

# Synthesis of Graft Copolymers from Natural Rubber Using Cumene Hydroperoxide Redox Initiator

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**ABSTRACT:** The graft copolymerization of 50/50 (w/w) styrene/methyl methacrylate mixtures onto natural rubber seed latex were carried out by using cumene hydroperoxide/sodium formaldehyde sulfoxylate dihydrate/EDTA-chelated Fe<sup>2+</sup> as a redox initiator. 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) and grafting level (GL) are reported. The mechanism of graft copolymerization was investigated. The synthesized graft copolymers were purified and then characterized by proton nuclear magnetic resonance (<sup>1</sup>H-NMR) analysis. Transmission electron microscopy (TEM) was used to study the morphology of the graft copolymers. It appears that the formation of graft copolymers occurs on the surface of the latex particles through a chain-transfer process. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2993–3001, 2002; DOI 10.1002/app.2328

**Key words:** graft copolymerization; natural rubber modification; styrene; methyl methacrylate; redox initiator

## INTRODUCTION

Natural rubber (NR) has an attractive range of modifying properties, which can be devised to give more desirable properties. Because there is an increased consciousness about environmental preservation and an increased emphasis on the use of renewable resources, a considerable amount of research has been involved with the improvement of the properties of natural rubber, thus enabling it to compete with synthetic rubbers. Furthermore, the improved products from natural rubber have potentially wide application

as a result of physical or chemical modification. 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.<sup>1–4</sup> 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.<sup>5,6</sup> 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.<sup>7</sup> Graft copolymers are produced when vinyl monomers are attached to the backbone unsaturation in natural rubber through carbon-to-carbon bonds. Enyiegbulam and Aloka<sup>8</sup> reported that graft copolymers of natural rubber and methyl methacrylate were produced by poly-

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merizing 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). Lenka et al.<sup>9</sup> reported that the graft copolymerization of methyl methacrylate onto rubber using potassium peroxydisulfate catalyzed by silver ion was temperature dependent. A number of reports<sup>10–13</sup> 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.<sup>14,15</sup>

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.<sup>15</sup> 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.<sup>16</sup> 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. During the course of a seeded emulsion polymerization, the phase separation leads to a variety of particles of different phase structure, for example, “raspberry-like,” “acorn-like,” “sandwich-like,” and “inverted” structure.<sup>17</sup>

The purpose of this work was to investigate the influence of the process factors on the graft copolymerization, factors such as initiator, amount used in the secondary polymerization, polymerization temperature, the amount of emulsifier and chain-transfer agent, and monomer-to-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<sup>2+</sup> 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 homopoly-

merization. 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. Moreover, the produced iron (III) ions, in turn, oxidize the reducing agent, being themselves reduced to iron (II) ions once again.<sup>18</sup>

## EXPERIMENTAL

### Materials

Natural rubber latex used was 60% dry rubber content (DRC), commercial high-ammonia natural rubber latex. Reagent-grade styrene (purity ~ 99%; Aldrich, Milwaukee, WI) and methyl methacrylate (purity ~ 99%; Aldrich) 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 dodecylsulfate (SDS, purity ~ 98%; Aldrich); the stabilizer isopropanol; the buffer potassium hydroxide (KOH, Aldrich); the initiators, redox initiator system, cumene hydroperoxide (CHPO, C<sub>9</sub>H<sub>12</sub>O<sub>2</sub>, purity ~ 80%; Aldrich); the reducing agent sodium formaldehyde sulfoxylate (SFS, CH<sub>3</sub>NaO<sub>3</sub>S·2H<sub>2</sub>O; Aldrich); iron (II) sulfate heptahydrate (FeSO<sub>4</sub>·7H<sub>2</sub>O, purity ~ 98%; Fluka, Milwaukee, WI); and ethylenediamine tetraacetic acid (EDTA; Aldrich) were used as received. Deionized water was used throughout the work. A redox solution was prepared from SFS and EDTA-chelated Fe<sup>2+</sup>, as described by Prince and Spitz.<sup>19</sup> The ratio of the components in the redox system, CHPO/SFS/EDTA-chelated Fe<sup>2+</sup>, was 1.0/1.0/0.08 (w/w/w), giving reasonable polymerization rates at low temperature.<sup>20</sup>

### 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, still providing 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 SFS solution and EDTA-chelated Fe<sup>2+</sup> 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 was performed at the stirring speed of 200 rpm and the desired temperature for 8 h. The polymerization temperature was maintained using a constant-temperature water bath and 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°C. The recipes and variable factors for the graft copolymerization are shown in Tables I and II.

Ungrafted natural rubber was washed out in a Soxhlet extractor using 60–80°C boiling point petroleum ether for 24 h. The residue was dried to constant weight in an oven at 40°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. Weights of both the initial sample and the extracted samples were measured for the determination of graft copolymer and free copolymer contents.

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) (PSt/MMA) are referred to as free copolymers. Graft copolymers are referred to as NR-*g*-PMMA, NR-*g*-PSt, and NR-*g*-PSt/MMA. The grafting level (GL) and

**Table I** Graft Copolymerization Recipe<sup>a</sup>

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

<sup>a</sup> In parts by weight.

**Table II** Parameters of Various Experiments

Factor	Variable
Reaction temperature	50, 60, 70, 80 (°C)
Sodium dodecylsulfate amount	0.5, 1.0, 1.5, 2.0 (phr)
<i>n</i> -Dodecyl mercaptan amount	0, 0.5, 1.0, 1.5 (phr)
CHPO amount	0.5, 1.0, 1.5, 2.0, 2.5 (phr)
Monomer-to-rubber ratio	0.75, 1.0, 1.25, 1.5

the grafting efficiency (GE) were calculated using the following relationships:

Grafting level (GL, %)

$$= \frac{\text{total weight of graft copolymers}}{\text{total weight of rubber grafted}} \times 100 \quad (1)$$

Grafting efficiency (GE, %)

$$= \frac{\text{total weight of monomers grafted}}{\text{total weight of monomers polymerized}} \times 100 \quad (2)$$

### 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<sub>4</sub> 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.

### Nuclear Magnetic Resonance

<sup>1</sup>H-NMR spectra were run on a Bruker 250-MHz instrument (Bruker Instruments, Billerica, MA) using 5–10% (w/v) solution in deuterated chloroform (CDCl<sub>3</sub>).

## RESULTS AND DISCUSSION

### Mechanism of Grafting

The cumene hydroperoxides in the dilute aqueous solution induced by the iron (II) ions decompose to yield alkoxy radicals (RO·). 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 either 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  $\alpha$ -methylene hydrogen atoms in the natural rubber, which are more active, to become the sites of graft copolymerization. The alkoxy radicals not only can attack the  $\alpha$ -methylene hydrogen atoms to produce polyisoprene radicals, which initiate monomers to form the graft copolymers, but can also initiate monomers to form free polymer radicals, which combine with polyisoprene radicals to terminate or transfer to natural rubber to form graft copolymers. Moreover, 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

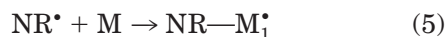
Attacking monomer:



Attacking rubber:

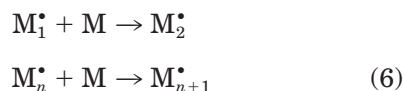


Reinitiation:

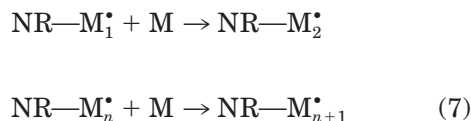


#### Propagation

Propagation of free polymerization:

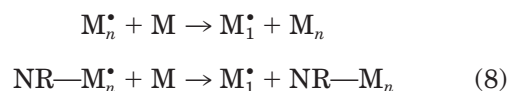


Propagation of graft polymerization:

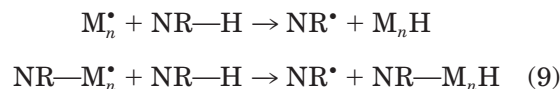


#### Chain Transfer to Macromolecules

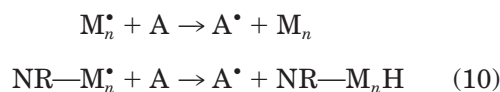
Transfer to monomer:



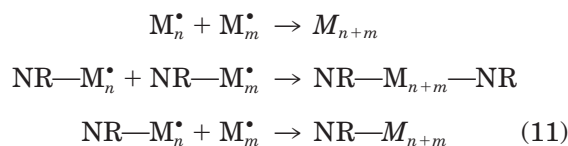
Transfer to rubber:



Transfer to chain-transfer agent:



#### Termination by Combination



where  $\text{RO}^\bullet$  is an alkoxy radical;  $\text{M}$  is a vinyl monomer;  $\text{M}_n^\bullet$  is a vinyl polymer radical;  $\text{NR—H}$  is natural rubber;  $\text{H}$  is the  $\alpha$ -methylene hydrogen atom;  $\text{NR}^\bullet$  is the polyisoprene radical;  $\text{NR—M}_n^\bullet$  is the growing graft polymer radical chain; and  $\text{A}$  is the chain-transfer agent.

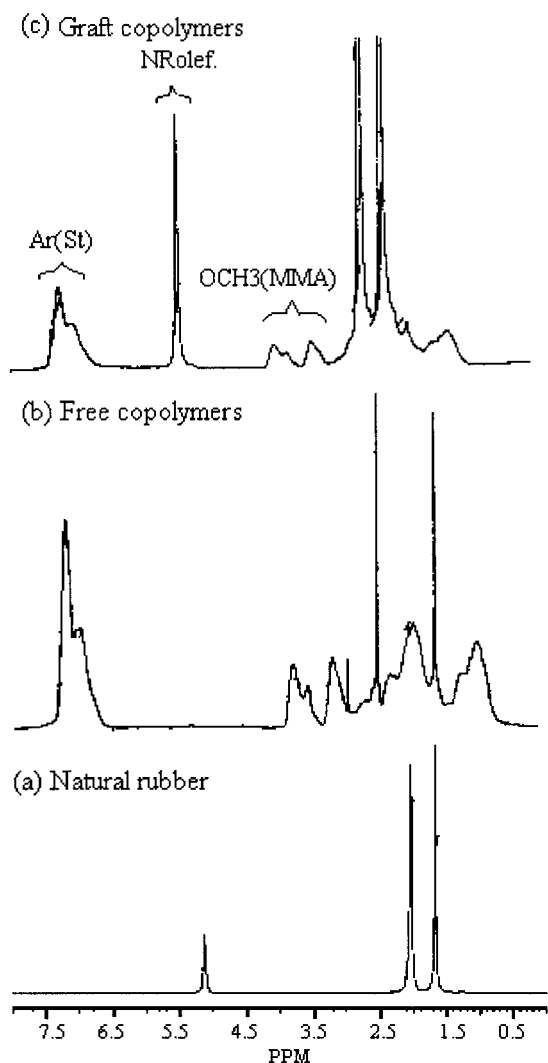
To determine the presence of the graft copolymers, the products were extracted by petroleum ether and the mixture of acetone and MEK, respectively. After the solvent extraction, the graft copolymers were analyzed by  $^1\text{H-NMR}$ . Figure 1 illustrates the  $^1\text{H-NMR}$  spectrum of the polymers. The peaks at 5.15 ppm are assigned to the olefinic proton 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  $^1\text{H-NMR}$  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 cannot be neglected. Allen et al.<sup>21</sup> studied the mechanism of the graft copolymerization of methyl methacrylate in the presence of polyisoprene and suggested that the

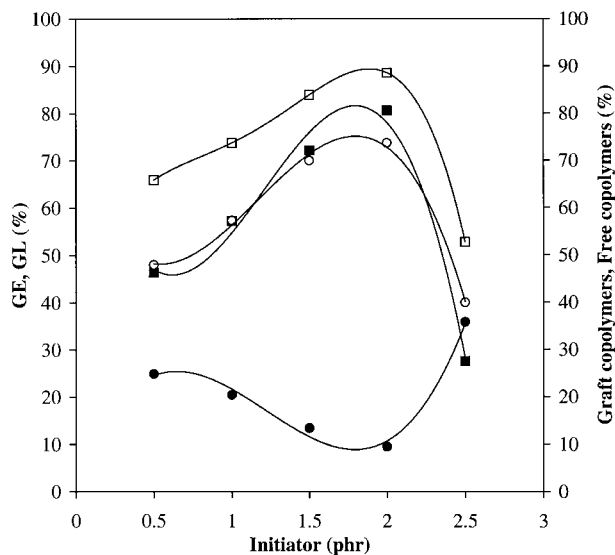
formation of graft copolymers involved the chain-transfer reaction when benzoyl peroxide was used as initiator. A similar observation was made by Merkel et al.<sup>22</sup> in the case of grafting of methyl methacrylate onto polybutadiene.

### 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



**Figure 1**  $^1\text{H-NMR}$  spectra (250 MHz) 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<sub>3</sub>(MMA) represents the resonance of the methoxy protons.



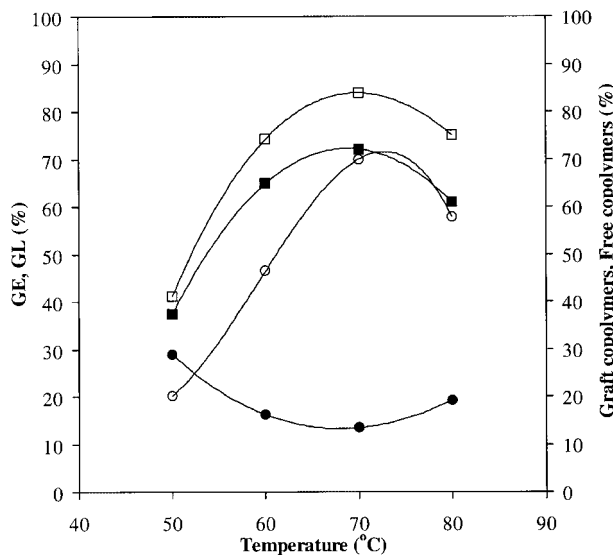
**Figure 2** Effect of the amount of initiator on grafting efficiency (■), grafting level (□), free copolymers (●), and graft copolymers (○). SDS = 1.5 phr, nDM = 0 phr, monomer-to-rubber ratio = 1, and  $T = 70^\circ\text{C}$ .

GL were seen to increase with an increase in the amount of initiator from 0.5 to 2.0 phr (Fig. 2). 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, which results from 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 radicals is promoted more at high initiator content (Fig. 2). 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 et al.<sup>9–11</sup> in the case of grafting methyl methacrylate onto natural rubber.

### Effect of Polymerization Temperature

The rate of decomposition of the initiator depends on the reaction temperature. With an increase in reaction temperature, more alkoxy radicals are



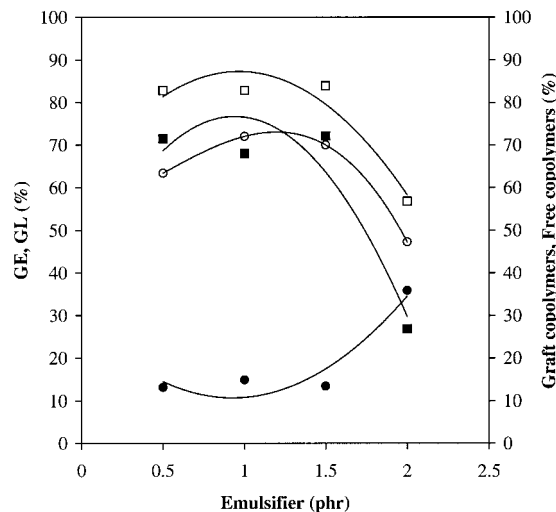


**Figure 3** Effect of temperature on grafting efficiency (■), grafting level (□), free copolymers (●), and graft copolymers (○). CHPO = 1.5 phr, SDS = 1.5 phr, nDM = 0 phr, and monomer-to-rubber ratio = 1.

produced. It is also known that the transfer of alkoxy radicals to the rubber chain produces the graft copolymers. So, perusal of the results indicates that the GE and GL increase as the polymerization temperature is increased up to 70°C (Fig. 3); then both GE and GL decrease with further increases in the reaction temperature. This may result from 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 that, however, fails to produce both the corresponding ungrafted and graft copolymers.

#### 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 (Fig. 4). The results indicate that the amount of emulsifier has little effect on GE and GL because of the nonoccurrence 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.<sup>16</sup> observed similar results for the graft copolymerization of styrene and methyl methacrylate onto styrene-butadiene rubber. The possibility of polymerization is that there will be more free micelles existing in the water phase,

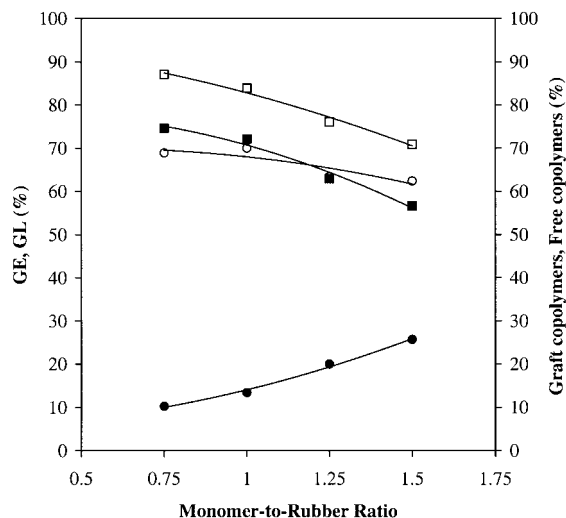


**Figure 4** Effect of the amount of emulsifier on grafting efficiency (■), grafting level (□), free copolymers (●), and graft copolymers (○). CHPO = 1.5 phr, nDM = 0 phr, monomer-to-rubber ratio = 1, and  $T = 70^{\circ}\text{C}$ .

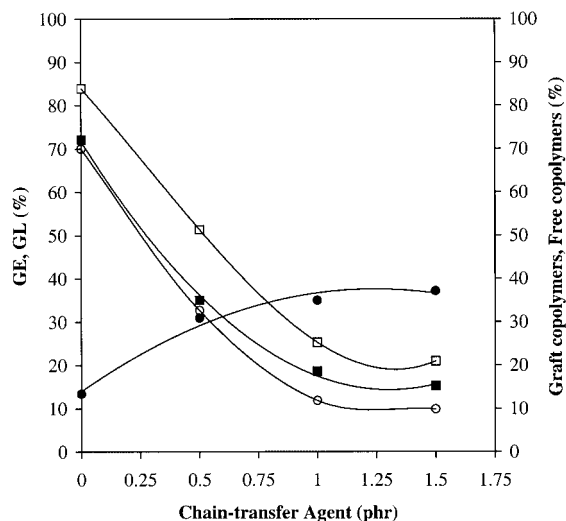
resulting in the increasing formation of free copolymers. Thus, there will be less monomer for grafting onto the NR latex backbone and free copolymerization is preferred to graft copolymerization.

#### Effect of Monomer-to-Rubber Ratio

Figure 5 shows the relationship between GE and GL and monomer-to-rubber ratio in the two-stage



**Figure 5** Effect of monomer-to-rubber ratio on grafting efficiency (■), grafting level (□), free copolymers (●), and graft copolymers (○). CHPO = 1.5 phr, SDS = 1.5 phr, nDM = 0 phr, and  $T = 70^{\circ}\text{C}$ .



**Figure 6** Effect of the amount of chain-transfer agent on grafting efficiency (■), grafting level (□), free copolymers (●), and graft copolymers (○). CHPO = 1.5 phr, SDS = 1.5 phr, monomer-to-rubber ratio = 1, and  $T = 70^{\circ}\text{C}$ .

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 was previously reported.<sup>16,22</sup> This suggests that the graft reactions occur mainly on the surface of the latex particles such that 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.

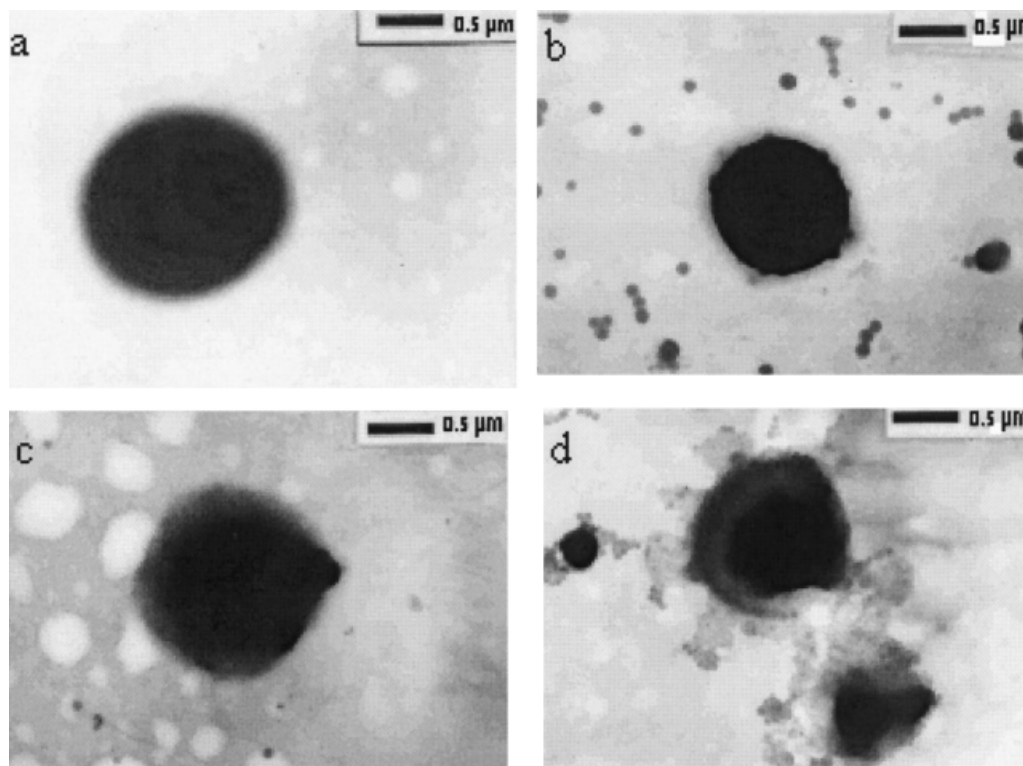
#### Effect of Chain-Transfer Agent

Aliphatic mercaptans are widely used in polymerization 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 6. 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 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 (Fig. 6), thus enhancing the transfer reaction of radicals to chain-transfer agent. Aerdts et al.<sup>23</sup> 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, given that the presence of mercaptans in the reaction mixture provides no ability to continue the propagation of the chains.

#### Effect of Grafting Efficiency on Particle Morphology

The grafting of styrene and methyl methacrylate onto 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 levels of grafting efficiency is shown in Figure 7. The darker areas represent the natural rubber core regions, whereas the lighter areas are PSt/MMA film as shell. The surface of the natural rubber latex particle is smooth [Fig. 7(a)]. The presence of nodules on the surface of the graft copolymers may be attributed 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 demonstrated that grafting of the second-stage polymer onto the core particle produces heterogeneous structures (core-shell structures), which are formed by phase separation 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 [Fig. 7(b)], the natural rubber seed particle was a compact packing of PSt/MMA particles. When the grafting efficiency increased, the PSt/MMA particles enhanced the encapsula-



**Figure 7** Transmission electron micrographs of polymers: (a) natural rubber; (b) 15% GE; (c) 61% GE; (d) 72% GE ( $\times 30,000$ ).

tion of the core and then fused to give a shell layer with a smooth surface [Fig. 7(c) and (d)]. Figure 7 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.

## CONCLUSIONS

The graft copolymerization of styrene and methyl methacrylate mixtures onto natural rubber seed latex using the redox initiation 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. 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. The emulsifier amount has a small effect on grafting sty-

rene 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 because of the decrease of macroradical formation.

Characterization of the graft copolymers by  $^1\text{H-NMR}$  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. Furthermore, it was confirmed that the graft copolymerization is a surface-controlled process.

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