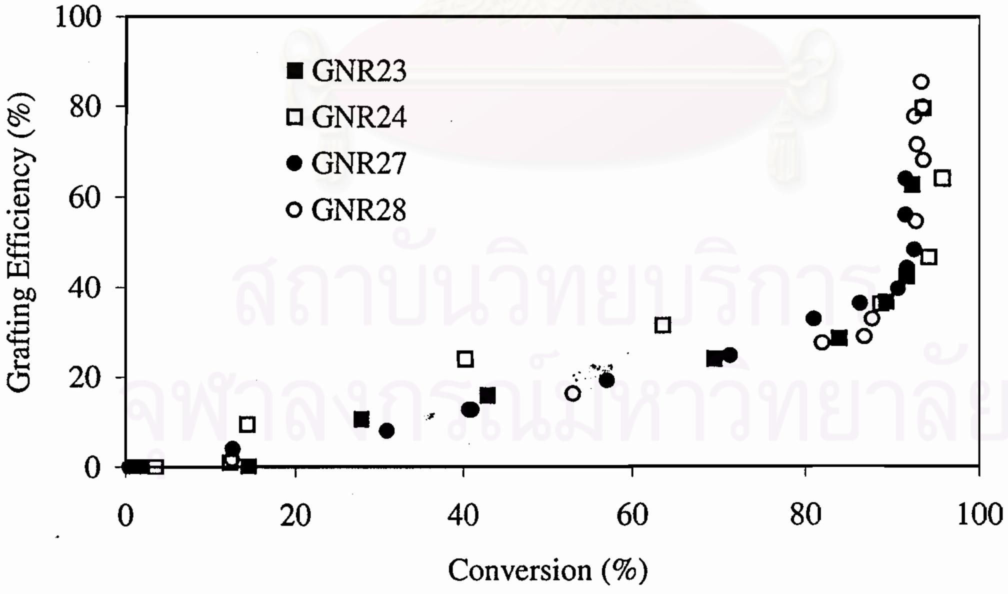


Figure 3.3b Grafting efficiency as a function of conversions for GNR23, GNR24, GNR27, and GNR28 (high level TEMP and low level CTA).

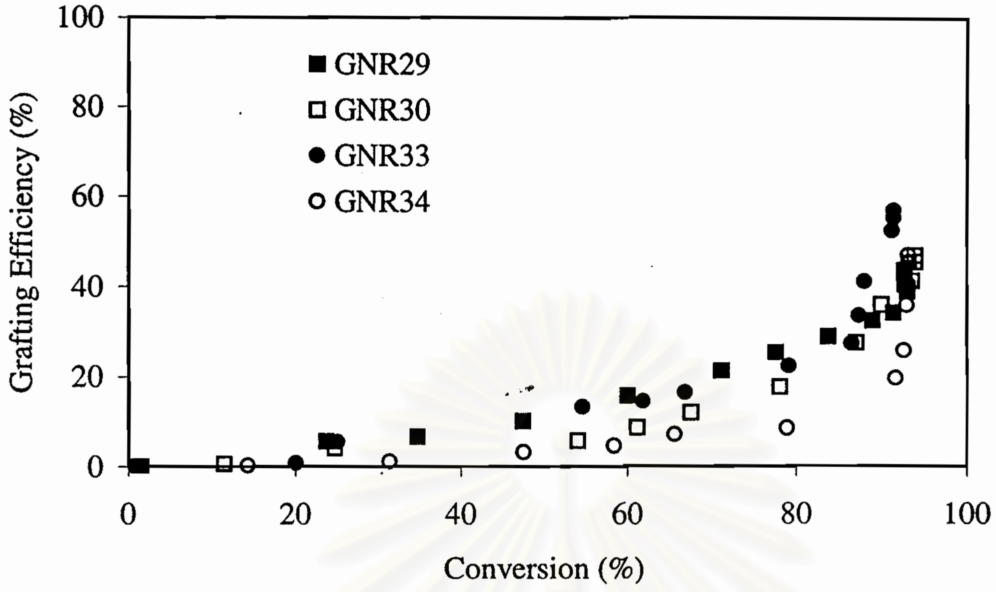


Figure 3.3c Grafting efficiency as a function of conversions for GNR29, GNR30, GNR33, and GNR34 (low level TEMP and high level CTA).

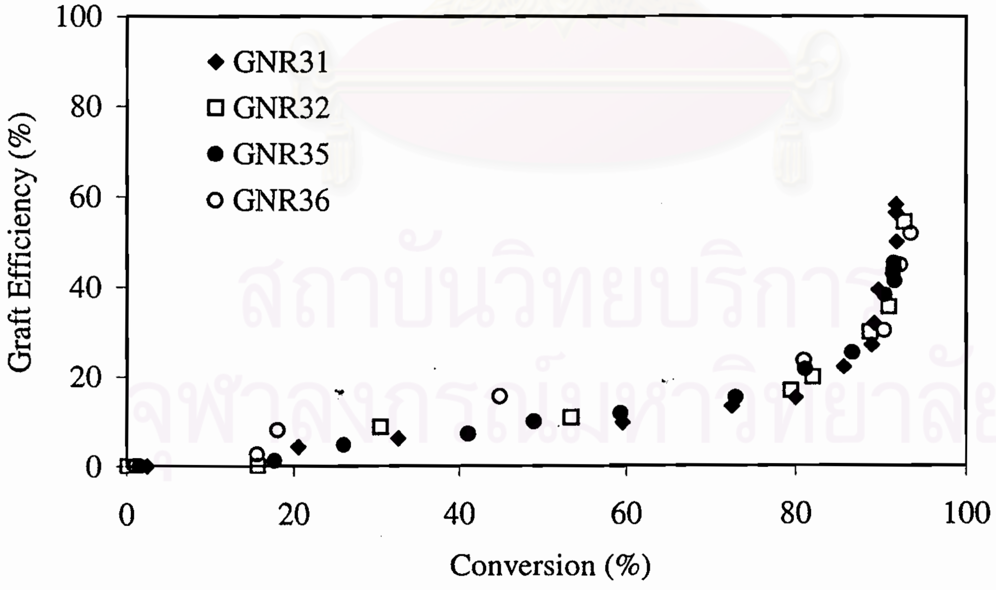


Figure 3.3d Grafting efficiency as a function of conversions for GNR31, GNR32, GNR35, and GNR36 (high level TEMP and high level CTA).

latex particle because of long chain characteristics and chain entanglements. At the beginning, most of monomers may be polymerized to form new growing polymer molecule, which can move by molecular motion or by propagation event, and this causes an effective increase in conversion. The growing polymeric radical, preferentially concentrated at the surface layer 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 high conversion. The extent of graft copolymers formation depends upon time. Transfer reactions are certainly dependent on the mobility of the monomer. Similar results of graft copolymerization of styrene and methyl methacrylate onto polybutadiene were observed by Aderts et al. [9].

3.4.2 The Influence of Process Variables

Within this framework, the process variables including the concentrations of initiator, emulsifier, and chain-transfer agent, the reaction temperature, the ratio of monomer mixture, and monomer to rubber ratio were investigated. The grafting efficiency was analyzed using analysis of variance (ANOVA). To ensure that the assumptions of normality and constant variance were met, the response variable, grafting efficiency, was calculated. According to the definition, the main effect of the controlled independent variable is the mean of the difference between the values at the high level (+) and the values at low level (-). Results for the mean grafting efficiency are shown in Table 3.6.

The F test was used to evaluate if a factor has a significant effect (F > 18.5). Results for main effects and two-factor interactions are shown in Table 3.7. Table 3.7 shows the F test of effects of the process variables on grafting efficiency. The effects

Table 3.6 The effect of process variables on mean grafting efficiency for NR.

Statistical experimental design	Mean	-95% Cnf. Limt	95% Cnf. Limt
CTA			
-1	63.77	57.47	70.06
+1	50.52	44.22	56.81
TEMP			
-1	51.61	45.31	57.90
+1	62.68	56.39	68.98
M/R			
-1	61.23	54.94	67.53
+1	53.05	46.76	59.35
ST/MMA			
-1	54.01	47.72	60.31
+1	60.27	53.98	66.57
INT			
-1	54.24	47.94	60.53
+1	60.058	53.75	66.34
EMUL			
-1	58.66	52.36	64.95
+1	55.63	49.34	61.92

Note: Std. Errs. for mean = 2.78

Table 3.7 Results for main effects and two-factor interactions for response and the analysis of variance of % GE for NR.

Effect Name	GE(%)	SS	df	MS	F[a]	Signif.
Mean	57.14					
INT	5.81	134.90	1.00	134.90	8.80	No
TEMP	11.07	490.60	1.00	490.60	32.00	Yes
EMUL	-3.03	36.65	1.00	36.65	2.39	No
CTA	-13.25	702.19	1.00	702.19	45.81	Yes
ST/MMA	6.26	156.65	1.00	156.65	10.22	No
M/R	-8.18	267.61	1.00	267.61	17.46	?[b]
INT by TEMP	4.46	79.63	1.00	79.63	5.20	No
INT by EMUL	-2.55	25.91	1.00	25.91	1.69	No
INT by CTA	-6.73	181.08	1.00	181.08	11.81	No
INT by ST/MMA	0.98	3.83	1.00	3.82	0.25	No
INT by M/R	-0.43	0.73	1.00	0.72	0.05	No
TEMP by CTA	-7.24	209.86	1.00	209.86	13.69	No
TEMP by M/R	2.54	25.80	1.00	25.80	1.68	No
Error		30.66	2.00	15.33		
Total SS	2346.09	15.00				
R^2=0.98693						

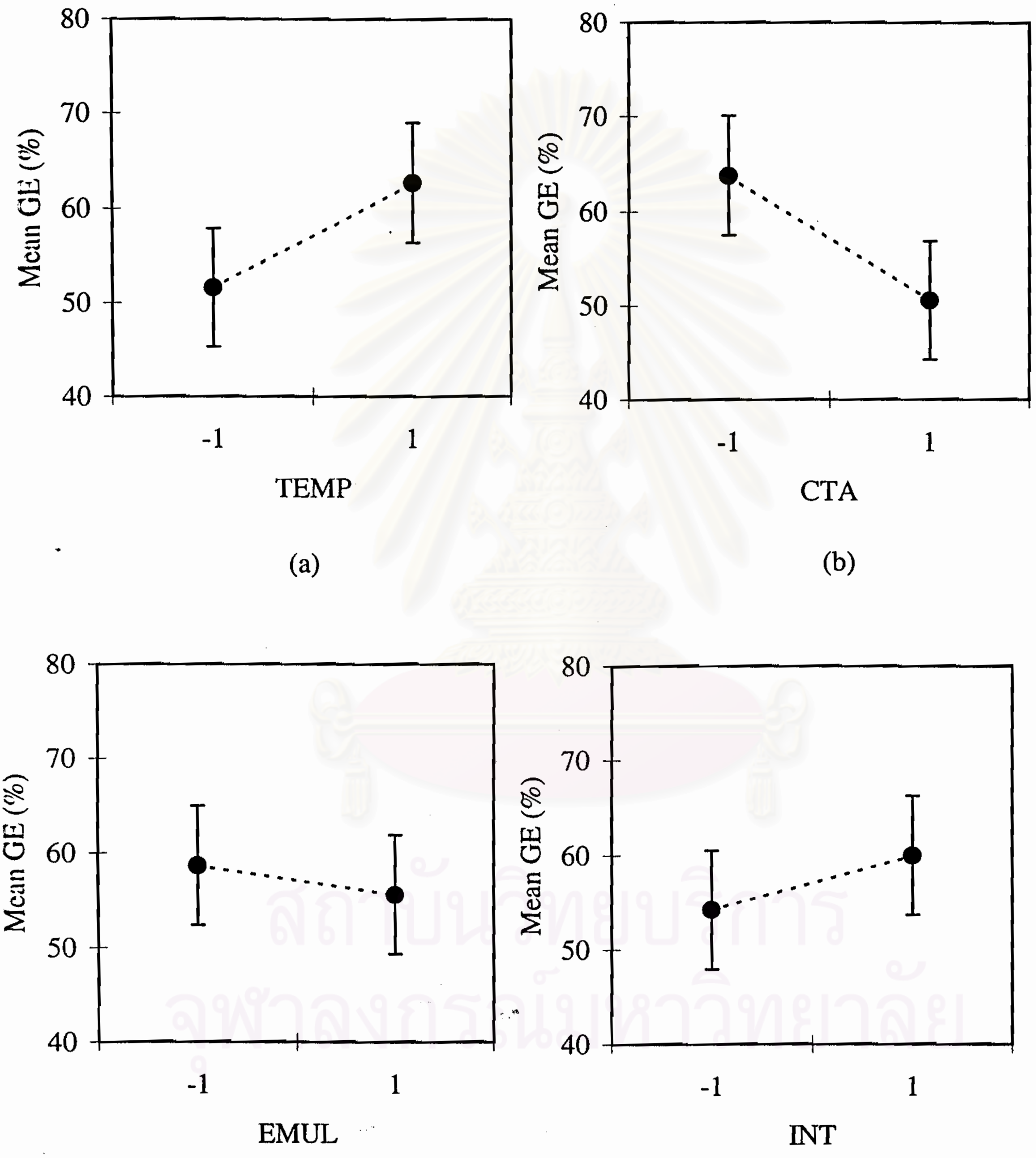
[a] F(1,2) = 18.5 with $\alpha = 0.05$. If $F < 18.5$, then the variable is not significant.

[b] this variable is marginally significant.

of the variables and any interactions, which are significant with respect to grafting efficiency, can be identified. An “effect” is defined as the change in the response (in this case the grafting efficiency) on changing the variable from the “-” level to the “+” level.

Regarding the decision about which terms were significant, for the purposes of this study, the 95% confidence interval ($F_{1,\,2} > 18.5$) was used. In this design two significant effects with respect to grafting efficiency were CTA and TEMP and one marginally significant effect was M/R. All interactions could be eliminated because of no significance (see in Table 3.7).

The negative effect, EMUL, has a small effect on the grafting efficiency when the amount of emulsifier changes from a low level to a high level (Figure 3.4). The seeded batch graft copolymerizations were performed in the so-called stage III of emulsion polymerization. The emulsifier, adding in the second stage emulsion polymerization, was ineffective in stabilizing the particles. The emulsifier concentration on the seed particle surface has little effect on GE in the absence of coagulation or renucleation of particles when the emulsifier-to monomer weight ratio is less than 2% [10]. It is assumed that during this reaction the chemically bonded sulfate groups do not become shielded, thus maintaining latex stability. At a high level of emulsifier concentration, the grafting efficiency slightly decreased, due to the occurrence of second nucleation This indicates that under such conditions, more free micelles exit in the water phase; these could be initiated to form a new crop of particles, so there would be less monomer left for grafting. The increase of grafting efficiency at a low level amount of emulsifier can be explained by the enhanced presence of initiator at the surface. Some parts of the redox initiator systems are in the aqueous phase and others in the oil phase, therefore it is expected that the initiator will be most active at the surface.



(a) (b)

(c) (d)

Figure 3.4 Effect of (a) TEMP, (b) CTA, (c) EMUL and (d) INT on mean grafting efficiency.

INT had a positive effect since the GE increased with increasing amount of initiator (Figure 3.4). The mean grafting efficiency increased from 54.24 to 60.05 when the amount of initiator was increased from 1.0 to 2.0 phr respectively. The increase in the initiator concentration caused the increased rate of radical entry. This can be explained by the fact that the radicals transfer to either rubber or monomer, producing macroradicals, resulting in an increase in grafting. As the initiator concentration is increased, it is probable that the number of grafting sites increase while more free copolymers are produced, therefore, the overall amount of graft copolymers increase slightly.

The positive effect of ST/MMA ratio on grafting efficiency was examined. The mean grafting efficiency increased from 54.01 to 60.27 when the ST/MMA ratio was increased from 0.75 to 1 respectively. For GNR27 and GNR28 (Table 3.4) two variables were ST/MMA and INT. The ratio of ST/MMA mainly affected the composition of the graft copolymers. Figure 3.5 shows that the fraction of ST and MMA in the free copolymer decreased dramatically with increasing conversion. There are some differences in the fraction of ST and MMA in the graft copolymers and free copolymers between the two experiments, GNR27 (ST/MMA ratio = 0.75) and GNR28 (ST/MMA = 1). The fraction of ST and MMA in the free copolymers of GNR27 was higher than that of GNR28. The fraction of ST and MMA in the graft copolymers of GNR27 was lower than that of GNR28. This indicates that when the amount of styrene in the monomer mixture was increased, a more favorable condition resulted to produce graft copolymers rather than free copolymers. Thus ST was grafted and left a substantial amount of MMA in the water and polymer phase. It can be concluded that high grafting efficiency was achieved a high level ST/MMA.

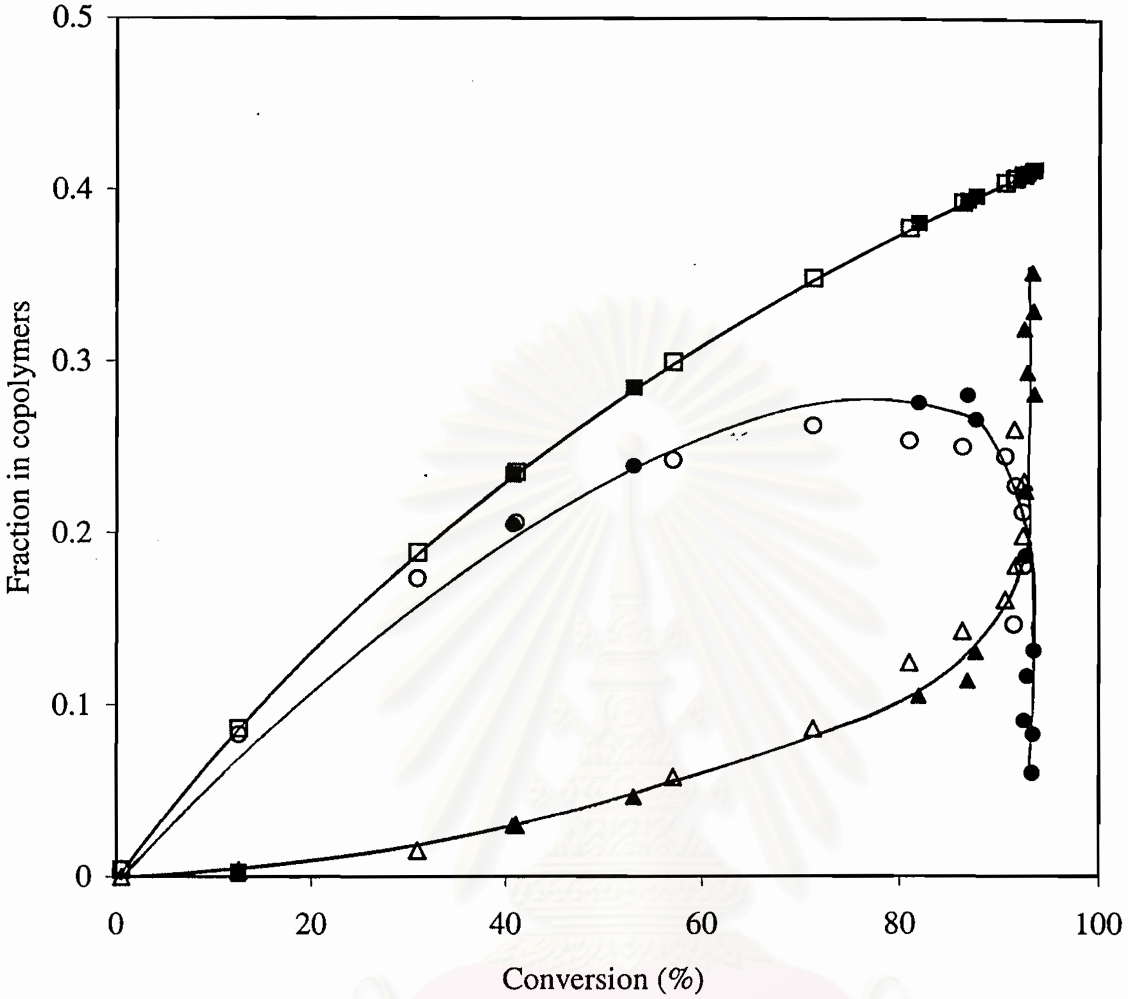


Figure 3.5 Variation of fraction of ST and MMA with conversion

▲, in graft copolymers; ●, in free copolymers; ■, total

polymerization for GNR28 (high level ST/MMA)

△, in graft copolymers; ○, in free copolymers; □, total

polymerization for GNR27 (low level ST/MMA).

On the other hand, for the styrene/methyl methacrylate grafting system, the attack of alkoxy radicals on *cis*-polyisoprene occurs most likely by chain transfer to form the polyisoprenyl radical. This polyisoprenyl radical, in a styrene polymerization environment, can compete for the styrene monomer and form graft copolymers since the reactivity of the polystyryl radical is about the same as that of the polyisoprenyl radical (both are stabilized by resonance). So, ST is grafted easier than MMA. Further evidence for this will be presented later, (Section 3.4.3).

Statistical analysis of the data (F test in Table 3.7) showed that only CTA and TEMP had a significant effect on GE. When the mean at the low (-) level is compared with the mean at the high (+) level, it can be seen that GE is negatively affected by CTA., CTA had the strongest effect on GE. The mean grafting efficiency decreased from 63.77 to 50.52 when the amount of chain-transfer agent was increased from 0 to 0.5 phr, respectively. Figure 3.6 shows the grafting efficiency *vs* conversion for GNR28 (low level of chain-transfer agent and high level of initiator concentration) and GNR31 (high level of chain-transfer agent and low level of initiator concentration). Addition of chain-transfer agent would affect mainly the transfer reactions altering graft chains. It is not perceived to affect the primary radical production. From the F test results shown in Table 3.7, the effect of the amount of initiator does not significant, Thus, amount of chain-transfer agent is the only remaining variable. For GNR28, where no mercaptan is used, the GE is increased with conversion. For GNR31, mercaptan is added, GE remains constant over a wide conversion range and steeply increased at a high conversion. This can be explained on the basis that the radicals of a graft chain or polymer backbone is most likely to transfer to the chain-transfer agent and then the new chains formed by this chain-transfer agent radical grafts again. For GNR28, there is no transfer to chain-transfer agent, so more transfer to polymer backbone and monomers takes place and as a result more grafting will occur at an earlier stage of the reaction. However, the GE of both experiments is approximately the same in the beginning of the polymerization (<40% conversion). At the end of the reaction, the GE of GNR31 (0.5% nDM) is less than that of GNR28 (0% nDM). This implies that the presence of mercaptans in the reaction mixture hinders the propagation of the chains. Thus, GE decreased in the presence of a chain-transfer agent.

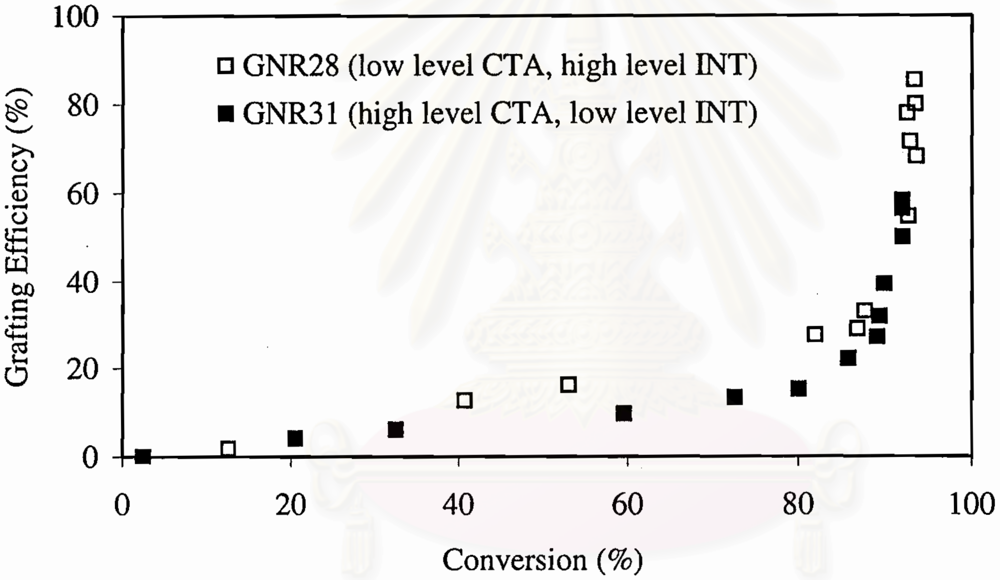


Figure 3.6 Grafting efficiency as a function of conversion for GNR28 and GNR31.

The polymerization temperature, TEMP, had a positive effect on grafting efficiency. The mean grafting efficiency increased from 51.61 to 60.05 when the temperature was increased from 50°C to 70°C respectively. Figure 3.7 shows the grafting efficiency *vs* time for GNR22 (the low level of emulsifier and temperature) and GNR28 (the high level of emulsifier and temperature). The emulsifier only served to enhance the particle stability and would not likely affect the radical generation. The

GE of GNR28 (high level temperature) is higher than that of GNR22 (low level temperature). The percentage of grafting efficiency increases, with increasing temperature, this is due to swellability of rubber, solubility of monomer, and its high diffusion rate, and the rate of decomposition of the initiator, which depend on the temperature. On the other hand, higher temperature may reduce the viscosity of the system and increase the mobility of the molecular chains to facilitate the grafting reaction. Furthermore, Sundberg et al. [6] states that the major influence of temperature is that the actual concentration of monomer in the particle can be very low at higher temperatures. This means that the monomer/rubber ratio in the rubber phase may be very low throughout the entire reaction process, which should promote higher grafting efficiency.

The graft efficiency decreases with increasing M/R ratio (see Table 3.6). The mean grafting efficiency decreased from 61.23 to 53.05 when the monomer to rubber ratio was increased from 1:1 to 1.25 respectively. In order to explain the reduced grafting, as a function of the increase in M/R ratio, recall the Section 2.3.6 in which grafting occurs mainly on the surface of the particles. When the M/R ratio increases, the contact area between monomer and natural rubber decreases gradually. As a result, the grafting efficiency decreases with increasing M/R ratio. There were three variables for experiment GNR29 and GNR34; these variables were amount of initiator, amount of emulsifier and M/R ratio. The F test results shown in Table 3.7 indicate that the different amounts of initiator and emulsifier are not significant. Therefore, the M/R ratio is the only remaining variable, which affects the grafting efficiency. Figure 3.8 shows that the grafting efficiency of GNR29, is higher than that of GNR34 at the beginning and then lower than that of GNR34 at the end of graft

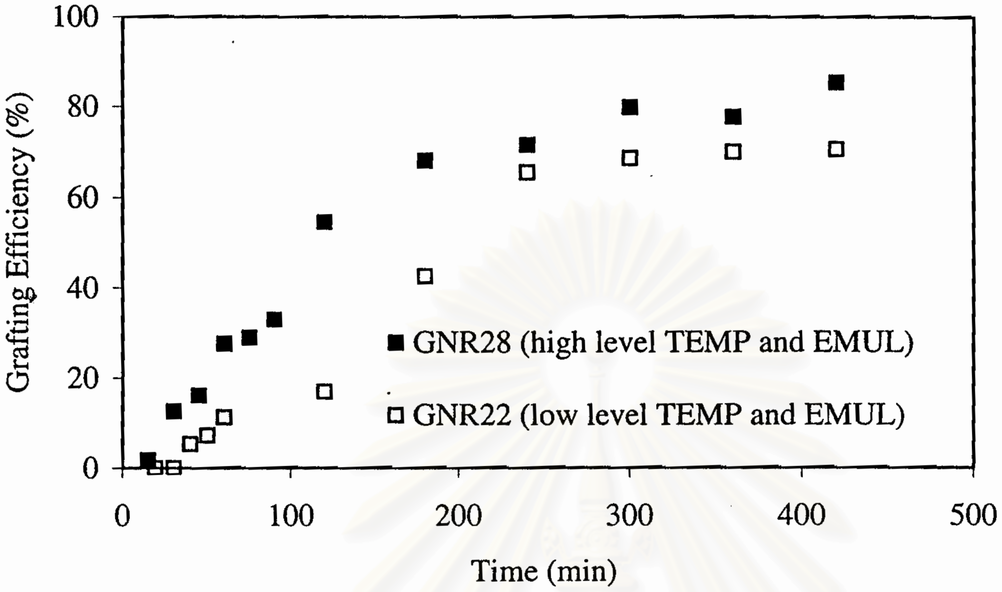


Figure 3.7 Grafting efficiency *vs* time profiles for GNR22 and GNR28.

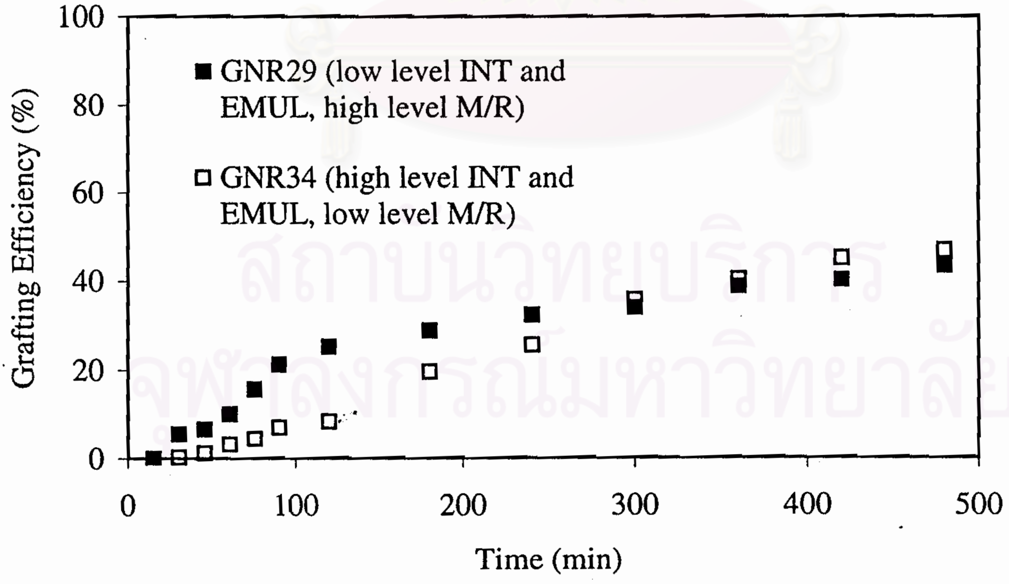


Figure 3.8 Grafting efficiency *vs* time profiles for GNR29 and GNR34.

reaction. As grafting proceeds and a certain shell thickness of grafted material is reached, grafting decreases due to the reduced availability of the polymer backbone. Therefore, more free copolymers are produced than graft copolymers. Also, systems with higher monomer to rubber ratio have lower surface area at the reaction site, and the rate of free copolymer termination of P(ST/MMA) is more favored than the rate of transfer of the polymeric radical to natural rubber, thus accounting for the reduced grafting efficiency with increased monomer to rubber ratio. This experiment was performed to confirm that grafting is a surface-controlled process.

3.4.3 The Graft Copolymer Composition

The graft copolymerization of styrene and methyl methacrylate in the presence of rubber latex using redox initiator gave the products of ungrafted natural rubber, polystyrene, poly(methyl methacrylate), and poly(isoprene-*graft*-[methyl methacrylate-*co*-styene]). The free rubber and free copolymers were removed from the product (crude sample) by extraction with petroleum ether and methyl ethyl ketone/acetone, respectively. The copolymer composition was determined from the ^{1}H-NMR spectrum of graft copolymers. The ^{1}H-NMR spectra of natural rubber and the graft copolymers are shown in Figure 3.9. The results are given in Table 3.8.

The nature of the initiator is important in graft copolymerization because it serves two functions. The first is to initiate the polymerization of the monomer resulting in polymeric radicals which then may attack the backbone polymer to produce a radical site along the backbone. The second is that the primary radical

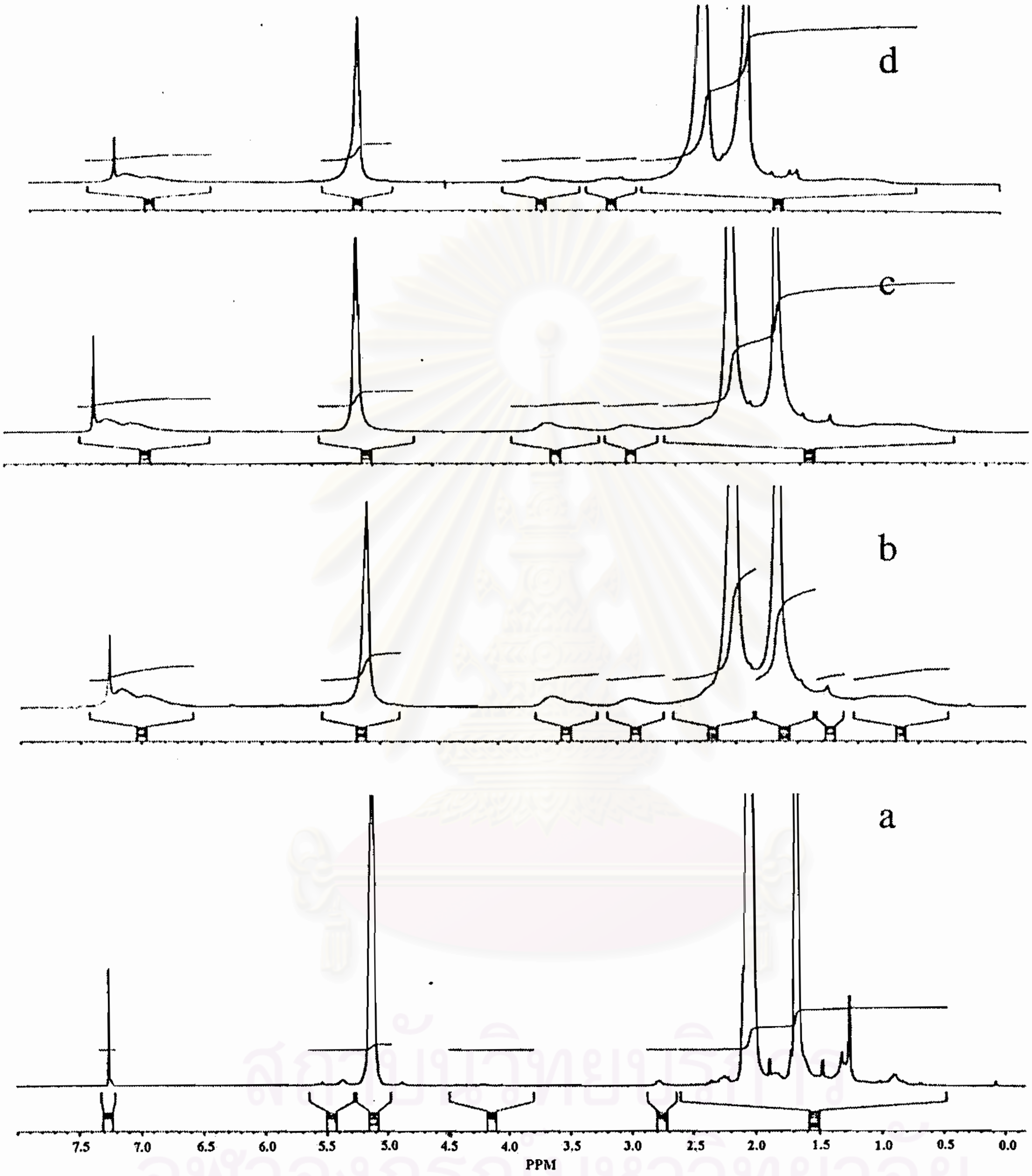


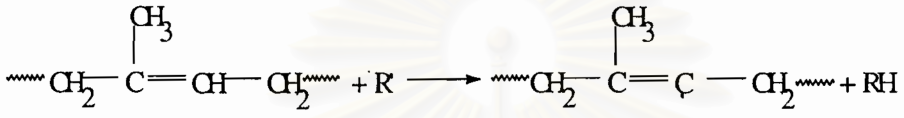
Figure 3.9 250 MHz ^{1}H-NMR spectra of (a) NR, (b) GNR21, (c) GNR26, and GNR34

Table 3.8 Graft copolymer compositions for NR.

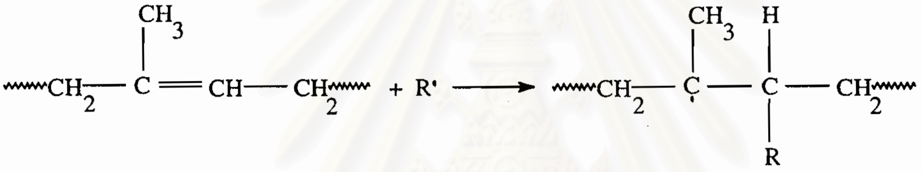
Experiment	ST (%wt)	Isoprene (%wt)	MMA (%wt)	F_{ST}-g	F_{MMA}-g	GE (%)
GNR21	10.6	81.5	7.9	0.563	0.437	53.5
GNR22	16.4	77.4	6.2	0.718	0.282	70.5
GNR23	14.2	77.1	8.7	0.613	0.387	62.8
GNR24	15.3	77.2	7.6	0.723	0.277	79.5
GNR25	15.4	79.2	5.4	0.733	0.267	49.8
GNR26	12.9	79.8	7.3	0.629	0.371	44.7
GNR27	15.3	77.9	6.8	0.686	0.314	64.0
GNR28	14.9	73.0	12.1	0.541	0.459	85.4
GNR29	9.2	85.4	5.4	0.620	0.380	43.6
GNR30	13.0	82.5	4.5	0.734	0.266	46.9
GNR31	10.5	79.0	10.5	0.519	0.481	58.1
GNR32	12.6	79.1	8.3	0.592	0.408	54.5
GNR33	10.7	82.8	6.5	0.610	0.390	56.9
GNR34	9.0	84.8	6.2	0.583	0.417	47.0
GNR35	13.0	82.7	4.3	0.744	0.256	45.3
GNR36	13.0	78.6	8.4	0.599	0.401	51.9

derived from the initiator itself may also attack the backbone polymer directly to produce a radical site along the backbone.

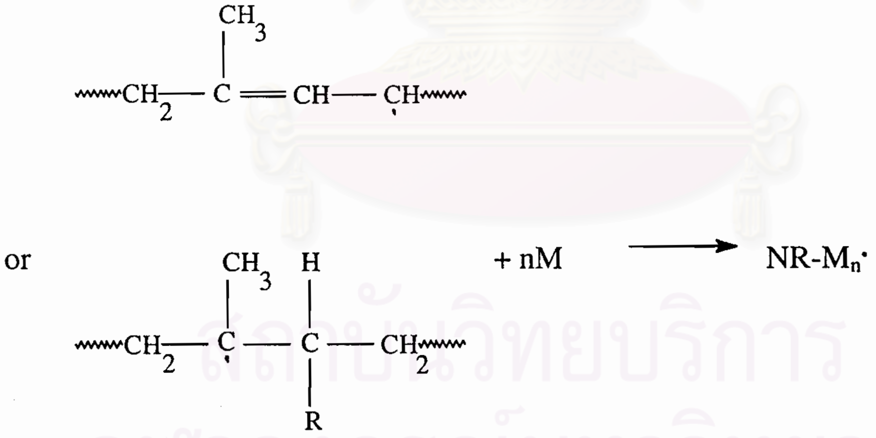
Allen et al. [11] proposed the grafting mechanism by using tracer methods of the graft polymerization of methyl methacrylate onto gutta-percha (tran-1,4-polyisoprene) in benzene solution at 60 °C. The reaction mechanism is as follows:



$$\sim CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2\sim + R^{\cdot} \longrightarrow \sim CH_2-\overset{CH_3}{\overset{|}{C}}=\underset{\cdot}{C}-CH_2\sim + RH \quad (3.7)$$



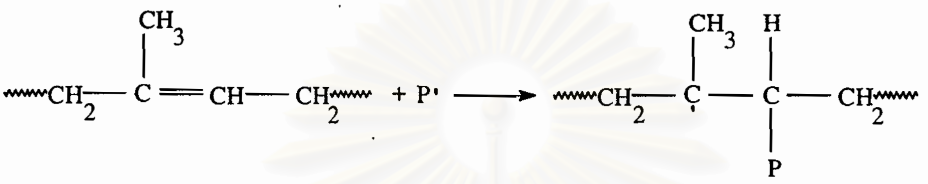
$$\sim CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2\sim + R^{\cdot} \longrightarrow \sim CH_2-\overset{CH_3}{\overset{|}{\underset{\cdot}{C}}}-\overset{H}{\overset{|}{\underset{R}{\underset{|}{C}}}}-CH_2\sim \quad (3.8)$$



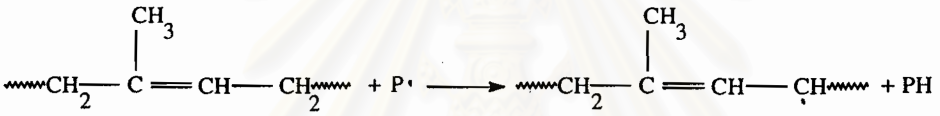
$$\left.\begin{array}{l}\sim CH_2-\overset{CH_3}{\overset{|}{C}}=CH-\underset{\cdot}{CH}\sim \\ \text{or} \\ \sim CH_2-\overset{CH_3}{\overset{|}{\underset{\cdot}{C}}}-\overset{H}{\overset{|}{\underset{R}{\underset{|}{C}}}}-CH_2\sim\end{array}\right. + nM \longrightarrow NR\text{-}M_n^{\cdot} \quad (3.9)$$

The results are consistent with the view that benzoyl peroxide initiates graft polymerization by direct reaction of the derived phenyl ($C_6H_5^{\cdot}$) and benzoyloxy ($C_6H_5\text{-}CO^{\cdot}O^{\cdot}$) radicals with the isoprene, (1) by addition to the isoprenic double bond (reaction 3.8), and (2) by abstracting α-methylenic hydrogen atom (reaction 3.7). They found that both chain transfer and double bond addition mechanism contributed to grafting site generation. However, the addition reaction (3.8) plays a minor role in relation to the transfer reaction (3.7).

The grafting reaction was proposed to occur by chain transfer reaction from propagating radicals to polymer chains [12].



$$\sim CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2\sim + P^{\bullet} \longrightarrow \sim CH_2-\overset{CH_3}{\overset{|}{\underset{\bullet}{C}}}-\underset{P}{\overset{H}{C}}-CH_2\sim \qquad (3.10)$$



$$\sim CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2\sim + P^{\bullet} \longrightarrow \sim CH_2-\overset{CH_3}{\overset{|}{C}}=CH-\underset{\bullet}{C}H\sim + PH \qquad (3.11)$$

The nature of the monomer is a very important factor in determining the reactivity of the polymeric radical. A rule of thumb is proposed that the most reactive monomer gives the least reactive polymeric radicals the least reactive monomers yields the most reactive polymeric radicals [13-15]. Aerdts et al. [16] reported a large difference in reactivity ratios, namely $r_{MMA} = 0.19 \pm 0.05$ and $r_{ST} = 0.73 \pm 0.05$, and by the large difference in water solubility between the monomers, i.e. $[ST]_{max} = 3$ $mmoll^{-1}$ and $[MMA]_{max} = 600$ $mmoll^{-1}$ at 323K. The reactivity of styrene and methyl methacrylate is in the following order:

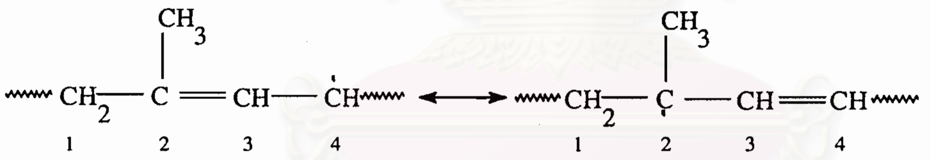
styrene > methyl methacrylate

and the reactivity of the polymeric radicals formed from these monomers is in the reverse order (via the rule thumb of Mayo):

Polystyrenyl radical < Poly(methyl methacrylate) radical-

This is an important consideration in the analysis of graft copolymers composition results.

Regardless of the origin of the radical site on the backbone polymer, the ability of this site to participate in a grafting reaction is dependent on its reactivity. If the radical site on the backbone polymer is much more stable than the polymeric radical generated from the monomer, then monomer does not readily add onto the backbone polymer and this radical is not effective as a grafting site. Thus, it is important to distinguish between the reactivity of all the radical species relative to their tendency to react with monomer. The polyisoprene molecule, the two methylene groups in the isoprene residue are not equivalent and it seems likely that the attack occurs preferentiaaly at carbon 4 so that the methyl group can exert the greatest stabilizing influence on the resulting allylic radical [17].



$$\sim\underset{1}{CH_2}-\underset{2}{\overset{CH_3}{C}}=\underset{3}{CH}-\underset{4}{\dot{C}H}\sim \longleftrightarrow \sim\underset{1}{CH_2}-\underset{2}{\overset{CH_3}{\dot{C}}}-\underset{3}{CH}=\underset{4}{CH}\sim \qquad (3.12)$$

In the styrene grafting system, the attack of alkoxy radicals on *cis*-polyisoprene is most likely by chain transfer to form the polyisoprenyl radical. This polyisoprenyl radical when it is in a styrene polymerization environment, can compete for styrene monomer and form graft copolymers because the reactivity of the polystyryl radical is about the same as the polyisoprenyl radical (both are stabilized by resonance). In addition, styrene monomer is one of the most active of the vinyl monomers, and in spite of the low reactivity of the polyisoprenyl radical, styrene monomer can still be grafted onto it. However, when the polyisoprenyl radical is in a methyl methacrylate environment, the situation is quite different. Methyl methacrylate is quite an inactive monomer compared to styrene. Conversely, the poly(methyl methacrylate) radical is a very active polymeric radical compared to the polystyryl radical. Therefore, the polyisoprenyl radical could not complete with the more active poly(methyl methacrylate) radical.

Table 3.8 shows the results of the composition of ST and MMA in graft copolymers. In Figure 3.10, the grafting efficiency is plotted against fraction of monomer in the graft copolymers. It can be seen that the level of styrene in the graft copolymers is higher than that of methyl methacrylate. It can be concluded that grafting can take place onto a polyisoprene seed. The chemical native of isoprene is similar to styrene (stabilized by resonance), this leads to the assumption that the grafting can take place due to the abstraction of a hydrogen atom from the polymer backbone.

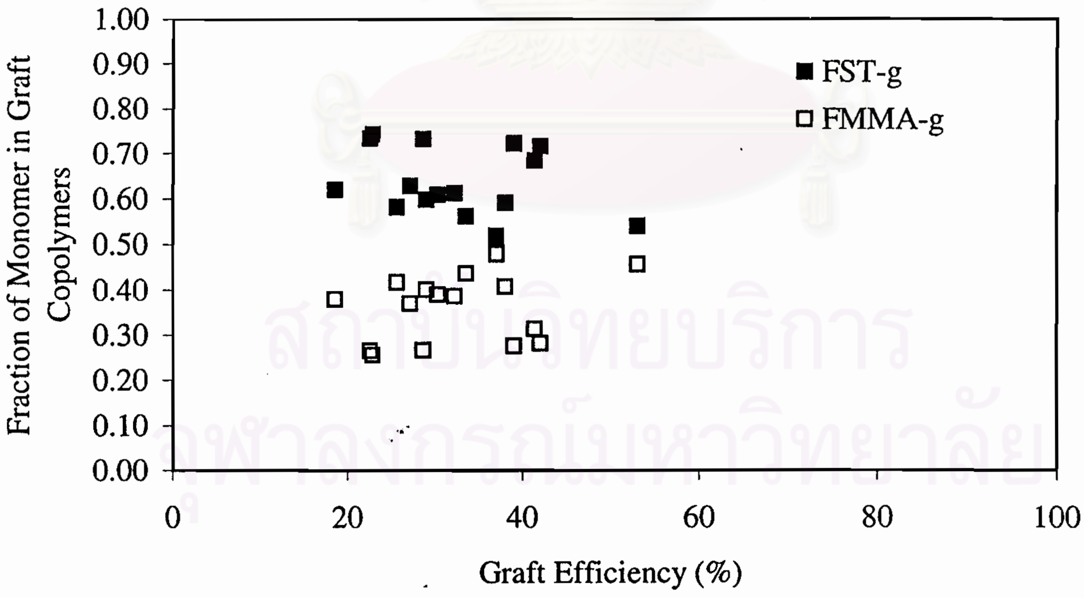


Figure 3.10 Fraction of styrene and methyl methacrylate in graft copolymers *vs* grafting efficiency.

It was postulated that the primary radical generated from the CHPO initiator most likely reacts with *cis*-polyisoprene by a chain transfer mechanism creating a polyisoprenyl radical. This radical is rather inactive but can effectively compete with polystyrenyl radicals more than poly(methyl methacrylate) radicals. Therefore, in the styrene and methacrylate systems, primary or monomeric radicals abstract α-methylenic hydrogen atom as the dominant mode of grafting site initiation.

3.4.4 Glass Transition Temperatures

To investigate the microstructure of graft copolymers, an analytical technique like ^{1}H-NMR has been employed. However, DSC, the effective conventional characterization technique is used explore the macromolecule chains motion. The glass transition temperatures of graft copolymers with various GE are given in Table 3.9. Figures 3.11 shows the DSC curves of graft copolymers with different levels of grafting efficiency as well as the natural rubber.

For natural rubber (Figure 3.11a), three peaks were observed. The most intense peak (B peak) at –65°C is attributed to the glass transition temperature. The β transition temperature (A peak) at about -88°C corresponds to the motion of short sections of the main chain or of side chain. The α′ transition temperature (C peak) is observed at 73°C due to the motion of the low-molecular weight components of a polymer with a broad molecular-weight distribution.

From the DSC curves (Figure 3.11b-d) of the graft copolymers with different GE, the β and α′ transition temperature shift toward the lower temperature side with increasing grafting efficiency. Figure 3.12 indicates the lowering of β transition temperature of the graft copolymer. The β transition temperature is dependent on the number and size of side chains, and as a function of the increase of grafting efficiency

Table 3.9 Transition temperatures of grafted NR.

Experiment	GE (%)	β Transition Temperature (°C) (A Peak)	T_g (°C) (B Peak)	α′ Transition Temperature (°C) (C Peak)
NR	-	-88.0	-65.1	73.4
GNR22	70.5	-113.7	-65.4	79.5
GNR23	62.7	-102.0	-65.9	76.3
GNR25	49.8	-102.7	-65.3	83.6
GNR26	44.7	-104.7	-65.3	78.3
GNR27	64.0	-112.9	-65.4	78.4
GNR28	85.4	-113.3	-66.6	73.8
GNR29	43.6	-113.0	-65.1	76.6
GNR31	58.1	-112.1	-65.4	72.2
GNR32	54.5	-102.1	-65.6	73.1
GNR33	56.9	-105.6	-65.2	74.1
GNR35	45.3	-106.0	-64.9	74.2
GNR36	51.9	-108.5	-65.7	73.3

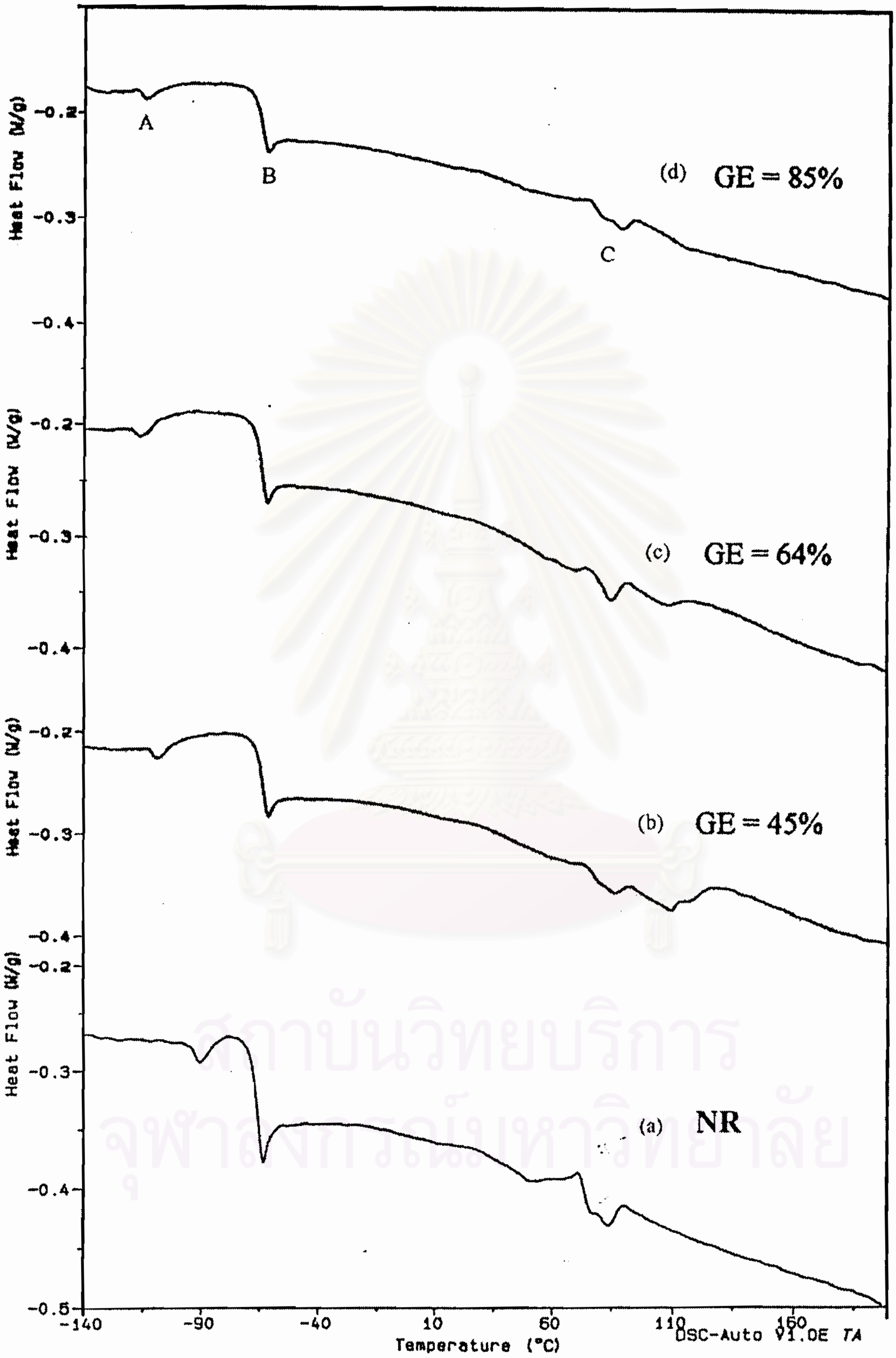


Figure 3.11 DSC curves for (a) NR, (b) GNR35, (c) GNR27, and (d) GNR28.

with a progressively lowering of the β transition temperature. It also can be seen that the β transition temperature decreases in area with increasing the grafting efficiency, reflecting the extent of mobility of the number of chain segments at that temperature (Figure 3.11). The β transition peak is seen to be related to grafting side chain; i. e., the β transition peak decreased in intensity and area with increasing grafting efficiency.

For graft copolymers, there is a two phase morphology, as confirmed by TEM (Figure 3.13). It is evident that at the highest grafting efficiency (GNR28), the PST/MMA shell encapsulates NR, as the core. Graft copolymers, the components of which are a rubber and two plastics, should exhibit three widely separated glass transition temperatures. The lower glass transition temperatures are close to the value expected for unmodified natural rubber ($T_{g,NR}$ = -65°C). The two upper glass transition temperatures should also be close to that expected for PMMA ($T_{g,MMA}$ = 110) and PST ($T_{g,ST}$ = 90°C). The latter is not found in the respective curve shown in Figure 3.11.

From the data provided in Table 3.9, several interesting observations can be made. It is evident that there is no shift in the glass transition temperature of NR (core) and no glass transition temperatures of PST/MMA (shell) in all graft copolymers is observed. The T_g is affected by size and the mobility of the chain. The majority of these polymers have relatively few graft chains, insufficient to affect the free volume available to the backbone, and the T_g of the backbone. The T_g of the backbone will initially be the same as for the NR. And the T_g of the components of the glassy shell can not be observed. This is also confirmed by the two phase morphology (Figure 3.13) that at the highest grafting efficiency (GNR28), NR core was encapsulated by a relatively thin shell of the ST and MMA. On the other hand,

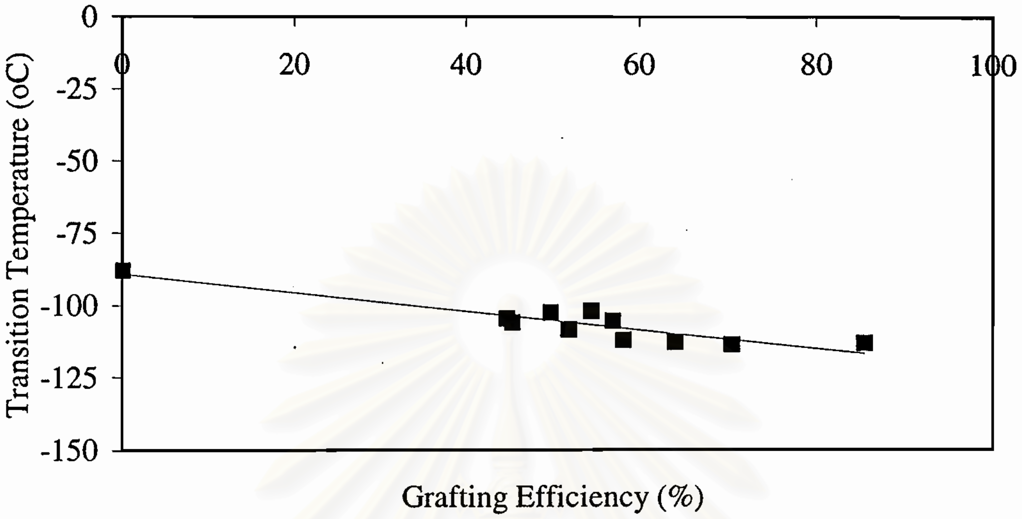


Figure 3.12 β transition temperature *vs* grafting efficiency.

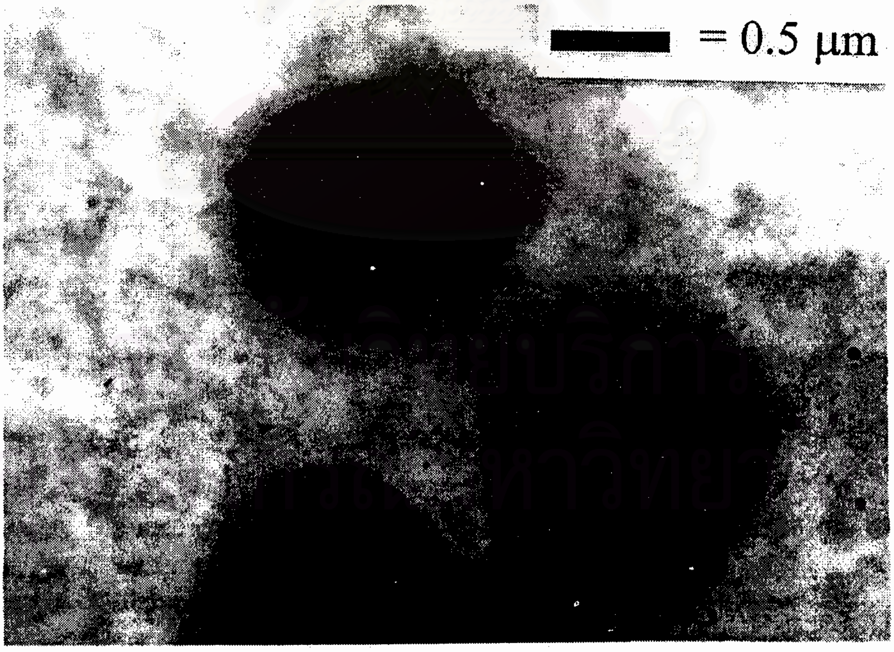


Figure 3.13 Transmission electron micrographs of GNR28 (×30000).

there are relatively few graft chains, grafted onto the rubber core. However, the experimental data support the fact that the number and size of the graft chains of the graft copolymers influence the β and α' transition temperature of the graft copolymers as indicated by the observation that with increasing grafting efficiency the β and α' transition temperatures decrease. The transition temperatures are shifted to higher or lower temperatures as a function of composition [18].

3.5 Conclusion

The process of graft copolymerization of styrene and methyl methacrylate onto natural rubber latex using amine-activated hydroperoxide in emulsion process was investigated. Graft copolymerization is a surface-controlled process because the bipolar redox initiator couple CHPO/TEPA favors the particle/water interface as the locus of polymerization.

The primary radical generated from CHPO initiator most likely reacts with *cis*-polyisoprene by a chain transfer mechanism. For natural rubber grafted styrene and methyl methacrylate monomers, the graft site formation is due to CHPO initiator radical attack onto the backbone via α-methylenic hydrogen atom abstraction.

The 2^{6-2}_{IV} design experimental method has been shown to be a very useful tool in order to study the influence of the process conditions on the grafting properties. Statistical analysis of the data showed that only CTA and TEMP, in the range of the tests conducted had a significant effect on GE. The extent of graft copolymer formation depends upon the time, temperature of reaction and the amount of mercaptan. The grafting efficiency increases with increasing temperature and decreasing concentration of chain-transfer agent. The grafting efficiency and graft copolymers composition depends upon the relative concentrations of monomer and backbone polymer but not upon the level of initiator. The addition of emulsifier only serves to enhance the particle stability.

The composition of graft copolymers shifts more strongly to higher styrene content than methyl methacrylate content. Moreover, the higher fractions of ST in the graft copolymers may be caused by a chain transfer mechanism creating a polyisoprenyl radical. This radical is rather inactive but can effectively compete with polystyryl radicals or poly(methyl methacrylate) radicals for styrene or methyl methacrylate monomers. For the grafting of styrene and methyl methacrylate onto natural rubber latex, the higher the amount of styrene in the monomer mixture, the higher the grafting efficiency. Results of the DSC curves for the graft copolymers indicate that the β transition temperature shifts toward the lower temperature side as grafting efficiency increases. Highlighted in row 8 of Table 3.5 is the experiment GNR28 found to have the highest grafting efficiency for all 16 experiments. That is, the highest grafting efficiency, a slight thin shell of the ST and MMA of the graft copolymers produced. However, if the number of graft chains is small, the glass transition temperatures of the resulting graft copolymers are essentially the glass transition temperatures of the unmodified polymers.

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CHAPTER 4

GRAFT COPOLYMERIZATION OF STYRENE AND METHYL METHACRYLATE ONTO SBR AND PBD USING AMINE ACTIVATED HYDROPEROXIDE

4.1 Introduction

The production of two-phase latex particles with core-shell 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 that has been synthesized in a graft copolymerization. In this study, a rubber core-glassy shell latex particle was required which could be used as a toughening agent for PVC. 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. The rubber component of the impact modifier should have a T_g lower than the β-relaxation temperature of PVC (-40°C) to confer toughness at lower temperature [1]. The lower the T_g of the modifier, the better the impact resistance [2]. Styrene-butadiene rubber (SBR) and polybutadiene (PBD) were chosen to be the core polymers because of their low glass transition temperatures.

In the previous chapter, the graft copolymerization of ST and MMA onto NR was performed using amine activated hydroperoxide. By extension, the graft copolymerization of ST and MMA onto other diene-based polymers can be accomplished in the same way. In this chapter, attention is directed to the synthesis of graft copolymers of ST and MMA onto SBR and PBD. The goal of the investigation for these polymers is not to provide a thorough study of reaction conditions but to elucidate the most influential process parameters on the graft copolymerization. The grafting efficiency was used for studying the effect of each process variable on grafting. The factorial experimental design is one of the most commonly used methods to understand the effects of some independent variables that significantly affect the final experimental results. The analysis of the data collected during the factorial designs is discussed. Results from two factorial designs are presented.

4.2 Experimental

4.2.1 Materials

Styrene-butadiene rubber latex (21.7% DRC), containing about 72.8% butadiene and 27.2 % styrene was supplied by Bayer Co Ltd. Polybutadiene latex was synthesized by classical emulsion polymerization technique. The recipes used for emulsion synthesis of the polybutadiene core seed particles are shown in Table 4.1.

Table 4.1 Standard polymerization recipes (in parts by weight).

Ingredients	Quantities
Water	100 g
Butadiene	30 g
Emulsifier (sodium dodecyl sulfate)	1.5 g
Initiator (potassium persulfate)	0.1 g
Dodecyl mercaptan	0.15 g
Ethanol	13 g

The butadiene was discharged from its cylinder through a drying tube containing Ascarite (to remove the inhibitor) into a trap placed in an ice-salt bath. Sufficient condensed butadiene was added from the trap to a cooled flask to introduce the correct amount of monomer. The polymerization was performed in a stainless steel reactor (1.5 lit Parr reactor) fitted with two six-bladed turbine impellers. The reactor was charged under N_2 with all ingredients except the butadiene. The system was free from inert gas by flushing the gas cap with gaseous butadiene, followed by evacuation. Lastly, the freshly distilled liquid butadiene was added from the flask.

The stirrer speed was maintained at 200 rpm and the temperature of the polymerization was normally 50°C. The reaction was allowed to proceed for 24 h, after the reaction was complete, the latex was warmed with steam, and the unreacted butadiene flashed off and poured through a screen to remove any coagulum formed. The percentage solids was usually about 15.5%.

The same materials used in the synthesis of the graft copolymers from NR latex mentioned in Section 3.2.1 were used in the synthesis of the graft copolymers from SBR and PBD latex.

4.2.2 Preparation of Grafted Rubber from SBR and PBD

The graft copolymerization of the styrene and methyl methacrylate onto SBR and PBD latex was carried out similar to the preparation of grafted NR mentioned in Section 3.2.2. The only difference was the amount of percentage solid in the seed latex.

4.2.3 Analytical Techniques

The analytical techniques used for determination of the total percent conversion, grafting efficiency, graft copolymer composition, and glass transition temperature were identical to that described in Section 3.2.3 to 3.2.6.

Table 4.2 ^{1}H-NMR Signal assignments for graft copolymers with diene-based rubber.

Unit	Type of proton	ppm
Butadiene	Olefinic protons of *cis* and *trans* unit	5.4
	Olefin CH_2 of the vinyl 1,2-sequence	4.9
Styrene	Aromatic protons	7.5-6.5
Methyl methacrylate	Methoxy protons	3.7
Butadiene Styrene Methyl methacrylate	All aliphatic protons	3.7-0.2

The ^{1}H-NMR signal assignments for graft copolymers are shown in Table 4.2. From the different signal areas, the amount of styrene per proton (ST), the amount of butadiene per proton (NR), and the amount of MMA per proton (MMA) can be calculated by using the following equations:

$$ST = \frac{A_{\delta=7.5-6.5}}{5} \tag{4.1}$$

$$MMA = \frac{A_{\delta=3.7}}{3} \tag{4.2}$$

$$PBD = \frac{A_{\delta=5.4} - \frac{1}{2}A_{\delta=4.9}}{2} + \frac{A_{\delta=4.9}}{2} \tag{4.3}$$

With these formulae, the fractions of styrene (F_{ST}-g) and methyl methacrylate (F_{MMA}-g) in graft copolymers are calculated by using equation (4.1)-(4.3):

$$F_{ST}\text{-g} = ST/(ST+MMA) \qquad (4.4)$$

$$F_{MMA}\text{-g} = MMA/(ST+MMA) \qquad (4.5)$$

The graft copolymerization experiments were conducted as part of a 2^{6-2}_{IV} fractional factorial design set of experiments. The methodology used was provided previously in Section 3.3. The recipe ingredients are listed for SBR and PB latex in Table 4.3. The independent variables are the same as that described in Table 3.3. The coding scheme of 16 experiments is similar to that described in Table 3.4, GSBR01 - GSBR16 for SBR latex and GPB01 - GPB16 for PBD latex. The experiments were performed at a constant agitation rate of 200 rpm and a total amount of solid in seed latex was 30 g. The results for the graft copolymerization are shown in Table 4.4 and 4.5 for SBR latex and PBD latex, respectively.

Table 4.3 Standard recipes used for graft copolymerization.

Ingredients	SBR (21.7% DRC) Quantities	PBD (15.5% DRC) Quantities
Latex	138.2 g	193.5 g
Water	61.8g	6.5 g
Stabilizer amount	3 g	3 g
Buffer amount	0.12 g	0.12 g
Redox initiator amount, CHPO:TEPA = 1:1	Variable	Variable
Surfactant amount	Variable	Variable
Chain-transfer agent	Variable	Variable
Styrene amount	Variable	Variable
Metyl methacrylate amount	Variable	Variable

4.3 Results and Discussion

4.3.1 The Influence of Process Variables

Within this framework, the influence of process variables including the concentrations of initiator, emulsifier, and chain-transfer agent, the reaction temperature, the ratio of monomer mixture, and monomer to rubber ratio were investigated. Statistical analysis was used to study the influence of each process variable irrespective of and in combination with the other process variables on the grafting efficiency. Table 4.6 shows the effect of process variables on mean grafting efficiency of grafted SBR and grafted PB compared with grafted NR. The F test was used to evaluate if a factor has a significant effect ($F > 18.5$). Results for main effects and two-factor interactions of graft copolymerization onto with SBR and PBD are shown in Table 4.7 and 4.8, respectively. These tables show the F test of effects of the process variables on grafting efficiency. An "effect" is defined as the change in the response (in this case the grafting efficiency) on changing the variable from the "-" level to the "+" level. The effects of the variables and any interactions, which are significant ($F_{1,2} > 18.5$) with respect to grafting efficiency, can be identified.

From Table 4.6, the effect of low level and high level CTA, TEMP, M/R, INT, and EMUL on grafting efficiency shows the similar trend for grafted SBR, grafted PB and grafted NR. Figure 4.1 shows the effect of level of emulsifier and initiator on the mean grafting efficiency for three different grafted rubbers. The emulsifier concentration on the seed particle surface has little effect on the grafting efficiency in the absence of coagulation. When more emulsifier was charged, the possibility of polymerization that was free of grafting onto the backbone polymer increased and the grafting efficiency decreased (Figure 4.1a). This is the result of the formation of new

Table 4.4 The Experimental results of graft copolymerization for SBR.

Experiment	Total conversion (%)	Free rubber (%)	Free polymer (%)	Graft copolymers (%)	Grafting efficiency (%)
GSBR01	87.9	0.7	11.2	88.0	71.8
GSBR02	98.5	2.1	11.7	86.2	72.4
GSBR03	92.4	0.2	10.9	88.9	77.3
GSBR04	87.9	0.5	8.8	90.7	81.1
GSBR05	94.9	0.5	15.6	83.9	68.0
GSBR06	92.4	2.7	14.9	82.4	68.9
GSBR07	95.1	1.1	5.6	93.3	86.6
GSBR08	94.4	1.5	6.6	91.9	84.1
GSBR09	95.0	2.2	20.0	77.8	59.0
GSBR10	97.1	2.0	24.0	74.0	51.2
GSBR11	73.9	5.7	10.9	83.4	69.4
GSBR12	89.8	4.8	16.1	79.1	60.0
GSBR13	90.8	2.8	21.0	76.3	48.3
GSBR14	89.6	4.2	17.2	78.6	57.2
GSBR15	89.0	3.1	25.7	71.2	45.5
GSBR16	81.0	3.0	19.2	77.8	57.1

Table 4.5 The experimental results of graft copolymerization for PBD.

Experiment	Total conversion (%)	Free rubber (%)	Free polymer (%)	Graft copolymers (%)	Grafting efficiency (%)
GPB01	92.0	20.8	14.7	64.6	64.0
GPB02	93.6	9.8	9.5	80.7	77.0
GPB03	94.2	16.4	13.3	70.3	72.6
GPB04	96.5	16.0	9.6	74.5	80.5
GPB05	92.6	10.0	17.5	72.5	63.6
GPB06	94.5	12.5	23.7	63.9	51.3
GPB07	91.2	17.4	10.9	71.7	73.1
GPB08	94.5	17.1	7.5	75.4	81.9
GPB09	91.8	9.7	22.9	67.5	52.2
GPB10	91.2	15.8	20.4	63.9	57.3
GPB11	92.5	15.2	13.1	71.8	68.1
GPB12	93.5	17.7	14.1	68.2	65.9
GPB13	92.2	23.7	14.0	62.3	65.7
GPB14	93.5	17.5	17.2	65.3	58.4
GPB15	91.1	18.3	21.9	59.7	54.0
GPB16	93.4	14.2	17.4	68.5	64.0

Table 4.6 The effect of process variables on mean grafting efficiency for grafted SBR, grafted PB and grafted NR.

Process Variable	NR[a,b] GE (%)			SBR[c] GE (%)			PBD[d] GE (%)		
	Mean	-95% Cnf.Limt.	95% Cnf.Limt	Mean	-95% Cnf.Limt	95% Cnf.Limt	Mean	-95% Cnf.Limt	95% Cnf.Limt
CTA									
-1	63.77	54.47	70.06	76.27	71.38	81.16	70.51	66.45	74.58
+1	50.52	44.22	56.81	55.95	51.06	60.84	60.69	56.63	64.75
TEMP									
-1	51.61	45.31	57.90	62.09	57.20	66.98	61.19	57.12	65.25
+1	62.68	56.39	68.98	70.14	65.24	75.03	70.02	65.95	74.08
M/R									
-1	61.23	54.94	67.53	68.71	63.82	73.60	69.27	65.21	73.33
+1	53.05	46.76	59.35	63.51	58.62	68.40	61.93	57.87	66.00
ST/MMA									
-1	54.01	47.72	60.31	66.26	61.36	71.15	62.43	58.37	66.50
+1	60.27	53.98	66.57	65.97	61.08	70.86	68.77	64.71	72.84
INT									
-1	54.24	47.94	60.53	65.73	60.84	70.62	64.17	60.10	68.23
+1	60.05	53.75	66.34	66.49	61.60	71.38	67.04	62.97	71.10
EMUL									
-1	58.66	52.36	64.95	67.78	62.87	72.67	67.20	63.14	71.27
+1	55.63	49.34	61.92	64.44	59.55	69.33	64.00	59.94	68.06

[a] Taken from Chapter 3
[b] Std.Errs. for mean=2.78
[c] Std.Errs. for mean=2.16
[d] Std.Errs. for mean=1.80

Table 4.7 Results for main effects and two-factor interactions for response and the analysis of variance of % GE for SBR.

Effect Name	GE(%)	SS	df	MS	F[a]	Signif.
Mean	66.11					
INT	0.77	2.34	1	2.34	0.04	No
TEMP	8.05	259.19	1	259.19	4.36	No
EMUL	-3.33	44.42	1	44.42	0.75	No
CTA	-20.31	1650.27	1	1650.27	27.76	Yes
ST/MMA	-0.29	0.33	1	0.33	0.01	No
M/R	-5.21	108.38	1	108.38	1.82	No
INT by TEMP	0.09	0.03	1	0.03	0.00	No
INT by EMUL	3.96	62.69	1	62.69	1.05	No
INT by CTA	0.04	0.01	1	0.01	0.00	No
INT by ST/MMA	-0.33	0.45	1	0.45	0.01	No
INT by M/R	1.37	7.53	1	7.53	0.13	No
TEMP by CTA	-3.97	63.04	1	63.04	1.06	No
TEMP by M/R	-4.58	83.81	1	83.81	1.41	No
Error		118.92	2	59.46		
Total SS						
R^2=0.95048						

[a] F(1,2) = 18.5 with $\alpha = 0.05$. If F < 18.5, then the variable is not significant.

Table 4.8 Results for main effects and two-factor interactions for response and the analysis of variance of % GE for PBD.

Effect Name	GE(%)	SS	df	MS	F[a]	Signif.
Mean	65.60					
INT	2.87	32.99	1	32.99	1.70	No
TEMP	8.83	312.11	1	312.11	16.10	No
EMUL	-3.20	41.04	1	41.04	2.12	No
CTA	-9.82	386.03	1	386.03	19.91	Yes
ST/MMA	6.34	160.80	1	160.80	8.29	No
M/R	-7.34	215.28	1	215.28	11.10	No
INT by TEMP	3.26	42.61	1	42.61	2.20	No
INT by EMUL	-3.08	37.94	1	37.94	1.96	No
INT by CTA	-1.47	8.59	1	8.59	0.44	No
INT by ST/MMA	-0.33	0.44	1	0.44	0.02	No
INT by M/R	-0.17	0.12	1	0.12	0.01	No
TEMP by CTA	-4.23	71.45	1	71.45	3.69	No
TEMP by M/R	2.85	32.43	1	32.43	1.67	No
Error		38.77	2	19.39		
Total SS		1380.59				
R^2=0.97191						

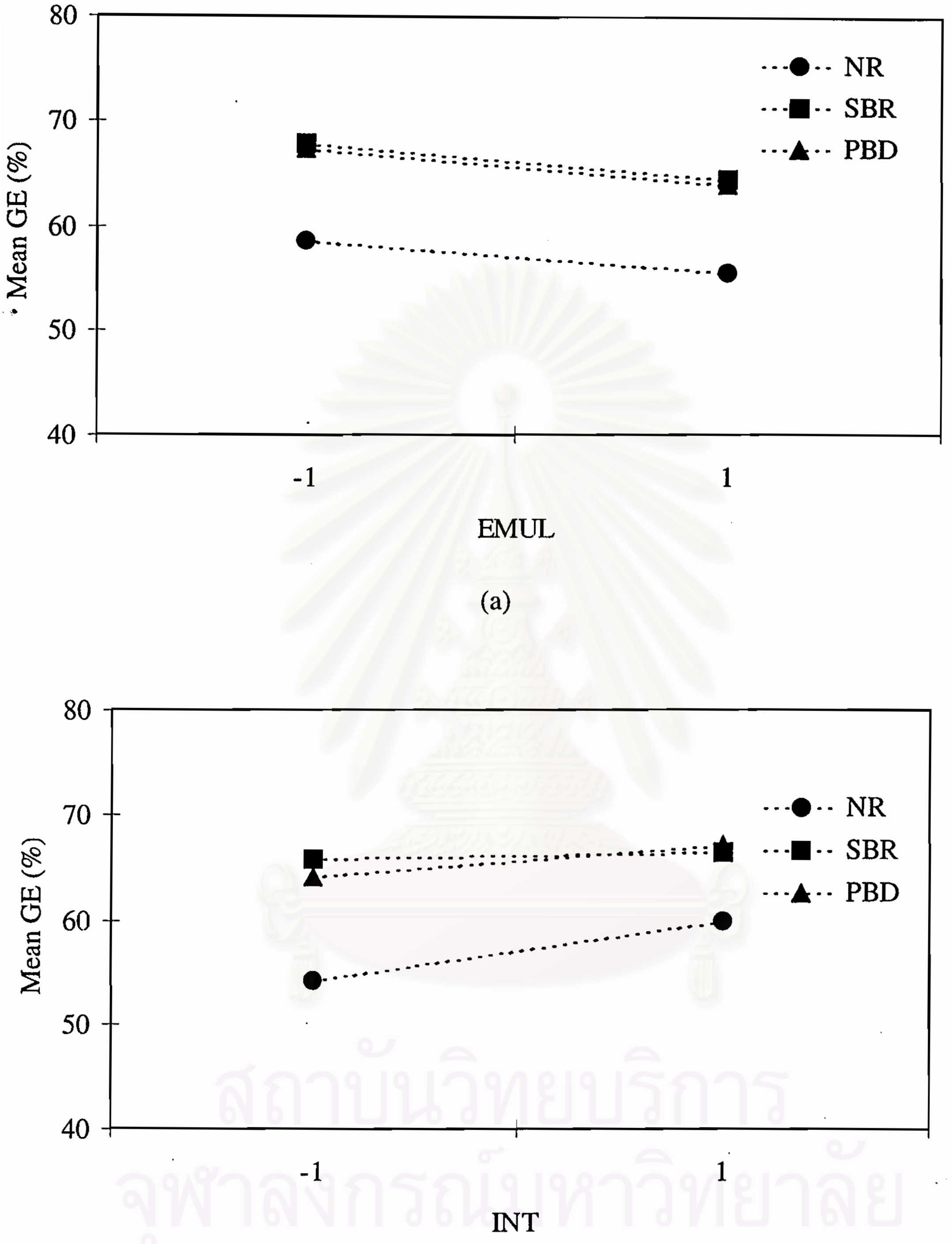
[a] F(1,2) = 18.5 with $\alpha = 0.05$. If F < 18.5, then the variable is not significant.

micelles in the aqueous phase, which, in turn, caused the formation of a new particle. From Figure 4.1b, the grafting efficiency increased with increasing radical generation and increased with increasing concentration. It is believed that the probability for the rate of radical generation increased, thus accounting for the increased levels of grafting with increased initiator concentrations.

Figure 4.2 shows the effect of the level of monomer to rubber ratio and temperature on the mean grafting efficiency for three different grafted rubbers. The grafting efficiency decreased when the monomer/rubber ratio was increased (Figure 4.2a). Accumulation of monomers around a seed particle would hinder the monomer from coming into contact with seed particle allowing more free copolymerization to take place, thus resulting in a lower grafting efficiency. From Figure 4.2b, the grafting efficiency increased with increasing temperature. The influence of temperature on the grafting efficiency can be explained by the temperature dependence of the rate constants and kinetics [3]. According to the Arrhenius relation both polymerization and diffusion rate are faster at higher temperature, therefore the grafting efficiency increases.

Figure 4.3 shows the effect of the level of chain-transfer agent and styrene to methyl methacrylate ratio on the mean grafting efficiency for three different grafted rubbers. The grafting efficiency strongly decreased when the chain-transfer agent was added (Figure 4.3a). When no mercaptan is used, there is no radical activity of a graft chain or backbone polymer transfered to the chain-transfer agent; greater transfer to polymers and monomers take place and as a result more grafting occurred.

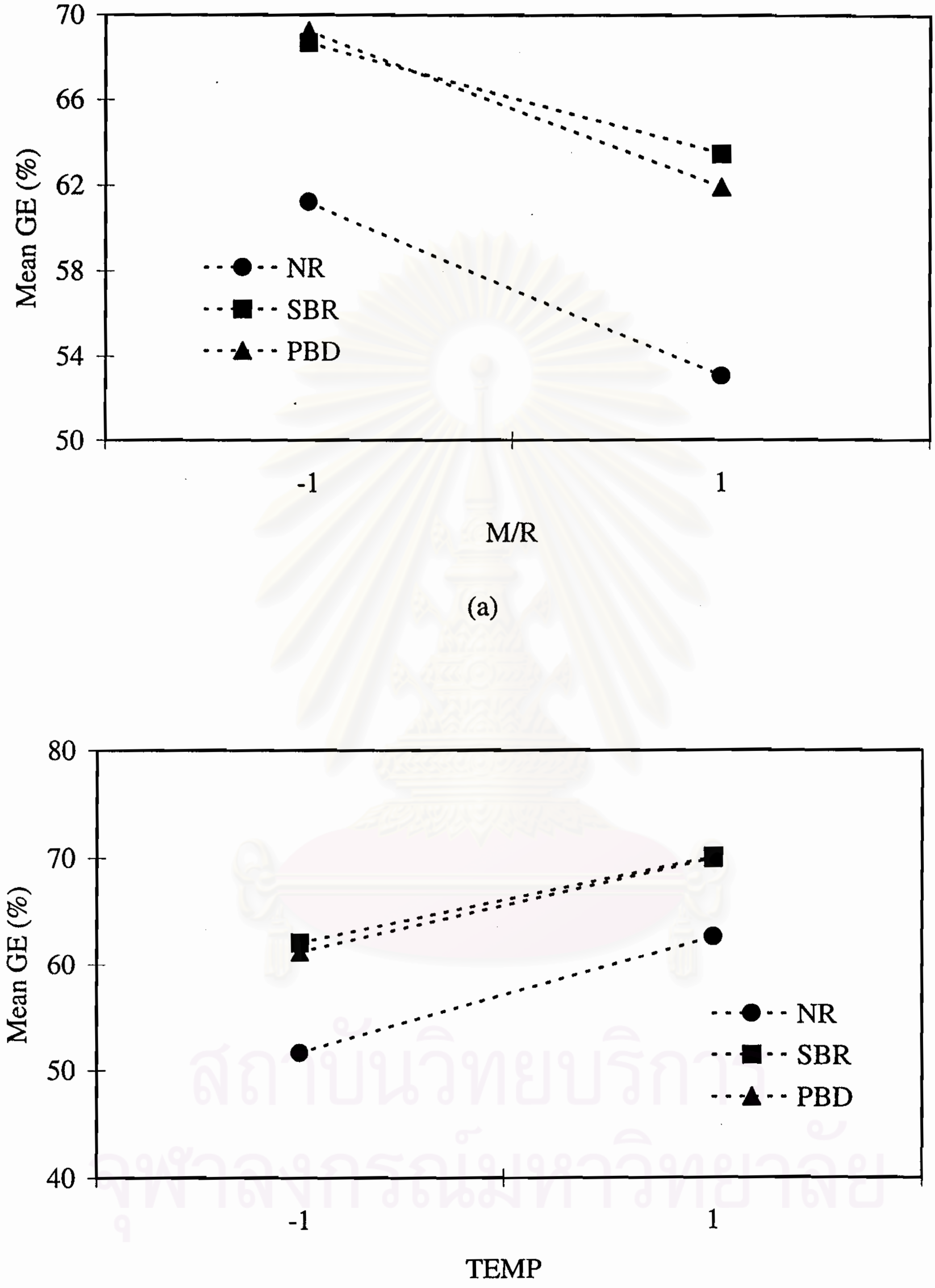
From Figure 4.3b, the grafting efficiency increased with increasing ST/MMA ratio for both NR and PBD while the grafting efficiency decreased with increasing ST/MMA ratio for SBR. The SBR shows a quite different grafting behavior compared



(a)

(b)

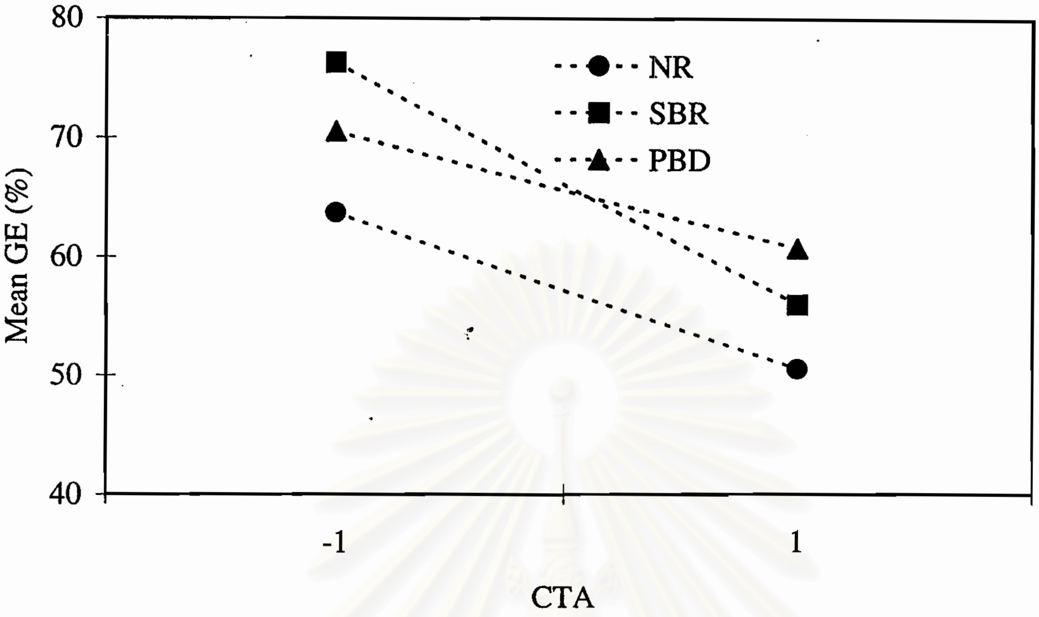
Figure 4.1 Effect of the level of emulsifier and initiator on mean GE for grafted SBR, grafted PBD and grafted NR.



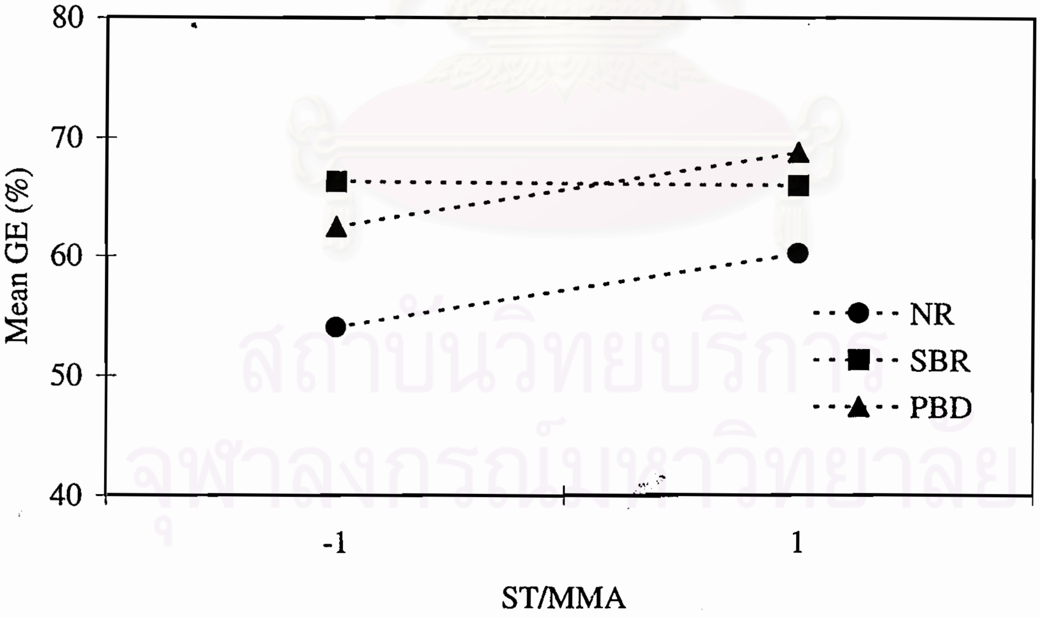
(a)

(b)

Figure 4.2 Effect of the level of monomer to rubber ratio and temperature on mean GE for grafted SBR, grafted PBD and grafted NR.



(a)



(b)

Figure 4.3 Effect of the level of chain-transfer agent and ST/MMA ratio on mean GE for grafted SBR, grafted PBD and grafted NR.

to NR and PBD, and this may be due to the presence of polystyrene segments in the copolymer. Because of the presence of polystyrene segments in the copolymer, the chemical structure of the backbone polymer was changed. The attack a of primary radical on SBR would generate a radical with no resonance stability and thus high reactivity. Such a radical along the backbone ought to compete effectively with the poly(methyl methacrylate) radical and thus lead to a decrease of grafting efficiency with increasing ST/MMA ratio.

With NR and PBD as backbone polymers, the grafting reaction occurred by the interaction of monomer with a radical, which was formed by removal of an allylic hydrogen from a backbone polymer. For a SBR backbone polymer, the reaction occurred through the interaction of a macroradical from the monomer with the addition of the double bond of the backbone polymer.

One can anticipate that graft copolymerization onto synthetic rubber (SBR and PB) results in a higher grafting efficiency than with natural rubber. However, the graft copolymerization onto synthetic rubbers and NR is similar with respect to influential variables and the course of the reaction depends on the particle size. The electron micrographs (Figure 4.4) of the SBR and NR latex particles coated with copolymers of ST and MMA, revealed regular shapes. The P(ST/MMA) is distributed discontinuously on the surface of the natural rubber particles. The particle size is an important factor when such an emulsion is used as seed latex. When the particle size of rubbery core increases, the probability of macroradicals to react with one another is decreased so they can precipitate at shorter chain lengths. Since the visible “lump” of P(ST/MMA) forms on the surface of the rubber seed particle, the shape or continuity of the final particle surface appears ragged as depicted in Figure 4.4. As the particle size is decreased, the surface becomes smoother and more continuous. Compare graft

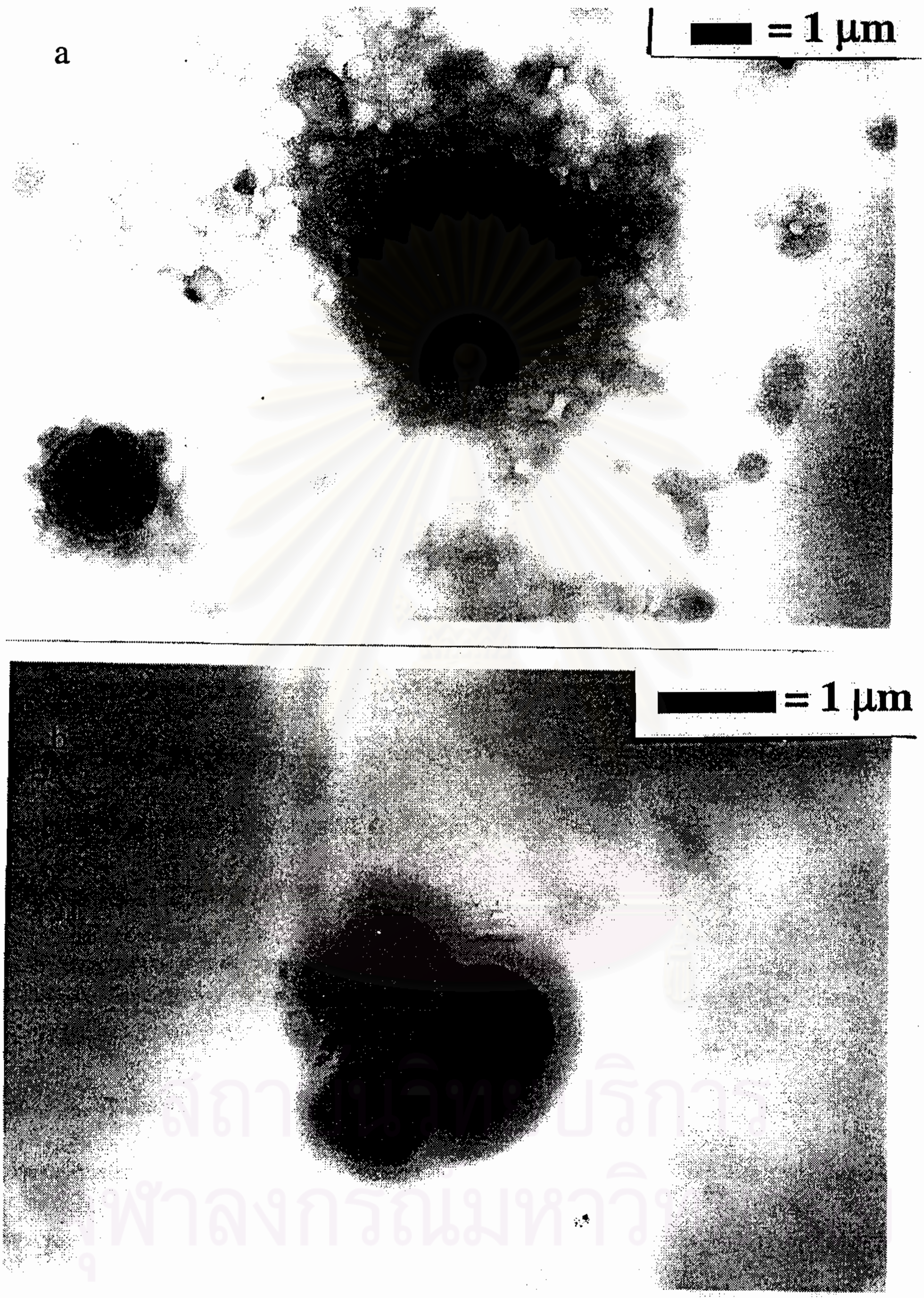


Figure 4.4 Transmission electron micrographs of grafted rubber:

(a) GNR33 (×82,500) and (b) GSBR13 (×150,000).

copolymers onto NR with graft copolymers onto SBR. The surface area of the SBR particle is higher (small particle size) but a fewer grafting efficiency was observed for graft copolymerization onto SBR with increasing ST/MMA ratio This is not surprising, since grafting efficiency is also possible to be due to the effect of the backbone polymer type. Hence, any change in rubber core properties can be directly attributed to the grafting efficiency of graft copolymers.

4.3.2 The Graft Copolymer Composition

^{1}H-NMR spectra of graft copolymers from graft copolymerization onto SBR and PBD are shown in Figures 4.5 and 4.6 respectively.

Table 4.9 and 4.10 provide the composition of graft copolymers, from SBR and PBD. Comparison of the compositions of the graft copolymers between grafted SBR and grafted PBD are also provided. It can be seen that the fraction of MMA is higher than fraction of ST in the grafted SBR while the fraction of MMA is lower than fraction of ST in the grafted PBD. The graft copolymerization of ST and MMA onto NR is similar to the results for the grafting onto PBD.

The graft copolymerization in diene-base rubber occurs at two positions; at the allylic positions and on the double bonds. To propose the mechanism of graft copolymerization, one needs to understand the properties of the monomer, which determines the reactivity of monomeric radicals. Mayo proposed a rule about the relationship between monomers and monomeric radicals: the most reactive monomer will be converted to the least reactive polymeric radical and the least reactive monomer will produce the most reactive polymeric radical.

The expectation of this work is that the graft copolymerization of ST and MMA onto PBD would occur by the replacement of the allylic hydrogen atom. For

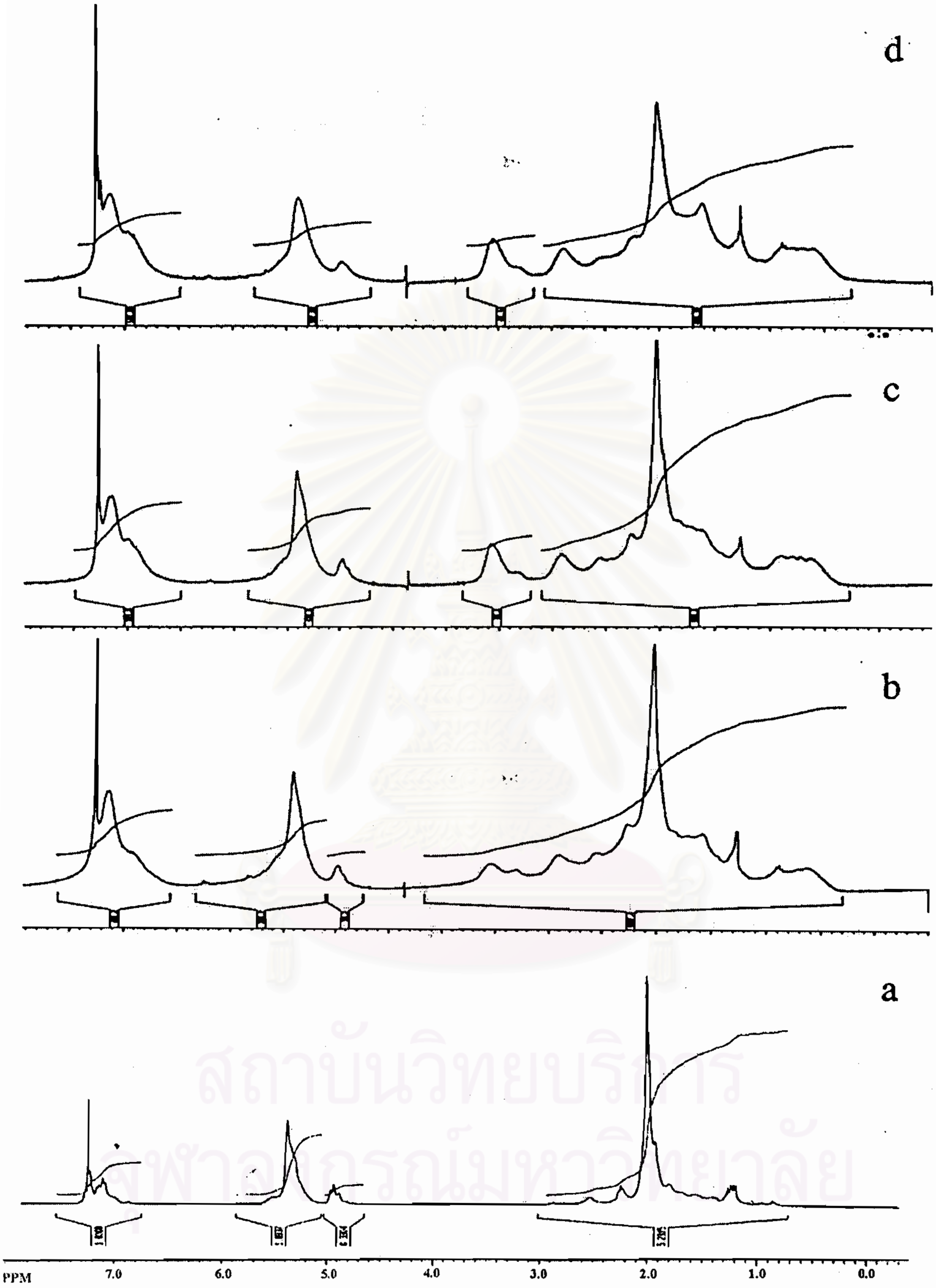


Figure 4.5 250 MHz ^{1}H NMR spectra in $CDCl_3$ at 298 K of (a) SBR, (b) GSBR15, (c) GSBR01, and (d) GSBR07.

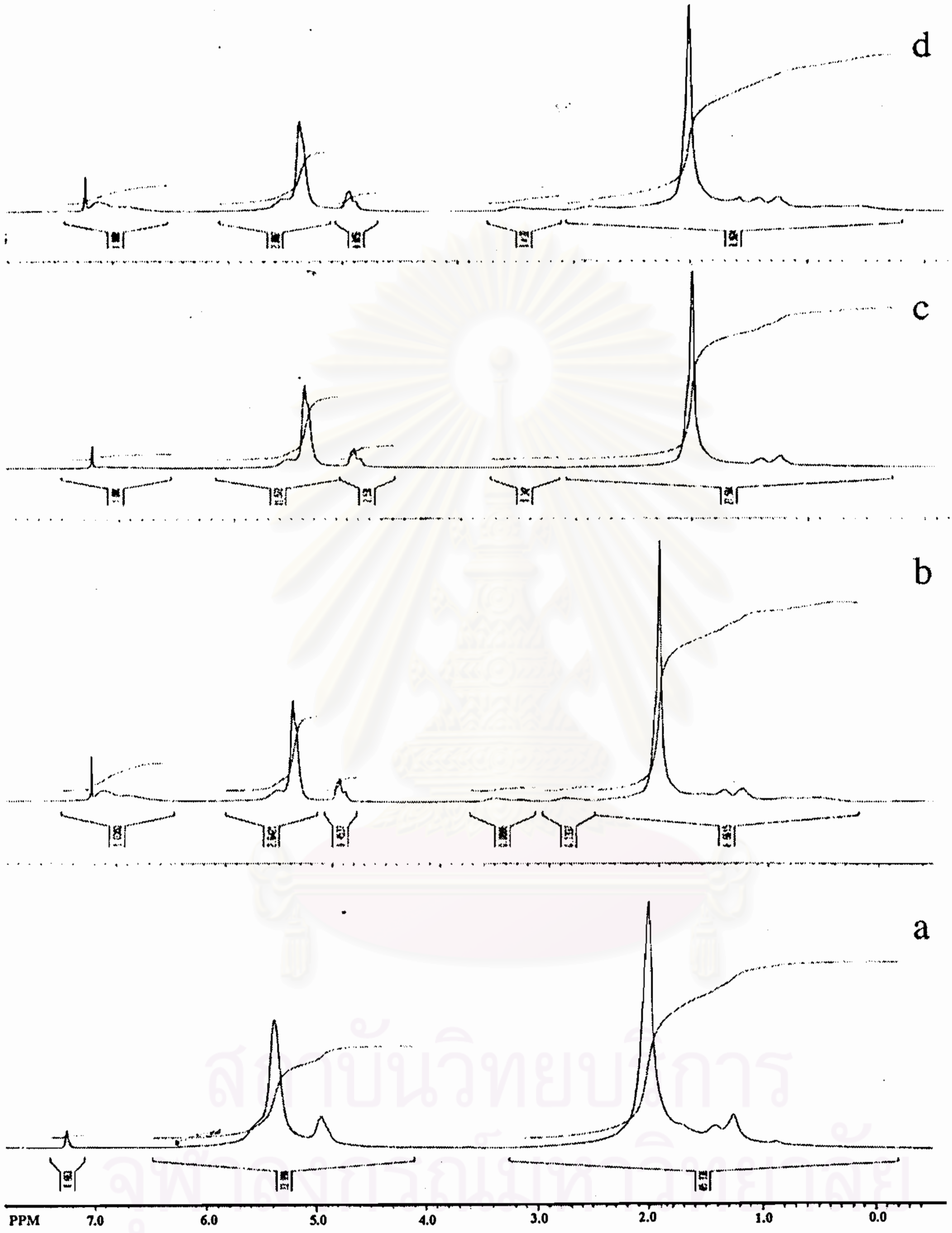


Figure 4.6 250 MHz ^{1}H NMR spectra in CDCl3 at 298 K of (a) PBD, (b) GPB09, (c) GPB01, and (d) GPB08.

Table 4.9 Grafting efficiency and composition of graft copolymers from SBR.

Experiment	ST (%wt)	SBR (%wt)	MMA (%wt)	F_{ST}-g	F_{MMA}-g	GE (%)
GSBR01	8.9	74.3	16.9	0.344	0.656	71.8
GSBR02	11.6	72.0	16.4	0.415	0.585	72.4
GSBR03	12.2	68.4	19.4	0.387	0.613	77.3
GSBR04	16.6	64.6	18.8	0.468	0.532	81.1
GSBR05	17.3	69.8	12.9	0.572	0.428	68.0
GSBR06	13.6	70.3	16.1	0.459	0.541	68.9
GSBR07	15.5	63.5	21.1	0.423	0.577	86.6
GSBR08	16.5	64.6	18.9	0.465	0.535	84.1
GSBR09	6.1	77.7	16.3	0.272	0.728	59.0
GSBR10	-	-	-	-	-	-
GSBR11	10.0	79.6	10.4	0.492	0.508	69.4
GSBR12	9.2	77.1	13.7	0.4	0.6	60.0
GSBR13	-	-	-	-	-	-
GSBR14	7.9	79.5	12.6	0.383	0.617	57.2
GSBR15	5.5	81.1	13.5	0.288	0.712	45.5
GSBR16	12.9	74.8	12.3	0.513	0.487	57.1

Table 4.10 Grafting efficiency and composition of graft copolymers from PBD.

Experiment	ST (%wt)	PB (%wt)	MMA (%wt)	F_{ST}-g	F_{MMA}-g	GE (%)
GPB01	5.5	91.0	3.5	0.600	0.400	64.0
GPB02	-	-	-	-	-	-
GPB03	-	-	-	-	-	-
GPB04	17.2	71.4	11.4	0.593	0.407	80.5
GPB05	-	-	-	-	-	-
GPB06	-	-	-	-	-	-
GPB07	21.2	63.5	15.4	0.570	0.430	73.1
GPB08	18.2	73.7	8.1	0.683	0.317	81.9
GPB09	20.5	76.3	3.3	0.857	0.143	52.2
GPB10	6.5	92.5	1.0	0.857	0.143	57.3
GPB11	10.8	81.0	8.2	0.561	0.439	68.1
GPB12	5.1	87.7	7.3	0.401	0.599	65.9
GPB13	10.4	84.6	5.0	0.666	0.334	65.7
GPB14	-	-	-	-	-	-
GPB15	11.2	80.3	8.6	0.556	0.444	54.0
GPB16	9.6	85.7	4.7	0.661	0.339	64.0

the grafting of ST and MMA onto SBR, the reactive site should be the double bonds, since SBR has a different reaction mechanism from PBD.

When CHPO is used, the primary radical is reactive and thus can either abstract a hydrogen from an allylic position, or add to the double bond in the backbone. For graft copolymerization of ST and MMA onto PBD or NR, the reactive primary radical can initiate reactive monomer (ST) to form unreactive monomeric radical or abstract a hydrogen from the allylic position of backbone to form a resonance stabilized allylic radical which is also an unreactive backbone radical. These two types of unreactive radicals will compete with each other. So, the fraction of styrene in graft copolymers of PBD is higher than the fraction of MMA (see Table 4.10). The presence of polystyrene segments in the copolymer changed the chemical structure of the backbone polymer. The grafting site is most likely formed by a double bond addition mechanism. On the other hand, graft copolymerization of ST and MMA onto SBR, the primary radical can initiate unreactive monomer (MMA) to form a reactive monomeric radical, which can add to the double bond in the backbone effectively. Thus, the fraction of MMA in graft copolymers of SBR is higher than the fraction of styrene (see Table 4.9).

4.3.3 Glass Transition Temperatures

Differential scanning calorimetry (DSC) is a means, which can give some clue about the change in the microstructure of polymers. The DSC curves for both grafted SBR and PBD are shown in Figure 4.7 and 4.8, respectively. It can be seen that the backbone polymers show two endothermic peaks: one at below -50°C and the other one at above 50°C. The former corresponds to the glass transition temperature (T_g) and the latter is obviously from the motion of the low-molecular weight components

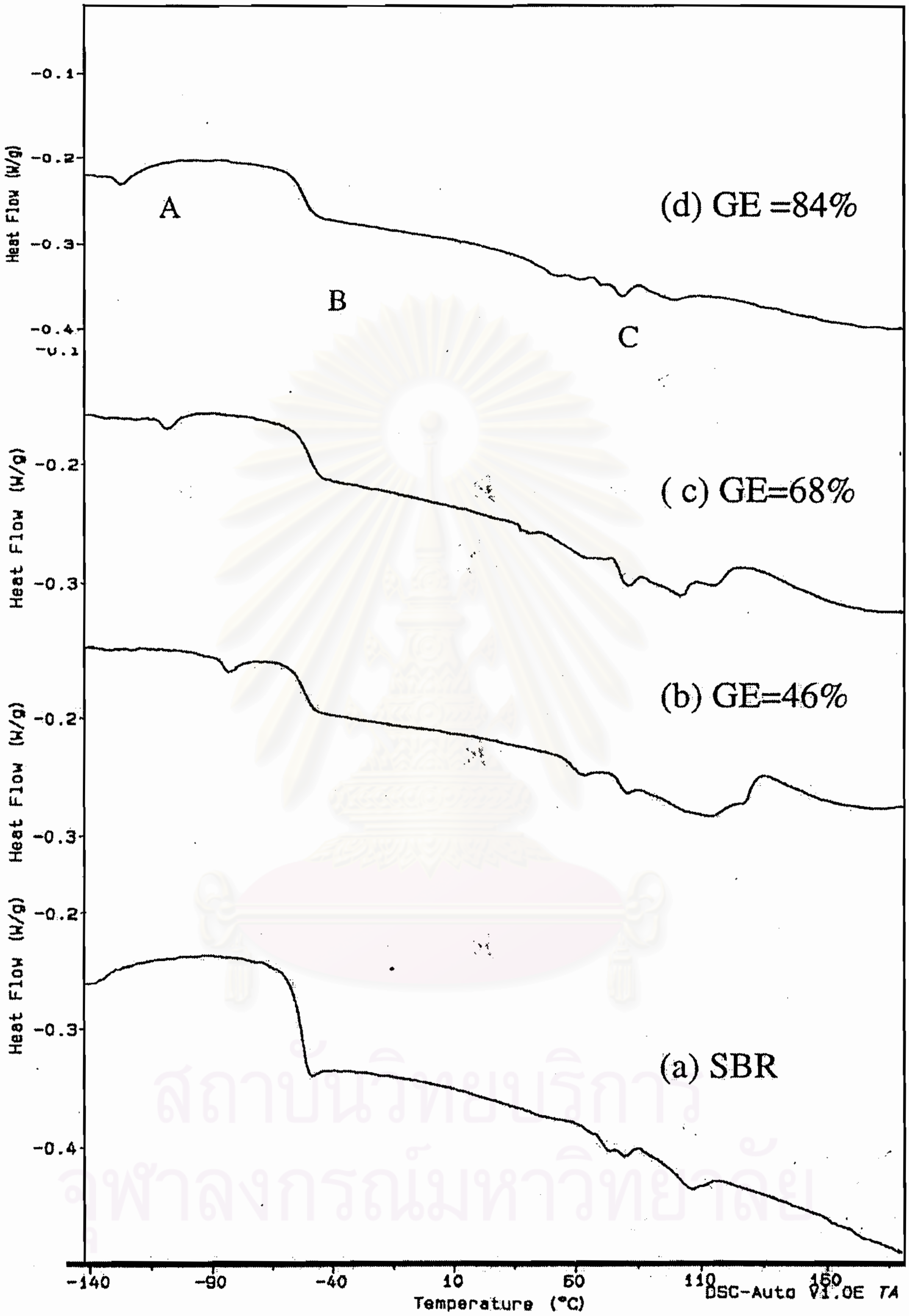


Figure 4.7 DSC curves for (a) SBR, (b) GSBR15, (c) GSBR05 and (d) GSBR08.

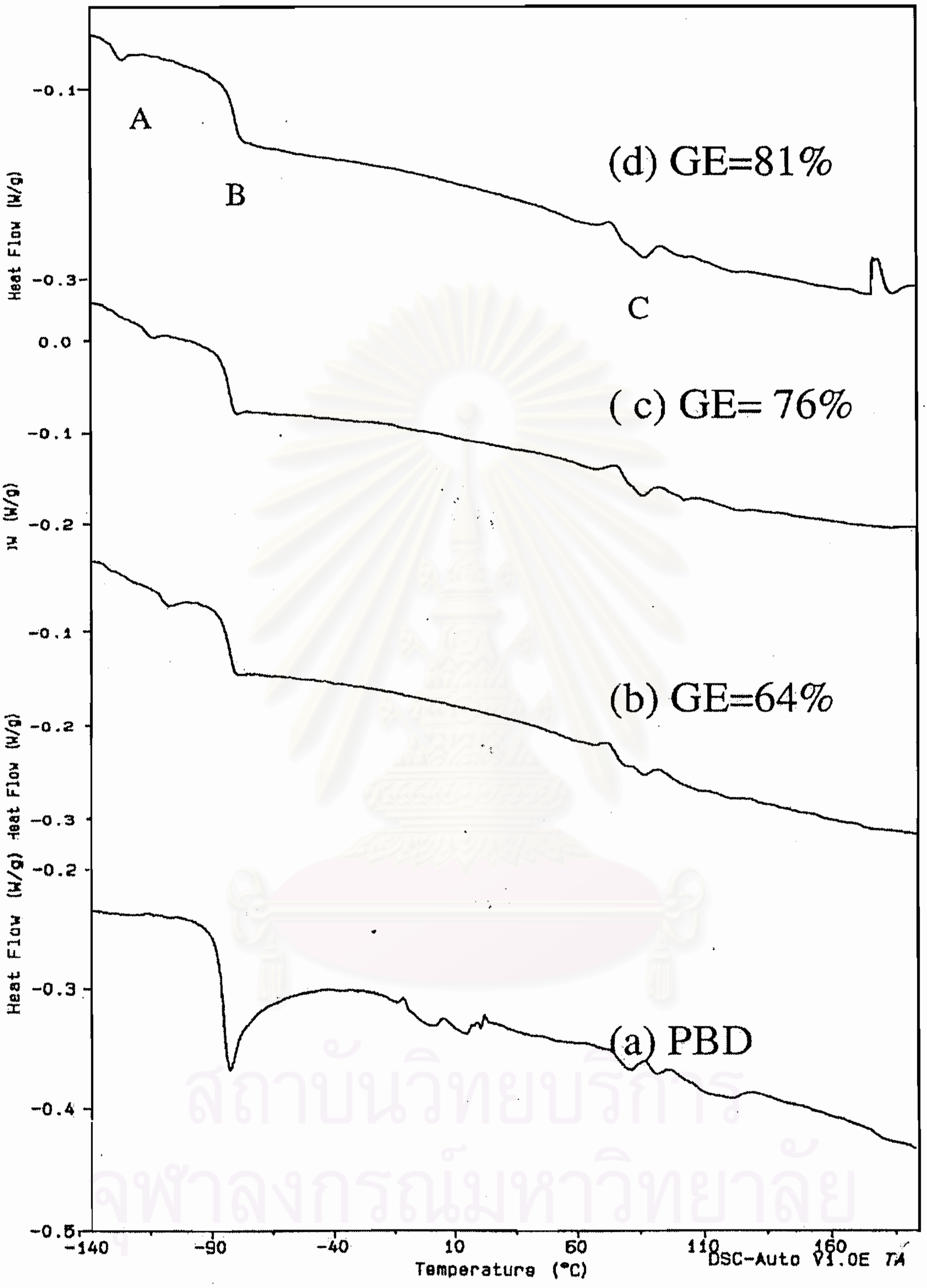


Figure 4.8 DSC curves for (a) PBD, (b) GPB01, (c) GPB02,

and (d) GPB08.

of a polymer with a broad molecular-weight distribution. The SBR and PBD backbone polymers exhibit peaks with maxim at –51.4°C and –85.5°C, respectively, attributed to the glass transition temperature. The glass transition of SBR and PBD become more broad with the increase in the level of grafting, and a lower peak (β transition temperature) appears at around –80 to –120°C for grafting onto SBR and at around –100 to –120°C for grafting onto PBD. Table 4.11 and 4.12 provide the transition temperatures of grafted SBR and grafted PBD.

Figure 4.9 and 4.10 show the effect of grafting efficiency on the β transition temperature and the lower glass transition temperature, respectively. It was found that the grafting efficiency affected the β transition temperature but did not change the lower glass transition temperature for both SBR and PBD cores. The lower peak can be associated with the increase of the graft site in the backbone chain. In addition, the β transition temperature of the core shifts slightly to the lower temperature with increasing grafting efficiency (Figure 4.9). The β transition temperature shifted slightly to the lower temperature; resulting in increased motion of segments or side groups, thus the grafting efficiency increased. Tough ductile glassy polymers and those with high impact strength have prominent β transition temperature (A peak).

From the DSC curves (Figure 4.7 and 4.8) of graft copolymers, the glass transition of the rubber based core system appear to be little affected by the grafting efficiency (Figure 4.10). Only a small change of T_g (less than 3°C) was observed with the increased grafting efficiency. This result is similar to that observed for graft copolymers of natural rubber. The lower glass transition temperature (T_g) decreased with increasing grafting efficiency. The evidence presented is not conclusive but indicative of a trend, particularly since there is no difference between the T_g of the unmodified polymers or graft copolymers if the few graft sites were performed.

Table 4.11 Transition temperature of grafted SBR.

Experiment	GE (%)	β transition temperature (°C) (A Peak)	Lower glass transition temperature (°C) (B Peak)	α′ transition temperature (°C) (C Peak)
SBR	0.0		-51.4	69.4
GSBR02	72.4	-109.1	-52.3	73.6
GSBR03	77.3	-110.8	-50.5	80.9
GSBR04	81.1	-113.2	-51.4	73.9
GSBR05	68.0	-106.3	-50.6	77.1
GSBR06	68.9	-108.9		
GSBR07	86.6	-114.4	-51.1	77.4
GSBR09	59.0	-91.5		74.8
GSBR10	51.2	-93.7	-51.8	85.1
GSBR11	69.4	-109.2	-50.9	77.6
GSBR12	60.0	-102.4	-52.6	76.8
GSBR13	48.3	-90.1	-51.5	79.4
GSBR14	57.2	-95.8	-50.3	75.3
GSBR15	45.5	-85.0	-50.3	61.7
GSBR16	57.0			

Table 4.12 Transition temperature of grafted PBD.

Experiment	GE (%)	β transition temperature (°C) (A Peak)	Lower glass transition temperature (°C) (B Peak)	α′ transition temperature (°C) (C Peak)
PBD	0.0		-85.5	
GPB01	64.0	-109.5	-82.2	74.6
GPB02	77.0	-115.7	-82.4	76.4
GPB03	72.6	-116.0	-82.7	79.7
GPB04	80.5	-116.5	-85.0	
GPB05	63.6	-112.5	-81.8	76.9
GPB06	51.3	-101.3	-82.5	79.6
GPB07	73.1	-115.1	-82.0	74.9
GPB09	52.2	-101.9	-82.4	74.8
GPB10	57.3	-106.2	-82.1	77.9
GPB11	68.1	-112.3	-82.2	88.2
GPB12	65.9	-106.9	-82.0	74.3
GPB13	65.7	-113.9	-82.1	78.3
GPB14	58.4		-82.2	78.0
GPB15	54.0		-82.5	74.8

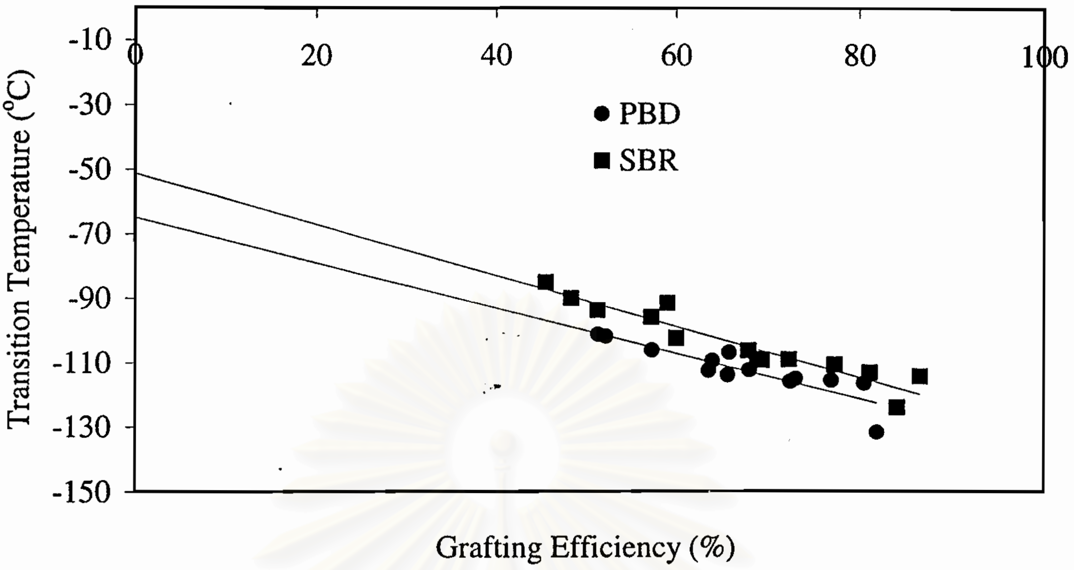


Figure 4.9 Effect of grafting efficiency on the β transition temperature

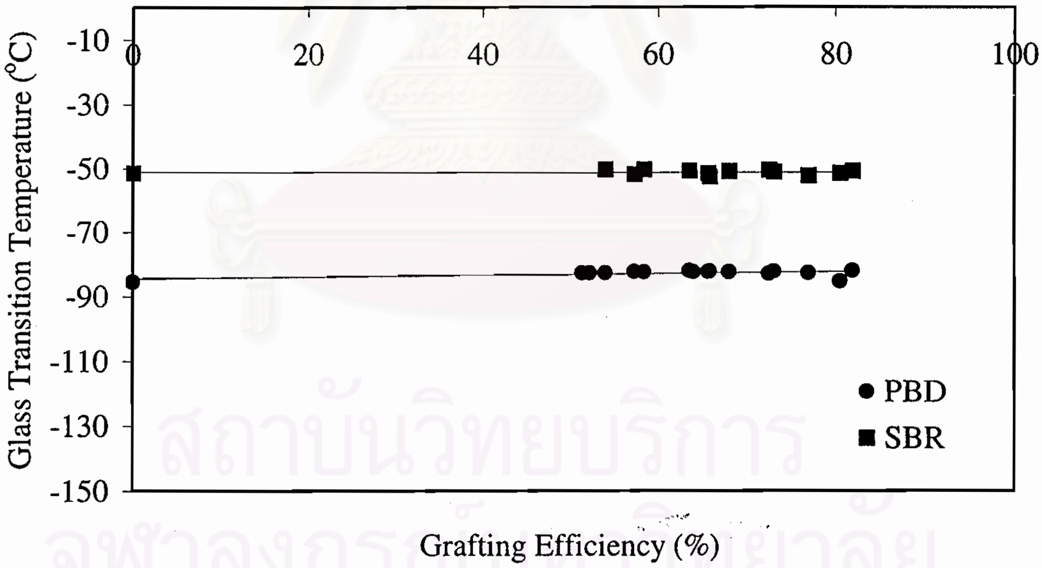


Figure 4.10 Effect of grafting efficiency on the lower glass transition temperature

4.4 Conclusion

The process of graft copolymerization of styrene and methyl methacrylate onto various rubber base systems for the core-shell emulsion process was investigated. Base on a statistical analysis, the extent of the graft copolymerization is dependent on the concentrations of all reactants and reaction temperature. The grafting efficiency increases as the ST/MMA ratio increases for PBD but decreases for SBR. From the observed results, the grafting efficiency of grafted synthetic rubber is slightly higher than that of natural rubber. For a comparison between graft copolymerization onto various polymers, the graft efficiency is a good indication of the graft copolymerization process. The influences of the process variables on the grafting efficiency are listed in Table 4.13

Table 4.13 Qualitative effect of process variables on grafting efficiency of graft copolymerization of ST and MMA onto various polymers.

	NR	SBR	PBD
[INI] ↑	↑	↑	↑
TEMP ↑	↑	↑	↑
[EMUL] ↑	↓	↓	↓
[CTA] ↑	↓	↓	↓
ST/MMA ↑	↑	↓	↑
M/R ↑	↓	↓	↓

Styrene and Methyl methacrylate may be graft copolymerized onto various backbone polymers by hydrogen abstraction or addition to double bond. For PBD and NR system, the graft copolymers are ordinarily produced from a primary radical or a polymeric radical, which abstracts a hydrogen atom to form a graft site. For SBR, the graft copolymer must be dominantly obtained by the addition of primary radical or monomeric radical to the backbone double bond.

The glass transition of graft copolymer change very slightly because the graft copolymers had relatively few graft chains, which was insufficient to affect the free volume available to the backbone. So, the T_g of the graft copolymer was almost the same as that of the ungrafted rubber. However, the β transition temperature had a significant change due to the movement of the graft sites on the main chain.

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CHAPTER 5

PVC IMPACT MODIFICATION USING GRAFTED RUBBER

5.1 Introduction

Polymer blends can combine attractive properties of several polymers into one, or can improve deficient characteristics of a particular polymer. It is well known that the introduction of a small amount of compatibilizer can lead to major changes in mechanical properties [1,2]. It has been reported that a homopolymer as well as block or graft copolymer can be used effectively as a compatibilizer [3-6]. In this study, a rubber core-glassy shell latex particle was required which could be used as a toughening agent for PVC. 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.

A large number of tests are utilized to simulate the various conditions that promote failure in PVC [5]. The test ideally must be both easy to perform and give a reasonable measure of a material impact performance. The material impact properties are directly related to the ability of the material to absorb applied energy. Impact testing represents an attempt to model the most severe abuse to which a material can be subjected.

The mode of failure of a PVC sample under impact is strongly influenced by both the temperature and the rate of deformation [6]. A much more widely used measure of impact strength by manufacturers and supplier is the notched impact strength, either Izod or Charpy, depending on the notch configuration. The notches used are much more blunt than those for fracture mechanics measurements, and the impact strength is defined as the energy required to initiate and propagate a crack from a blunt notch in a bar of square cross-section under impact conditions. As a result of the different notch configurations, there can be no direct comparison between Izod and Charpy values.

The objective of this study was to analyze the toughening effect that the graft copolymers as impact modifier could impart to PVC. The effect of grafting properties and the graft copolymers loading on the impact resistance and tensile properties of PVC blends were investigated. The Izod test at room temperature was performed for the sake of simplicity and to maximize the rubber toughening effect.

5.2 Experimental

5.2.1 Materials

The PVC powder (K-value = 65) and MBS (methyl methacrylate-Butadiene-Styrene terpolymer) were supplied by Thai Plastic and Chemicals Co. Ltd. Other additives were industrial products.

Three graft copolymers with different grafting efficiency and properties (GNR28, GNR33, and GSBR13) were prepared from natural rubber and SBR. The graft properties of graft copolymers are presented in Table 5.1

Table 5.1 Properties of graft copolymers.

	GNR28	GNR33	GSBR13
Total conversion (%)	93.3	91.5	90.8
Grafting efficiency (%)	85.4	56.9	48.3
Graft Properties			
Graft copolymers (%)	73.9	62.5	76.3
Free rubber (%)	20.1	20.0	2.7
Free copolymers (%)	6.0	17.5	21.0
Particle size (μm)	≈ 2-3[a]	≈ 2-3[b]	< 1.0[c]

[a] take from Figure 3.13
[b,c] take from Figure 4.4

5.2.2 Blend Preparation

PVC resin was mixed with the solid additives in the high speed mixer at 2000 rpm for 3 min. The various impact modifiers were added in 5, 8, 10, or 15 phr. Table 5.2 gives the recipes for unmodified and modified PVC. This powder mixtures were hand-mixed thoroughly at proper composition, followed by melt blending using 2-roll mill at 180°C for 5 min and roll gap 1.1 mm.

5.2.3 Preparation of Compression Molding

All physical test specimens were molded on a compression molding machine. The material was placed into the test bar mold and heat up to the molding temperature of 180°C. The sheet was pressed at the pressure of 150 kg_f/cm^2 for 3 min. Finally, the mold was cooled to 60°C at a slow rate (~25°C/min) by compressed air through cooling channels in the mold plates.

Table 5.2 PVC formulation.

Material	UnModified PVC (phr)	Impact modified PVC (phr)
PVC	100	100
OGP 103 (heat stabilizer)	3	3
PE Wax (internal lubricant)	1	1
PR 88C (processing aid)	5	5
graft copolymers impact modifier		
MBS	-	5 and 10
GNR28	-	5, 8, 10, and 15
GNR33	-	5, 8, 10, and 15
GSBR13	-	5, 8, 10, and 15

5.2.4 Physical Characterization

5.2.4.1 Izod Impact Strength

The Izod impact strength of samples was measured according to the ASTM D256 test method. The dimensions of the 2.5 mm notch marked specimens used were 1.27 × 6.35 × 0.3 cm. The impact energy was obtained by the potential energy of the falling hammer before and after impact. Impact energy per unit breadth of the sample is expressed as the impact strength. The machine used in the present investigation was a Toyoseiki; model 612. The average values of at least six tests were reported in every case.

5.2.4.2 Tensile Properties Testing

The tensile properties of the blends were determined by tensile strength and elongation tests according to the JIS K 6723 using a type II dumbbell specimen with 1 mm thickness. A Toyoseiki; model RS-500 testing machine was used at a crosshead speed of 300 mm/min. The results were averaged with at least six measurements.

5.3 Results and Discussion

The effects of graft copolymer modifier loading on the mechanical properties of PVC blends were investigated. The Izod impact strength and tensile strength of PVC blends are presented in Table 5.3

5.3.1 Effect on Impact Strength

The variation of impact resistance of graft copolymer/PVC blends are shown in Figure 5.1. The impact strength increased essentially linearly with increasing of grafted natural rubber. However, the impact strength remains constant at 7 kg_f-cm/cm with loading of GSBR13. The PVC with no graft copolymers has a low impact strength. Therefore, PVC exhibits considerable impact improvement by the addition of the graft copolymer. The addition of the graft copolymers significantly increases the observed

Table 5.3 Properties of graft copolymers/PVC blends.

	Amount (phr)	Izod impact strength (kg_f-cm/cm)	Tensile strength (kg_f/mm^2)	Elongation (%)
Unmodified				
PVC	0	4	166	2
MBS	5	9	525	167
	10	18	413	144
GNR28	5	9	532	27
	8	13	482	11
	10	17	443	10
	15	88	385	65
GNR33	5	9	527	0.4
	8	11	485	37
	10	14	423	10
	15	NA	NA	13
GSBR13	5	7	497	5
	8	7	408	59
	10	7	443	12
	15	NA	NA	10

energy to rupture. So, the impact resistance can be improved by the increased rubber content.

MBS (methyl methacrylate-Butadiene-Styrene terpolymer) is widely used as an impact modifier in PVC. The increases of impact strength of the PVC with the grafted NR and MBS (10 phr) were 17 and 18 kg_f-cm/cm, respectively. For comparison between the grafted NR and MBS, the impact strength of the MBS/PVC blend was somewhat higher than that of the grafted NR/PVC blend. Therefore, the grafted NR is more or less acceptable as an impact modifier for rigid PVC.

To provide a reference point for mechanical property behavior for the synthesized graft copolymers modifier, PVC was blended containing a commercial modifier. This impact modifier is wildly used for PVC. It is possible that the commercial impact modifier MBS gave superior impact properties because of superior fusion with the PVC, primary better miscibility in, and adhesion of the modifier shell to the PVC chains.

Comparison of the graft copolymers GNR28 and GNR33, indicated that the higher grafting efficiency copolymers exhibit better mechanical properties due to the better adhesion between the components in the compatibilized system. Methyl methacrylate/styrene copolymers are used in formation of the shell for impact modifier. 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. The amount of polymer grafted is an important variable that affects the nature of graft layer. Typically, the higher the amount of the monomer polymerized, the higher is the fraction that is chemically bound to the rubber particle. Therefore, the graft layer becomes thicker and usually more uniform. Grafted rubbers that have a high level of non rubbery component (high grafting efficiency) provide better adhesion between the ST/MMA shell and the PVC results in better transfer of energy between the hard PVC phase and the rubbery phase. Interfacial adhesion increases with increasing shell layer and, consequently, the mechanical properties increase.

Comparison of graft copolymers GNR33 and GSBR13, suggest a series of grafted NR core exhibit better mechanical properties as compare to the grafted SBR core. When the PVC blend sample is subjected to shock or impact, the associated mechanical energy is first absorbed by the coherent PVC matrix (hard phase). The energy must be transferred immediately to the rubbery soft phase embedded in the matrix if brittle fracture is to be avoided. If the energy absorbed by the PVC matrix cannot be transferred to the rubbery phase, the energy remains in the hard PVC phase with the result that stress is concentrated at certain point, causing fracture. The energy absorption by the rubbery phase is typically viscoelastic with generation of heat, which in turn lowers the T_g of the PVC matrix near the interface with the modifier particle. The lower T_g of the PVC lowers the yield stress thereby converting brittle PVC into a tougher more ductile material. The T_g value of –65°C determined for NR is lower than that determined for SBR (-51°C) The rubber component of the impact modifier should have a T_g lower than the β-relaxation peak of PVC (-40°C) to impart toughness at lower temperatures [7]. The lower the T_g of the modifier, the better the impact resistance is [8]. From Table 5.2, The grafting efficiency of GSBR13 is lower than that of GNR33. Grafted rubbers that have a high level of grafting efficiency have better mechanical properties.

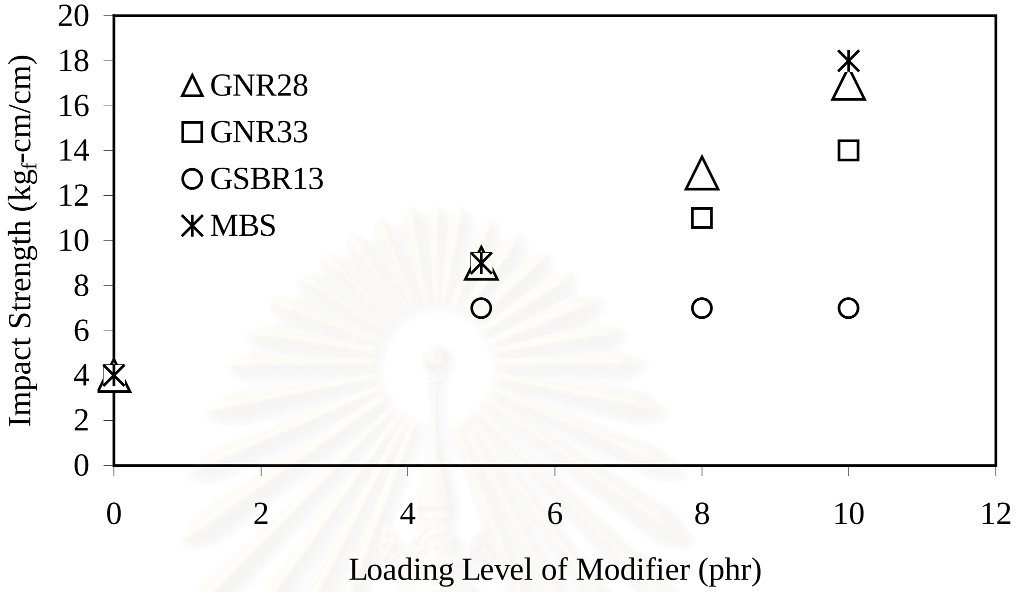

Figure 5.1 Effect of modifier content on impact resistance of PVC blends.

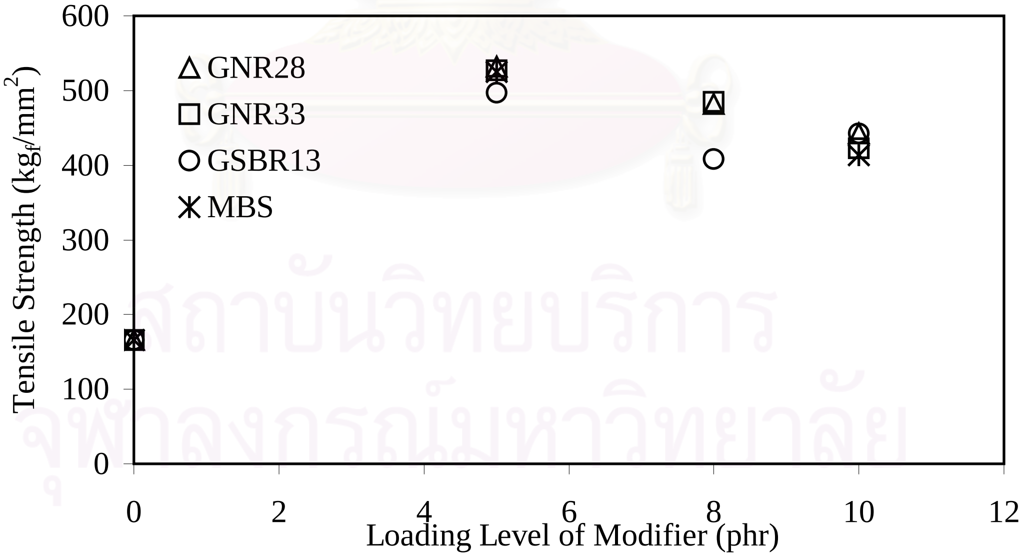

Figure 5.2 Effect of modifier content on tensile strength of PVC blends.

5.3.2 Effect on Tensile Strength.

In polymer blends, mechanical properties are very important parameters for various applications. From Figure 5.2 it is seen that the tensile strength of the PVC blends various with the graft copolymer concentration. The PVC with no graft copolymers has a low tensile strength and considerable strength improvement in PVC is provided by the addition of the graft copolymer. Tensile strength increased rapidly with increasing graft copolymer content at lower loading of copolymer. At the higher loading of graft copolymer (more than 8 phr), tensile strength decreased. However, increasing the concentration of the rubber phase decreases the tensile strength irrespective of whether the matrix is brittle or pseudo ductile [9].

5.4 Conclusion

The grafted natural rubber can be used as impact modifier for PVC to form PVC/grafted rubber blends by mechanical blending and compression molding. The impact strength increased essentially linearly with increasing of grafted natural rubber. The PVC/grafted rubber blends show a higher tensile strength in comparison to unmodified PVC. Good mechanical properties were obtained at 10 phr of the grafted natural rubber. This work has successfully produced an impact modifier from natural rubber similar to MBS for PVC impact improvement.

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CHAPTER 6

CONCLUSION AND RECOMENDATION

6.1 Conclusion

High impact resistance polymers are based on two-phase polymer systems, comprising continuous glassy phase and dispersed rubbery domains. Stabilization of these two domains is achieved by grafting the monomers in the second stage polymerization onto rubber. Seeded emulsion polymerization for the grafting reaction of methyl methacrylate and styrene onto rubber was found to be an appropriate and easy synthetic approach to produce core-shell particles of spherical morphology. The resulting graft copolymer composition and properties are affected by emulsion polymerization variables such as the amount and type of initiator, the amount of emulsifier, the amount of chain transfer agent, the amount of monomers, monomer-to-rubber ratio, styrene-to-methyl methacrylate ratio, and reaction temperature and time.

The work of this investigation attempts to provide a consistent overview of the effects of process variables on the grafting reaction. Initially, the grafting of methyl methacrylate and styrene onto natural rubber was carried out using two types of initiator (Chapter 2). It was found that, when the water soluble initiator (potassium persulfate) was used, the grafting efficiency of the copolymer was much lower than that when oil soluble initiator (cumene hydroperoxide) was employed. The hydroperoxide initiator is believed to produce the initiating radicals at or near the particle interface and it causes preferential copolymerization of the monomer in the region of the particle surface. A study of the effect of process variables led to the following preliminary conclusions: 1) an increase in the initiator concentration increased the grafting efficiency due to higher free radical concentration; 2) the grafting efficiency increased with increasing temperature depending on the free radicals, resulting from the decomposition of the initiator; 3) the emulsifier amount has a small effect on grafting styrene and methyl methacrylate onto natural rubber; 4) the grafting efficiency decreased as monomer-to-rubber ratio increased suggesting that the graft copolymerization occurs on the surface of the latex particles; 5)the grafting decreased as the amount of chain-transfer agent increased due to the decrease of macroradical formation.

Factorial design experiments is an efficient method for data collection. The two fractional factorial designs were employed to study the effects of six potentially influential process factors. The analysis of the results from the design showed that only the amount of chain transfer agent and temperature in the range of test had significant effects on grafting efficiency.

These observations were also made when performing analogous grafting onto styrene-butadiene rubber (SBR) and polybutadiene (PBD) as the rubbery core. It was found that grafting of styrene and methyl methacrylate onto synthetic rubber was in some ways similar to grafting onto natural rubber and in some ways was different, especially the graft copolymer composition for the SBR core. This suggests a different mechanism of grafting.

The mechanistic results presented in Chapters 2 through 4 indicated the occurrence of grafting on the natural rubber backbone in the core-shell latex particles. The growing polymeric chain, produced in water, might precipitate onto the surface of the latex particle and continue to propagate to form the shell layer. Furthermore, it is confirmed that the graft copolymerization is a surface-controlled process.

When cumene hydroperoxide is used as initiator, the primary radical is reactive and thus can either abstract a hydrogen from an allylic position, or add to the double bond in the backbone. Styrene and methyl methacrylate may be dominantly graft copolymerized onto NR and PBD latex by hydrogen abstraction. For grafting onto SBR, the graft copolymer may be obtained by the addition of the double bond. Differential scanning calorimetry also confirmed a two phase particle morphology. The T_g of the rubbery phase was unaffected by grafting efficiency, but the β transition temperature decreased as the efficiency of grafting was increased

The graft copolymer could be used as an impact modifier for PVC resin. The PVC/graft copolymer blends were prepared by melt blending and compression molding. PVC toughed with the addition of graft copolymers provided improved impact resistance. Impact resistance was found to be a function of both modifier loading and grafted rubber properties. PVC toughened with graft copolymer GNR28 was found to give superior impact properties similar to PVC toughened with commercial MBS at the same loading level.

6.2 Recommendation

For the area of modification of natural rubber latex and polymer blends, further study should be given to the following aspects:

1. Investigate methods to obtain narrow particle size distribution seed latex.
2. Investigate methods to determine the mechanism of grafting (direct attack of the double bond in backbone or hydrogen abstraction) by analysis of the chemical composition using FTIR.

3. Investigate methods to determine the particle size and the number of particles for studying the kinetics of seeded emulsion polymerization on the grafting reaction.

APPENDIX A

Raw Data of of Graft Copolymerization

Table A-1 Raw data of of graft copolymerization for NR (Chapter 2).

EXP.	Conv. (%)	Sample (g)	NR (g)	Monomers (g)	Free rubber (g)	Free copolymers (g)	Graft copolymers (g)	Free rubber (%)	Free copolymers (%)	Graft copolymers (%)	GE (%)
GNR01	92.5	5.019	2.607	2.412	0.836	0.672	3.511	16.7	13.4	69.9	72.1
GNR02	86.3	4.980	2.674	2.306	1.353	1.237	2.391	27.2	24.8	48.0	46.4
GNR03	91.1	5.020	2.627	2.393	1.121	1.023	2.876	22.3	20.4	57.3	57.3
GNR04	95.6	4.931	2.520	2.410	0.827	0.468	3.635	16.8	9.5	73.7	80.6
GNR05	97.6	4.935	2.498	2.438	1.196	1.767	1.972	24.2	35.8	40.0	27.5
GNR06	85.9	5.019	2.701	2.319	2.553	1.449	1.017	50.9	28.9	20.3	37.5
GNR07	85.4	5.172	2.790	2.382	1.932	0.837	2.403	37.4	16.2	46.5	64.9
GNR08	97.2	5.011	2.541	2.470	1.147	0.962	2.902	22.9	19.2	57.9	61.1
GNR09	90.5	6.819	3.579	3.240	2.489	2.106	2.224	36.5	30.9	32.6	35.0
GNR10	75.3	5.047	2.879	2.168	2.687	1.764	0.597	53.2	34.9	11.8	18.6
GNR11	77.9	5.084	2.858	2.226	2.697	1.887	0.500	53.0	37.1	9.8	15.2
GNR12	85.1	5.027	2.715	2.312	1.181	0.659	3.187	23.5	13.1	63.4	71.5
GNR13	86.6	5.228	2.802	2.427	0.688	0.777	3.764	13.1	14.9	72.0	68.0
GNR14	96.2	5.017	2.557	2.460	0.848	1.800	2.369	16.9	35.9	47.2	26.8
GNR15	90.1	5.164	3.082	2.082	1.080	0.529	3.556	20.9	10.2	68.8	74.6
GNR16	93.4	4.953	2.285	2.668	0.825	0.989	3.139	16.7	20.0	63.4	62.9
GNR17	96.1	5.004	2.050	2.954	0.604	1.281	3.119	12.1	25.6	62.3	56.6
GNR18	78.3	8.116	4.551	3.565	3.600	1.950	2.565	44.4	24.0	31.6	45.3
GNR19	79.8	7.382	4.105	3.276	2.828	2.548	2.005	38.3	34.5	27.2	22.2
GNR20	70.7	5.192	2.874	2.318	2.640	2.096	0.456	50.8	40.4	8.8	9.6

Table A-2 Raw data of of graft copolymerization for NR (Chapter 3).

EXP.	Conv. (%)	Sample (g)	NR (g)	Monomers (g)	Free rubber (g)	Free copolymers (g)	Graft copolymers (g)	Free rubber (%)	Free copolymers (%)	Graft copolymers (%)	GE (%)
GNR21	90.0	9.985	5.961	4.024	2.609	1.873	5.502	26.1	18.8	55.1	53.4
GNR22	92.6	7.279	4.295	2.984	1.609	0.880	4.790	22.1	12.1	65.8	70.5
GNR23	92.2	14.117	7.344	6.773	1.847	2.523	9.747	13.1	17.9	69.0	62.7
GNR24	93.5	13.318	6.883	6.435	1.809	1.318	10.191	13.6	9.9	76.5	79.5
GNR25	91.6	3.198	1.669	1.529	0.469	0.768	1.961	14.7	24.0	61.3	49.8
GNR26	93.5	14.563	7.528	7.035	2.200	3.889	8.474	15.1	26.7	58.2	44.7
GNR27	91.5	10.039	5.954	4.085	2.414	1.470	6.155	24.0	14.6	61.3	64.0
GNR28	93.3	9.126	5.369	3.757	1.838	0.548	6.741	20.1	6.0	73.9	85.4
GNR29	92.8	9.514	4.936	4.578	1.272	2.581	5.661	13.4	27.1	59.5	43.6
GNR30	93.9	7.769	4.006	3.763	0.779	1.999	4.991	10.0	25.7	64.2	46.9
GNR31	91.9	11.459	6.783	4.676	2.088	1.959	7.412	18.2	17.1	64.7	58.1
GNR32	92.8	14.202	8.373	5.829	2.671	2.655	8.876	18.8	18.7	62.5	54.5
GNR33	91.5	6.724	3.988	2.736	1.345	1.180	4.200	20.0	17.5	62.5	56.9
GNR34	93.1	11.654	6.861	4.793	2.391	2.538	6.724	20.5	21.8	57.7	47.0
GNR35	91.7	9.975	5.204	4.771	1.173	2.609	6.192	11.8	26.2	62.1	45.3
GNR36	93.6	9.253	4.779	4.474	0.775	2.153	6.324	8.4	23.3	68.4	51.9

Table A-3 Raw data of of graft copolymerization for SBR (Chapter 4).

EXP.	Conv. (%)	Sample (g)	NR (g)	Monomers (g)	Free rubber (g)	Free copolymers (g)	Graft copolymers (g)	Free rubber (%)	Free copolymers (%)	Graft copolymers (%)	GE (%)
GSBR01	87.9	10.197	6.146	4.051	0.075	0.765	9.357	0.7	7.5	91.8	81.1
GSBR02	98.5	8.945	5.145	3.800	0.186	0.862	7.897	2.1	9.6	88.3	77.3
GSBR03	92.4	6.805	3.537	3.268	0.012	1.058	5.735	0.2	15.5	84.3	67.6
GSBR04	87.9	8.795	4.681	4.114	0.044	1.277	7.474	0.5	14.5	85.0	69.0
GSBR05	94.9	13.352	6.851	6.501	0.065	0.872	12.415	0.5	6.5	93.0	86.6
GSBR06	92.4	14.533	7.554	6.979	0.388	1.111	13.034	2.7	7.6	89.7	84.1
GSBR07	95.1	6.940	4.051	2.889	0.075	0.816	6.049	1.1	11.8	87.2	71.8
GSBR08	94.4	8.176	4.787	3.389	0.121	0.936	7.119	1.5	11.4	87.1	72.4
GSBR09	95.0	13.192	6.765	6.427	0.290	3.503	9.399	2.2	26.6	71.2	45.5
GSBR10	97.1	12.249	6.215	6.034	0.245	2.592	9.412	2.0	21.2	76.8	57.0
GSBR11	73.9	7.993	5.143	2.850	0.455	1.474	6.064	5.7	18.4	75.9	48.3
GSBR12	89.8	7.937	4.743	3.194	0.382	1.368	6.187	4.8	17.2	78.0	57.2
GSBR13	90.8	11.326	6.738	4.588	0.313	1.882	9.131	2.8	16.6	80.6	59.0
GSBR14	89.6	13.041	7.800	5.241	0.551	1.602	10.888	4.2	12.3	83.5	69.4
GSBR15	89.0	9.542	5.049	4.493	0.296	3.192	6.054	3.1	33.5	63.4	29.0
GSBR16	81.0	11.565	6.390	5.175	0.347	2.070	9.148	3.0	17.9	79.1	60.0

Table A-4 Raw data of of graft copolymerization for PBD (Chapter 4).

EXP.	Conv. (%)	Sample (g)	NR (g)	Monomers (g)	Free rubber (g)	Free copolymers (g)	Graft copolymers (g)	Free rubber (%)	Free copolymers (%)	Graft copolymers (%)	GE (%)
GPB01	92.0	6.894	4.079	2.815	1.431	1.012	4.451	20.8	14.7	64.6	64.0
GPB02	93.6	5.335	3.135	2.201	0.524	0.507	4.305	9.8	9.5	80.7	77.0
GPB03	94.2	11.013	5.671	5.342	1.805	1.464	7.744	16.4	13.3	70.3	72.6
GPB04	96.5	9.188	4.676	4.512	1.468	0.878	6.841	16.0	9.6	74.5	80.5
GPB05	92.6	13.358	6.936	6.422	1.336	2.338	9.684	10.0	17.5	72.5	63.6
GPB06	94.5	11.923	6.130	5.793	1.484	2.821	7.618	12.5	23.7	63.9	51.3
GPB07	91.2	8.185	4.860	3.324	1.422	0.893	5.870	17.4	10.9	71.7	73.1
GPB08	94.5	7.618	4.458	3.160	1.299	0.572	5.747	17.1	7.5	75.4	81.9
GPB09	91.8	12.716	6.630	6.086	1.228	2.911	8.577	9.7	22.9	67.5	52.2
GPB10	91.2	9.895	5.175	4.720	1.559	2.016	6.320	15.8	20.4	63.9	57.3
GPB11	92.5	9.126	5.388	3.738	1.386	1.192	6.548	15.2	13.1	71.8	68.1
GPB12	93.5	9.945	5.845	4.099	1.764	1.397	6.783	17.7	14.1	68.2	65.9
GPB13	92.2	9.047	5.349	3.699	2.142	1.268	5.637	23.7	14.0	62.3	65.7
GPB14	93.5	7.860	4.620	3.240	1.379	1.349	5.132	17.5	17.2	65.3	58.4
GPB15	91.1	8.300	4.343	3.957	1.520	1.821	4.959	18.3	21.9	59.7	54.0
GPB16	93.4	8.218	4.249	3.969	1.163	1.429	5.626	14.2	17.4	68.5	64.0

APPENDIX B

The Composition of Styrene and Methyl Methacrylate in Grafted Rubber Calculated fromThe Specific Signal Areas of ^{1}H-NMR

Table B-1 The composition of styrene and methyl methacrylate in grafted NR calculated from the specific signal areas of ^{1}H-NMR.

Experiment	Signal areas at			Styrene (%)	Isoprene (%)	MMA (%)	F_{ST}-g	F_{MMA}-g
	Styrene (7.5-6.5 ppm)	Isoprene (5.1 ppm)	MMA (3.7 ppm)					
GNR21	0.3199	0.7564	0.1492	10.6	81.5	7.9	0.563	0.437
GNR22	19.49	28.21	4.6	16.4	77.4	6.2	0.718	0.282
GNR23	1.722	2.854	0.653	14.2	77.1	8.7	0.613	0.387
GNR24	19.5	22.43	4.48	19.5	73.3	7.2	0.723	0.277
GNR25	0.946	1.491	0.207	15.4	79.2	5.4	0.733	0.267
GNR26	18.76	35.48	6.64	12.9	79.8	7.3	0.629	0.371
GNR27	1.314	2.044	0.361	15.3	77.9	6.8	0.686	0.314
GNR28	25.28	37.93	12.86	14.9	73.0	12.1	0.541	0.459
GNR29	0.898	2.55	0.33	9.2	85.4	5.4	0.620	0.380
GNR30	0.856	1.67	0.186	13.0	82.5	4.5	0.734	0.266
GNR31	0.956	2.172	0.532	10.7	79.7	9.6	0.519	0.481
GNR32	1.182	2.272	0.488	12.6	79.1	8.3	0.592	0.408
GNR33	0.49	1.167	0.188	10.7	82.8	6.5	0.610	0.390
GNR34	0.3421	0.9878	0.1471	9.0	84.8	6.2	0.583	0.417
GNR35	0.2294	0.4476	0.0474	13.0	82.7	4.3	0.744	0.256
GNR36	10.17	18.87	4.09	13.0	78.6	8.4	0.599	0.401

Table B-2 The composition of styrene and methyl methacrylate in grafted SBR calculated from the specific signal areas of ^{1}H-NMR.

Experiment	Signal areas at				Styrene (%)	Butadiene (%)	MMA (%)	F_{ST}-g	F_{MMA}-g
	Styrene	Butadiene		MMA					
	(7.5 ppm)	(5.4 ppm)	(4.9 ppm)	(3.7 ppm)					
GSBR01	1.0	0.9	0.15	0.292	8.9	74.3	16.9	0.344	0.656
GSBR02	116.6	96.0	15.2	30.68	11.6	72.0	16.4	0.415	0.585
GSBR03	201.6	145.5	33.1	61.8	12.2	68.4	19.4	0.387	0.613
GSBR04	99.3	55.1	20.3	26.64	16.6	64.6	18.8	0.468	0.532
GSBR05	1.0	0.7	0.14	0.1811	17.3	69.8	12.9	0.572	0.428
GSBR06	93.5	67.3	17.2	22.97	13.6	70.3	16.1	0.459	0.541
GSBR07	149.5	88.1	19.6	46.14	15.4	63.5	21.1	0.423	0.577
GSBR08	13.5	8.2	1.35	3.664	16.5	64.6	18.9	0.465	0.535
GSBR09	230.4	245.8	46.2	70.2	6.1	77.7	16.3	0.272	0.728
GSBR10	-	-	-	-	-	-	-	-	-
GSBR11	196.8	193.7	39	34.2	10.0	79.6	10.4	0.492	0.508
GSBR12	1.0	1.0	0.12	0.2353	9.1	77.1	13.7	0.400	0.600
GSBR13	-	-	-	-	-	-	-	-	-
GSBR14	131.5	138.2	25.5	29.55	7.9	79.5	12.6	0.383	0.617
GSBR15	1.0	1.2	0.21	0.2576	5.5	81.1	13.5	0.288	0.712
GSBR16	553.4	455.6	99.6	105.7	12.9	74.8	12.3	0.513	0.487

Table B-3 The composition of styrene and methyl methacrylate in grafted PBD calculated from the specific signal areas of ^{1}H-NMR.

Experiment	Signal areas at				Styrene (%)	Butadiene (%)	MMA (%)	F_{ST}-g	F_{MMA}-g
	Styrene	Butadiene		MMA					
	(7.5 ppm)	(5.4 ppm)	(4.9 ppm)	(3.7 ppm)					
GPB01	1.0	11.6	2.53	0.4	5.5	91.0	3.5	0.600	0.400
GPB02	-	-	-	-	-	-	-	-	-
GPB03	-	-	-	-	-	-	-	-	-
GPB04	1.0	2.9	0.6058	0.4122	17.2	71.4	11.4	0.593	0.407
GPB05	-	-	-	-	-	-	-	-	-
GPB06	-	-	-	-	-	-	-	-	-
GPB07	1.0	2.1	0.4234	0.4523	21.2	63.5	15.4	0.570	0.430
GPB08	1.0	2.8	0.5772	0.278	18.2	73.7	8.1	0.683	0.317
GPB09	1.0	2.6	0.4537	0.1	20.5	76.3	3.3	0.857	0.143
GPB10	1.0	8.9	4.028	0.1	6.5	92.5	1.0	0.857	0.143
GPB11	1.0	5.0	1.421	0.47	10.8	81.0	8.2	0.561	0.439
GPB12	1.0	11.7	3.199	0.896	5.1	87.7	7.3	0.401	0.599
GPB13	1.0	5.7	1.247	0.301	10.4	84.6	5.0	0.666	0.334
GPB14	-	-	-	-	-	-	-	-	-
GPB15	1.0	5.0	1.11	0.479	11.2	80.3	8.6	0.556	0.444
GPB16	1.0	6.2	1.342	0.308	9.6	85.7	4.7	0.661	0.339

VITA

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