

Preparation of a Natural Rubber Core/Polymer Shell in a Nanomatrix by Graft Copolymerization

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ABSTRACT: The grafting of a vinyl monomer, methyl methacrylate (MMA) or styrene (ST), onto a natural rubber (NR) exhibited a core-shell structure, with NR as the core and poly(methyl methacrylate) or polystyrene as the shell. The grafting efficiency (GE) of the graft copolymer was determined by a solvent-extraction technique. The synthesized graft copolymer was purified and then characterized by Fourier transform infrared spectroscopy analysis. The effects of the graft parameters, including time, initiator content, and concentration, and the type of monomer, MMA or ST, were investigated. A longer time was favorable for the graft copolymerization. GE first increased and then decreased with increasing concentration of initiator. GE decreased with increasing monomer content, and it

was confirmed that the graft copolymerization was a surface-controlled process. The grafting ST monomer had a higher GE compared to MMA under the same conditions. The characterization of the particles by transmission electron microscopy and scanning electron microscopy confirmed the formation of a core-shell structure. From the micrographs, we inferred that at 71% GE, the NR seed particle had a complete closed shell several nanometers in thickness. Therefore, the NR particle was dispersed in a polymer nanomatrix. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2475–2482, 2008

Key words: core-shell polymers; graft copolymers; nanolayers; polystyrene; rubber

INTRODUCTION

Natural rubber latex (NRL) obtained from *Hevea brasiliensis* is a natural biosynthesis polymer with an attractive range of modifying properties that can be devised to provide more desirable properties. NRL is supplied as a natural latex that has a broad particle size distribution, ranging from 100 nm to 2 μ m, stabilized with ammonia.¹ In general, the improved products from natural rubber (NR) have potentially wide applications as a result of physical or chemical modification. Chemical modification of NR by grafting with vinyl monomers with various initiator systems has gained considerable importance in the modification of the properties of NR.^{2–6} The core-shell particles may be prepared by the graft copolymerization of NR in latex form because the NR, an unsaturated elastomer with double bonds in its chains, can be readily grafted with a variety of monomers with the well-established technique of seeded emulsion polymerization. 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.⁷ The graft copolymer of vinyl monomers, such as methyl methacrylate (MMA or C₅H₈O₂) or styrene (ST or C₈H₈) onto NR, comprising an inner soft polymer sphere, the core, and an outer hard polymer, the shell, can be expected to have better impact-resistance properties. A polymeric material composed of a thin matrix several nanometers in thickness (nanolayers) and dispersed a micrometer in diameter is proposed to be a multifunctional soft material, namely, a nanomatrix-dispersed polymer. The graft copolymer of vinyl monomers onto NR comprising the rubbery core makes up for the defects without the loss of the outstanding properties because NR is grafted with a small amount of functional polymer when the polymer forms a nanomatrix. A number of reports^{3,4,8–10} have appeared on the grafting of vinyl monomers onto NRL particles with an amine-activated hydroperoxide. Hydroperoxides have been found to be particularly susceptible to activation by polyalkylenepolyamines.¹⁰ A redox initiation system consisting of organic hydroperoxide and tetraethylene pentamine [TEPA or HN(CH₂CH₂NHCH₂CH₂NH₂)₂] was chosen for this study because it operates efficiently at the high pH values normally encountered in NRL.

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It is not sensitive to oxygen and works well when ammonia is present. Some articles have dealt with the effects of the process conditions on the grafting of vinyl monomers of MMA and/or ST on rubber latex. Gasperowicz et al.¹¹ investigated the grafting of ST onto poly(butyl acrylate) in emulsion form. The grafting efficiency (GE) was found to decrease with increasing reaction time, concentration of initiator, and monomer-to-polymer ratio. The same conclusions were also drawn by Xu et al.¹² for the grafting of ST onto poly(ethyl acrylate) in a seed emulsion process and by Merkel et al.¹³ for the graft copolymerization of MMA onto polybutadiene latex. Sundberg et al.¹⁴ investigated various factors, that is, the monomer-to-polymer ratio, the amount of initiator, the degree of conversion, and the concentration of chain-transfer agent governing the GE of ST onto polybutadiene latex. The GE increased with increasing temperature, whereas, it decreased with increasing concentration of a chain-transfer agent. Kawahara et al.¹⁵ reported that NR particles about 0.5 μm in diameter were dispersed in a polystyrene (PST) matrix about 15 nm thick when the feed of ST was 1.5 mol/kg of rubber in the case of the graft copolymerization of deproteinized NR initiated by *tert*-butyl hydroperoxide with 3.3×10^{-5} mol/kg of rubber with TEPA at 30°C.

The main objective of this study was to prepare a nanomatrix dispersed polymer based on grafted NR with a small amount of functional polymer. The graft copolymerization of NR as the core with MMA or ST as the shell monomer in a seeded emulsion process were carried out with a cumene hydroperoxide ($\text{C}_9\text{H}_{12}\text{O}_2$ or CHPO)/TEPA redox initiation system. The effects of the reaction time, amount of initiator, and concentration and type of monomer, MMA or ST, used in the secondary polymerization on the GE were investigated. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were used to study the morphology of the graft copolymer latex.

EXPERIMENTAL

Materials

The NRL used in this study had a 60 wt % dry rubber content and was obtained from Yala Latex Industry Co., Ltd. (Yala, Thailand). Reagent-grade ST (purity $\approx 99\%$, Fluka, Buchs, SG, Switzerland) and MMA (purity $\approx 99\%$, Fluka, Seelze, Germany) monomers were destabilized in the conventional way by washing with a 10% aqueous solution of NaOH and then with deionized water until neutrality was reached. The monomer was then stored in a refrigerator until it was needed. The emulsifier sodium dodecyl sulfate (SDS; purity $\approx 90\%$, BHD,

Leicestershire, England), the stabilizer isopropyl alcohol, the buffer potassium hydroxide (KOH; Aldrich, St. Louis, MO, USA), the initiator, the redox initiator system, CHPO (purity $\approx 80\%$, Fluka, Seelze, Germany), and the activator agent TEPA (purity $\approx 85\%$, Fluka, Buchs SG, Switzerland), were used as received. Deionized water was used throughout the study.

Preparation of grafted NR

The graft copolymerization reaction was carried out in a 2000-mL, four-necked, round-bottom flask equipped with a stirrer, thermometer, reflux condenser, and gas inlet tube. NRL and an aqueous solution of additives were charged to the reactor, and we removed the dissolved oxygen in the ingredients by purging nitrogen gas for at least 30 min through the mixture, while still providing a stable latex. If necessary, buffer was added to maintain the pH of the system at 10. The monomer and TEPA as an activator agent were fed into the reactor. The redox initiation system, consisting of CHPO and TEPA at a ratio of 1 : 1, was used. The NR seed latex was swollen with the monomer mixture for 1 h at the reaction temperature before the initiator was added. The polymerization reaction was performed at a stirring speed of 400 rpm for the desired time at a definite temperature 50°C. The polymerization was stopped by the addition of phenol. The posttreatment included the coagulation of the polymer latex and washing with deionized water. The gross polymer was recovered and dried to a constant mass in a vacuum oven at 40°C. The recipes for the graft copolymerization are shown in Table I.

Ungrafted NR was washed out in a Soxhlet extractor with 60–80°C boiling point petroleum ether for 24 h. The residue was dried to a constant weight in an oven at 40°C *in vacuo* for 24 h. To remove free polymer, the residue was extracted in a methyl ethyl ketone (MEK)/acetone (50 : 50 v/v) mixture. The

TABLE I
Graft Copolymerization Recipes

Ingredient	Amount
Water	500 g
NRL	250 g
KOH	0.60 g
Isopropyl alcohol	15 g
SDS	2.25 g
Temperature	50°C
Time	Variable (0–8 h)
Initiator (CHPO/TEPA = 1 : 1)	Variable (1.7×10^{-2} to 6.7×10^{-2} mmol/g of rubber)
Monomer	Variable (1.5–6.0 mmol/g of rubber)

weights of the initial sample and the extracted samples were measured for the determination of the graft copolymer and free-polymer contents.

In this system, there were many components in the gross polymer sample. Ungrafted poly(methyl methacrylate) (PMMA) or PST is referred to as free polymer. The graft copolymers are referred to as NR-g-PMMA and NR-g-PST. GE was calculated with the following relationship:

$$\text{GE (\%)} = \frac{\text{Total weight of the monomer grafted}}{\text{Total weight of the monomer polymerized}} \times 100 \quad (1)$$

The presence of functional groups within the graft copolymer was verified by Fourier transform infrared (FTIR) spectroscopy (Bruker model Tensor 27, Ettlingen, Germany).

The morphology of the latex particles was studied by two kinds of electron microscopic methods: latex TEM and latex SEM. General procedures for electron microscopic work were as follows.

The latex was diluted to a concentration of about 0.025% in distilled and deionized water to a total volume of 10 mL, and 1 mL of 2% aqueous osmium tetroxide was added [osmium tetroxide added to the residual bonds of the polyisoprene to render the core more dense in the electron beam than the polymer shell]. One drop of the stained latex was placed on a carbon-coated film on a 200-mesh stainless steel grid, and the sample was allowed to dry overnight in a dust-free environment. The sample was examined in a Jeol JEM-1220 transmission electron microscope (Tokyo) at 120 kV.

For SEM, the dried latex grids prepared as described previously were fixed to the substrate and sputter-coated with a thin gold layer. The three-dimensional shapes of the particle were then observed from those specimens with a Joel microscope (model JSM 5600 LV) at a magnification of 15,000 \times .

RESULTS AND DISCUSSION

Mechanism of grafting

For the graft copolymerization with CHPO in dilute aqueous solution as the initiator system, alkoxy radicals were readily formed. The alkoxy radicals quite likely interacted with the monomer or the rubber molecule to produce macroradicals, which initiated grafting. During the formation of the graft copolymer, the surface of the latex particles became the loci of polymerization. The alkoxy radicals not only attacked the backbone to produce polyisoprenyl radicals, which initiated the monomers to form the graft copolymer, but also initiated monomers to form free

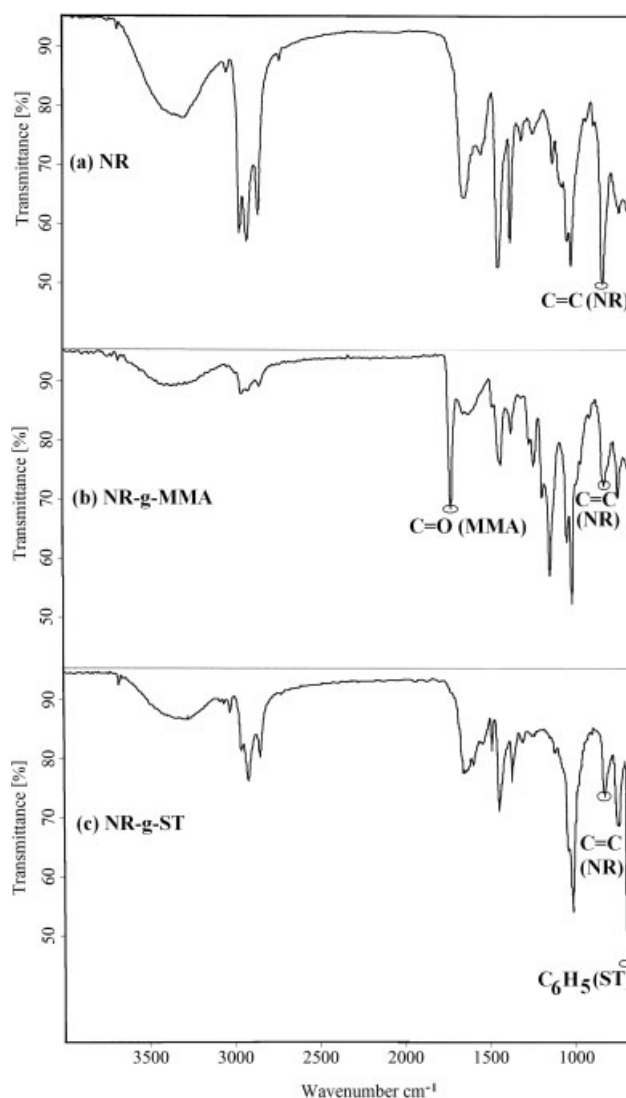


Figure 1 FTIR spectra of the polymers: (a) NR, (b) MMA-g-NR, and (c) ST-g-NR.

polymeric radicals, which combined with polyisoprenyl radicals to terminate or transfer to NR to form the graft copolymer. Some of the free polymeric radicals still terminated to form free polymer on the surfaces of the latex particles. The growing polymer chains, grafted or ungrafted, terminated by recombination with another macroradical, chain transfer, or disproportionation.

To determine the presence of the graft copolymer, the products were extracted by petroleum ether and a mixture of MEK and acetone, respectively. After solvent extraction, the graft copolymer was analyzed by FTIR spectroscopy. Figure 1 shows the FTIR spectrum for the residue (the graft copolymer). There were several characteristic peaks attributed to $R_2C=CHR$ of isoprene, $C=O$ stretching of ester groups of MMA, and the monosubstituted benzene ring of ST at wave numbers of 837, 1732, and 698 cm^{-1} , respectively. This provided evidence that the

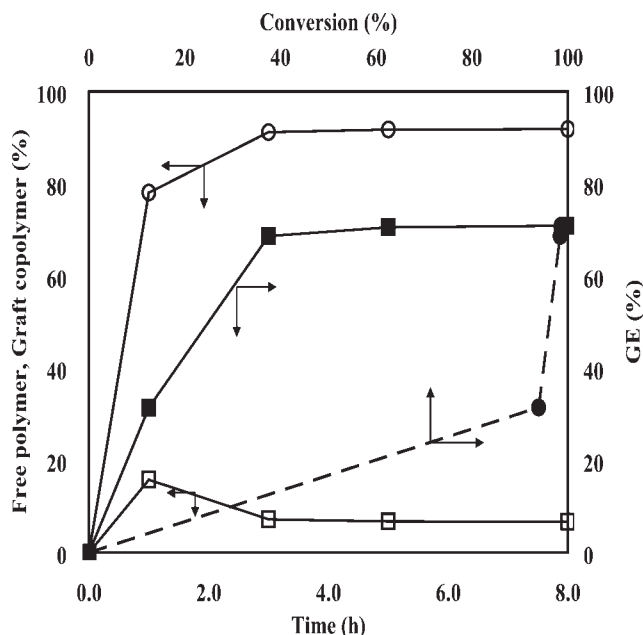


Figure 2 Effect of the reaction time on (■) GE, (□) the free polymer, and (○) the graft copolymer and effect of the conversion on (●) GE (CHPO = 3.3×10^{-2} mmol/g of rubber, MMA = 3.0 mmol/g of rubber).

graft copolymer was formed during the grafting of MMA or ST onto NR.

Effect of the reaction time

The effect of reaction time over the range 0–8 h on the GE of MMA grafting onto NR is shown in Figure 2. The reaction was carried out via emulsion polymerization with a MMA concentration of 3.0 mmol/g of rubber and CHPO (3.3×10^{-2} mmol/g of rubber) as the initiator at 50°C. In this case, GE increased continuously with increasing reaction time up to 5 h, and then, it leveled off with further increases in reaction time. The GE was 31.5% when the reaction time was 1 h. Furthermore, it reached a value of 70.5% when the reaction time increased to 5 h. After 5 h, the level-off result may have been caused by the decrease in the unreacted monomer concentration. On the other hand, grafted chains generally grow until the active sites are occupied completely and reach maximum grafting at that particular time, after which GE does not increase further. Figure 2 also shows good agreement between the graft copolymer and free-polymer values, in which at shorter times, there was a greater amount of free polymer than at longer times. The occurrence of the preferred homopolymerization of monomer at shorter times may have been due to the preference of the initiator radical to react with monomer present at a relatively high concentration in combination

with a higher diffusivity of the monomer and polymeric radical than the polyisoprene macromolecular chain. Then, the new growing polymer chains were chemically bonded to the surface of the NR particles, thus forming graft copolymer. The amount of free polymer was typically high at short times and decreased at longer times.

Figure 2 also shows the GE of MMA on the NR as a function of conversion. *Conversion* is defined as the fraction of monomer at a given time that has converted to polymer. GE first increased gradually up to about 31.5% conversion and then steeply increased. This suggested that the conversion at the beginning increased rapidly because most of the monomers were polymerized in the aqueous phase to form new polymeric radicals until the monomers were almost completely consumed, and it reached maximum conversion at that particular time. At that point, the new growing polymer chains were chemically bonded to the surface of the NR particles and thus formed graft copolymers, which led to a sudden increase in GE at high conversion. Similar behavior for the graft copolymerization of ST and MMA onto polybutadiene were observed by Aerdt et al.¹⁶

Effect of the initiator

The effect of the amount of initiator on the GE was studied over the range of approximately 1.7×10^{-2} to 6.7×10^{-2} mmol/g of rubber at 50°C for 5 h with the concentration of all of the other reagents kept constant. GE increased with increasing amount of initiator from 1.7×10^{-2} to 5.0×10^{-2} mmol/g of rubber (Fig. 3). This trend could be explained by the fact that the radicals transferred to either rubber or monomer to produce macroradicals, which was enhanced with an increase in the amount of initiator; this resulted in an increase in grafting. However, beyond the amount of initiator of 5.0×10^{-2} mmol/g of rubber, GE decreased with increasing initiator content. This was because the conversion of the free polymer increased again over 5.0×10^{-2} mmol/g of rubber. Under these conditions, the chain length of the grafts had hardly anything to do with the free-polymer radicals. The excessive free-polymer radicals reacted with each other to form free polymer more than they grafted onto the NR and decreased the chain length of the grafts. Therefore, the production of free polymer was promoted more greatly at high initiator contents (Fig. 3). On the other hand, the probability for the rate of chain transfer for the free-polymer radicals to the NR backbone was lower than the rate of termination of the free-polymer radicals, which favored the termination process of the free polymer over the chain-transfer process. A

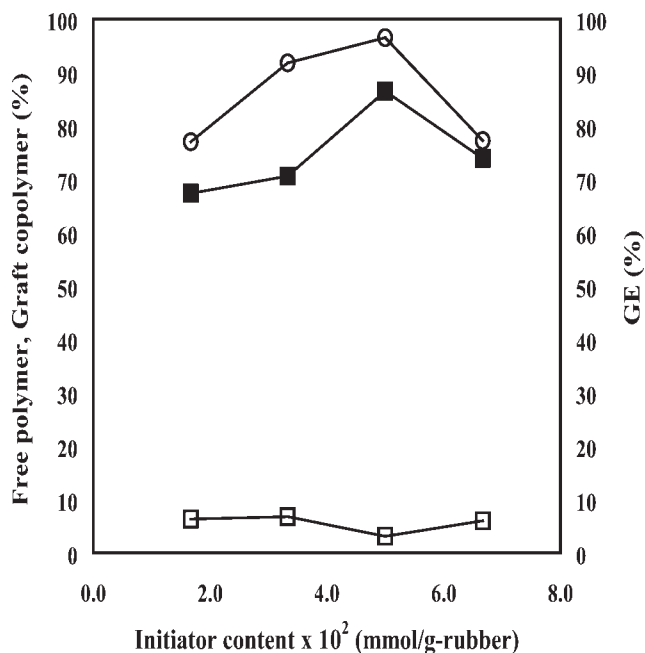


Figure 3 Effect of the amount of the initiator on (■) GE, (□) the free polymer, and (○) the graft copolymer (reaction time = 5 h, MMA = 3.0 mmol/g of rubber).

similar observation was made by Lenka and co-workers¹⁷⁻¹⁹ for the grafting of MMA onto NR.

Effect of the monomer content

Figure 4 shows the relationship between GE and monomer content in the two-stage emulsion poly-

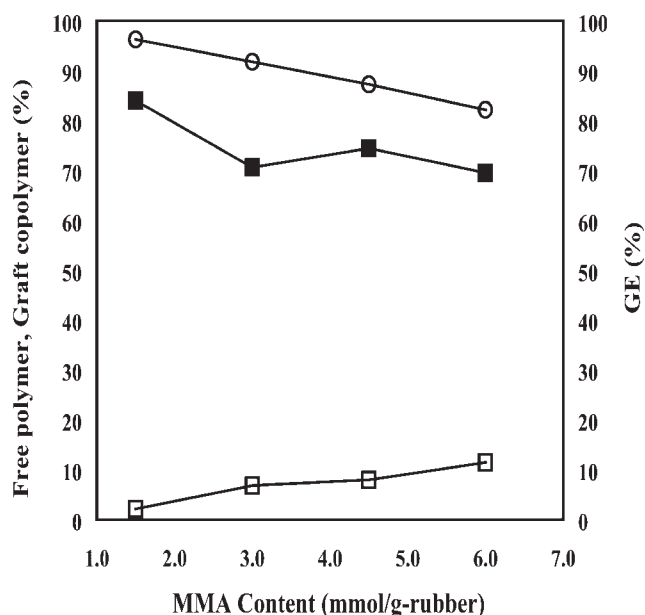


Figure 4 Effect of the amount of MMA on (■) GE, (□) the free polymer, and (○) the graft copolymer (reaction time = 5 h, CHPO = 3.3 × 10⁻² mmol/g of rubber).

merization. The reaction was performed via emulsion polymerization with a CHPO concentration of 3.3 × 10⁻² mmol/g of rubber as an initiator at 50°C for 5 h. The grafting decreased with increasing monomer content. This result may be explained by a mechanism involving a surface-controlled process, which was reported by Merkel et al.¹³ This suggests that the graft reactions occurred mainly on the surface of the latex particles, so the polymerization occurred mainly in the shell of the particles. As grafting proceeded and a certain shell thickness of the second-stage polymer was reached, the contact area between the monomer and rubber decreased. Therefore, it was more difficult for graft copolymerization to occur through the diffusion of the monomer to the rubber chain compared to the polymerization of monomers. As a result, GE decreased with increasing monomer content. Enyiegbulam and Aloka²⁰ found similar results when they studied the grafting of MMA onto NR.

Effect of ST and MMA

In Figure 5, GE as a function of the monomer content is shown, where grafting took place with the different monomers, MMA or ST. The reaction was carried out via emulsion polymerization with a CHPO concentration of 3.3 × 10⁻² mmol/g of rubber as an initiator at 50°C for 5 h. The GE of ST in the graft copolymer was higher than that of MMA.

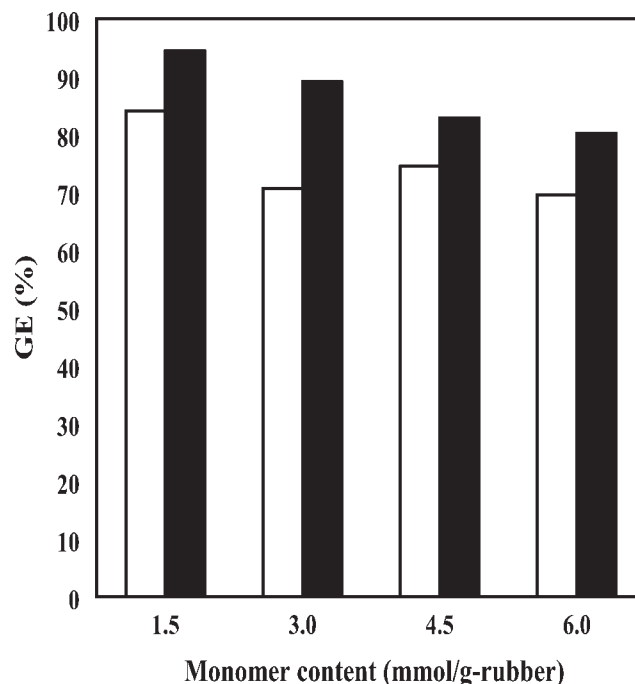


Figure 5 Effect of the type of monomer on GE: (□) grafting of MMA and (■) grafting of ST (reaction time = 5 h, CHPO = 3.3 × 10⁻² mmol/g of rubber).

The nature of the monomer is a very important factor in determining the reactivity of polymeric radicals. Aerdts et al.¹⁶ reported a large difference in reactivity ratios, namely, a MMA reactivity ratio of 0.19 ± 0.05 and a ST reactivity ratio of 0.73 ± 0.05 , at 323 K. A rule of thumb has been proposed, where the most reactive monomers give the least reactive polymeric radicals and the least reactive monomers yield the most reactive polymeric radicals.^{21–24} Thus, the reactivity of ST and MMA was in the following order: ST > MMA, and the reactivity of the polymeric radicals formed from these monomers was in the reverse order (via the rule thumb of Mayo): polystyryl radical < PMMA radical. In the grafting system, the attack of alkoxy radical on *cis*-polyisoprene most likely occurred by chain transfer to form the polyisoprenyl radical. The reactivity of the polystyryl radical was about the same as the polyisoprenyl radical (both were stabilized by resonance). In addition, ST monomer is one of the most active of vinyl monomers, and despite the low reactivity of the polyisoprenyl radical, the ST monomer could still be grafted onto it. However, MMA is a quite inactive monomer compared to ST. Conversely, the PMMA radical is as very active polymeric radical compared to the polystyryl radical. Therefore, the polyisoprenyl radical could not compete with the more active PMMA radical. The chemical reactivity of isoprene is similar to ST, which led to the higher GE of ST compared to that of MMA.

Effect of GE on particle morphology

The morphology of the particles was examined by TEM and SEM. The grafting of MMA onto the NR was a core-shell type emulsion copolymerization. The grafted NR particles consisted of the NR core and the compatibilized PMMA shell. The TEM micrographs of NR and the grafted NR with different GEs are shown in Figure 6. The darker areas represent the NR core regions, whereas the lighter areas represent the PMMA film as the shell. The surface of the NR particle was smooth [Fig. 6(a)]. The presence of nodules on the surface of the graft copolymer may have been due to the growing macroradical chains, which were grafted onto the surface of the NR particle and continued to propagate to form the shell layer. Furthermore, it was demonstrated that the grafting of the second-stage polymer onto the core particle produced heterogeneous structures (core-shell structures), which were formed by the phase separation of the incompatible polymer during polymerization. Most of the MMA polymerized in the aqueous phase to form secondary particles, which then flocculated with the NR seed particles. With the increase in the level of GE, the shell thickness became larger [Fig. 6(b–d)]. At low GE [Fig.

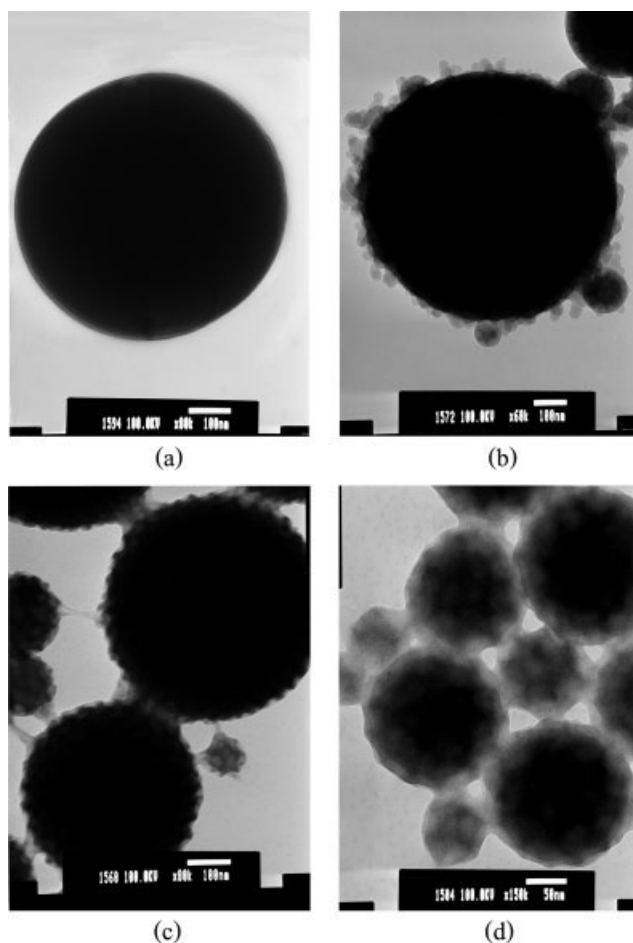


Figure 6 TEM micrographs of the polymers: (a) NR ($\times 80,000$), (b) 31% GE ($\times 60,000$), (c) 71% GE ($\times 80,000$), and (d) 86% GE ($\times 150,000$).

6(b)], the NR seed particle was a compact packing of PMMA particles. When GE increased, the PMMA particles enhanced the encapsulation of the core [Fig. 6(c)] and then fused to give a shell layer [Fig. 6(d)]. The TEM results show that the shell thicknesses were less than 50 nm, which depended on the level of GE. The NR seed particles had a complete closed shell at 71% GE, whereas they had an overly thick shell at 86% GE, which resulted in a loss of the rubbery nature. The corresponding images shown in Figure 6 indicate that at 71% GE, the NR particle was simply able to fully cover the inner rubbery core and be dispersed into the PMMA matrix. The thickness of the PMMA's graft layer was about 15 nm. These results indicate that the synthesis conditions have an application effect on the graft copolymer with different levels of GE for various products. A graft copolymer with a low GE is recommended for adhesive applications. Another application for a graft copolymer with a higher GE would combine the hardness and rigidity of the thermoplastic component with the high impact resistance.

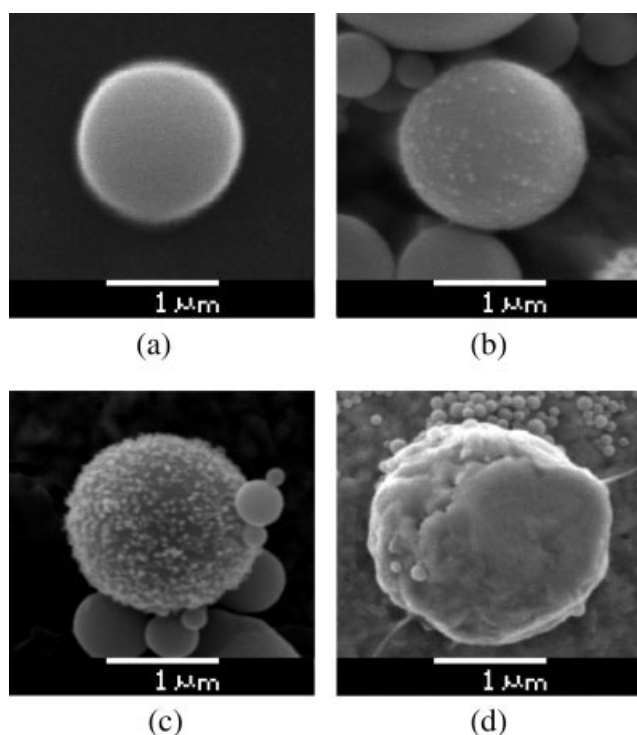


Figure 7 SEM micrographs of the polymers: (a) NR, (b) 31% GE, (c) 71% GE, and (d) 86% GE ($\times 15,000$).

Lee and Chang²⁵ reported that the shell thickness of a core-shell impact modifier was the single most important factor in the toughening of rigid poly(vinyl chloride). When the shell thickness was greater than a critical value of 15.8 nm, these core-shell elastomeric particles were able to remain structurally intact and well dispersed within the poly(vinyl chloride) matrix after melt blending. However, too thick a shell thickness resulted in a hard core (high modulus) for these core-shell particles and a loss of the rubbery nature required in an efficient impact modifier. Figure 7 shows the SEM micrographs of NR and the grafted NR with different GEs. The gloomy domain is NR, and the bright domain is PMMA. At the low GE, a few bright domains were scattered in the gloomy matrix [Fig. 7(b)]. When GE increased, the bright domain was able to fully cover the gloomy spheres [Fig. 7(c)] and then fused to give an overly thick shell layer [Fig. 6(d)]. The shell thickness of the particles obtained by graft copolymerization became larger with higher GE. As shown by the results (Figs. 6 and 7), to obtain a polymer shell of nanometer thickness, the most suitable GE was 71% for the graft copolymerization.

CONCLUSIONS

The graft copolymerization of a vinyl monomer onto a NR seed latex with a redox initiation system was

dependent on the main process factors, including the reaction time, amount of initiator, and amount and type monomer. GE dramatically increased with increasing reaction time up to 5 h and then hardly varied. GE increased with increasing amount of initiator up to 5.0×10^{-2} mmol/g of rubber and then decreased marginally, which suggested that an excess of free radicals may have combined by themselves and lessened the chain length of the grafts. GE decreased as monomer content increased, which indicated that the graft copolymerization occurred on the surface of the latex particles. The results show that the GE of the ST-grafted NR was higher than that of the MMA-grafted NR under the same conditions. The difference between the GE of the ST-grafted NR and that of the MMA-grafted NR was due to the nature of the monomer. The presence of the polymer on the NR microparticle surface was identified by FTIR, TEM, and SEM, which indicated the occurrence of grafting on the NR backbone in the core-shell latex particles. The level of GE efficiency has a great influence on shell thickness, which will affect the application of the graft copolymer in various products. A NR core with a nanoscale thickness of polymer shell was obtained by the grafting of a small amount of functional polymer onto the NR. TEM also gave an indication of the coating structure and revealed perfect coating at 71% GE. Therefore, NR particles were dispersed in a PMMA matrix about 15 nm thick. This may lead to an improvement in the field of impact modifiers.

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