Preparation of Graft Copolymers from Deproteinized and High Ammonia Concentrated Natural Rubber Latices with Methyl Methacrylate

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ABSTRACT: Deproteinized natural rubber (DPNR) latex was prepared by the incubation of fresh natural latex with a proteolytic enzyme. The DPNR latex was later used to prepare a graft copolymer with methyl methacrylate (MMA). High ammonia (HA) concentrated latex was also used to prepare a graft copolymer with MMA. The appropriate reaction time was 3 h at a reaction temperature of 50°C. The conversion percentage of the graft reaction with DPNR was higher than that of the system with HA. The grafting efficiency percentage decreased with an increasing concentration of MMA in the graft reaction. In a comparison of the two types of latices, it was found that the reaction with DPNR provided higher grafting efficiency. Furthermore, a larger quantity of grafted poly(methyl methacrylate), a larger average particle size, and fewer free natural rubber molecules were also observed in the grafting system with DPNR. The difference between the reactions of the DPNR and HA latices was attributed to the removal of proteins, which acted as free-radical scavengers. They terminated the free-radical species during the graft copolymerization. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 87: 68–75, 2003

Key words: rubber; graft copolymers; proteins

INTRODUCTION

Natural rubber (NR) contains 93–95% *cis*-1,4-polyisoprene.[1] It is an unsaturated elastomer with some good properties, such as high strength, outstanding resilience, and high elongation at break.[2] However, NR is very sensitive to heat and oxidation because of the double bonds in its chains.[3] Furthermore, NR has low tensile strength and tensile modulus and poor creep characteristics unless highly vulcanized.[4] These disadvantages of NR have limited its applications in industry. Some methods have been used to improve NR. One is the modification of NR by graft copolymerization with a vinyl monomer. The rubber samples used to prepare graft copolymers are generally in solution[5] or latex phases.[6–10] Various types of vinyl monomers, such as styrene, acrylonitrile, methacrylic acid, and methyl methacrylate (MMA), have been widely used.[11,12] The graft copolymerization of NR and MMA has been performed by free-radical polymerization in solution or latex states with various initiator systems, such as benzoyl peroxide and redox initiators.[5,13]

In this work, a graft copolymer of NR and MMA was prepared with a semibatch emulsion polymerization technique. A redox initiating system consisted of an initiator [*tert*-butyl hydroperoxide (*tert*-BuHP)] and a coinitiator [tetraethylene pentamine (TEPA)] was used. The initiation system proved to be very effective for the emulsion polymerization in the NR latex. That is, it was not sensitive to oxygen and worked well with ammonia present.[14] Two type of NR latices, deproteinized natural rubber (DPNR) latex and high ammonia (HA) concentrated latex were used to prepare the graft copolymer.

EXPERIMENTAL

Materials

An HA latex containing 61.1% dried rubber was supplied by Pattani Industrial, Ltd. (Pattani, Thailand). The proteolytic enzyme Opticlean was manufactured by Solvay Biosciences (Victoria, Australia). The MMA used to prepare the graft copolymers was manufactured by Merck (Munchen, Germany). *tert*-BuHP and TEPA used as redox initiators were manufactured by Fluka Chemie AG (Buchs, Switzerland). Potassium laurate, used to stabilize the latices, was prepared from the reaction of potassium hydroxide (Fluka Chemie AG, Buchs, Switzerland) and lauric acid (Lab Scan, Ltd., Ireland).

Preparation of DPNR

Fresh NR latex was obtained from a rubber plantation in the Pattani area. An ammonia solution of 0.7 wt %
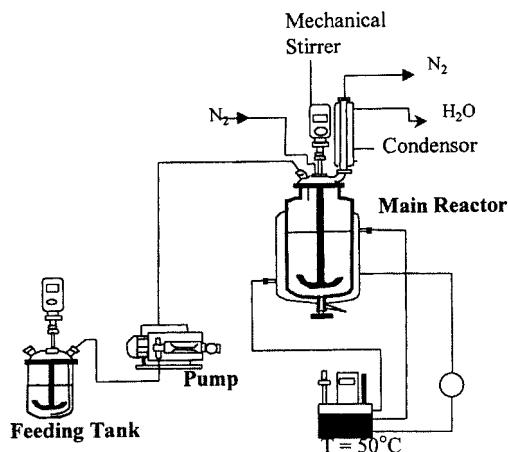
Figure 1 Apparatus used for the preparation of the graft copolymer of NR and MMA.

dried rubber was added to the latex. For the prevention of coagulation, the latex was preserved by the addition of potassium laurate with 0.5 wt % dried rubber. The proteolytic enzyme Opticlean, with 0.3 wt % fresh NR latex, was later incorporated. The mixture was incubated for 72 h and centrifuged on an Alfa Laval model 410 factory-scale centrifuge machine. The nitrogen contents in NR before and after incubation were analyzed.

Preparation of grafted NR

The DPNR latex with 60.37% dried rubber was placed into a 2-L main reactor (Fig. 1). TEPA (85 wt %, 2.12 g) and 87 mL of water were later added to the main reactor. The mixture was then thoroughly stirred and deoxygenated by the bubbling of nitrogen gas for approximately 30 min at the reaction temperature. The monomer MMA, 2.57 g of *tert*-BuHP (70 wt %), 9 g of potassium laurate (30 wt %), and 120 mL of water were incorporated into a 1-L feeding tank. The mixture was stirred for 20 min and pumped into the main reactor at a flow rate of 2.7 mL/min. The reaction was then performed for 3 h under continuous stirring. The average particle size of the resultant latex was quantified with a Coulter LS 230 particle size analyzer. The latex was then coagulated with a 10 wt % calcium chloride solution. The coagulum was separated, and a thin sheet was produced with a two-roll mill. The sheet was leached with distilled water for the removal of the coagulant (i.e., calcium chloride) and other water-soluble impurities. Finally, the sheet was dried in a vacuum oven at 40°C until it was thoroughly dry. A Soxhlet extractor was used to wash out the ungrafted NR (i.e., free NR) with petroleum ether and the free poly(methyl methacrylate) (PMMA) homopolymer with acetone.[5] The grafting efficiency and the grafted PMMA functional groups were later characterized.

The grafting efficiency is defined as the weight of the PMMA-grafted rubber divided by the total weight of the polymer produced (the free PMMA and the grafted rubber):[15]

Grafting efficiency

$$= \frac{\text{Weight of grafted copolymer} \times 100}{\text{Total weight of polymer formed}} \quad (1)$$

The HA latex with 61.1% dried rubber was also used to prepare graft copolymers for a comparison of the results. Various molar percentage ratios of NR to MMA (i.e., 95/5, 90/10, 80/20, 70/30, and 60/40) were used in the graft copolymerization (Table I).

RESULTS AND DISCUSSION

The DPNR latex was prepared with a proteolytic enzyme. The nitrogen content of the latex was reduced from 0.9 (the fresh NR latex) to 0.07 wt % (the DPNR latex). The graft copolymerization of MMA and NR latices (HA and DPNR) via a semibatch polymerization technique was then studied with a bipolar redox initiating system (i.e., *tert*-BuHP and TEPA). The appropriate concentrations of the initiator (*tert*-BuHP) and coinitiator (TEPA) were used according to our previous work.[16] The dependence of the conversion and grafting efficiency percentages on the reaction temperature and reaction time was examined. Furthermore, the dependence of the monomer concentration in terms of the molar percentage ratio of NR to MMA on the monomer conversion, average particle size of the graft copolymer, grafting efficiency percentage, and levels of grafted PMMA and ungrafted NR molecules was examined and compared with the results for the HA latex.

Effect of the reaction temperature

The graft copolymerization was carried out at four different temperatures ranging from 40 to 70°C with 300 g of DPNR, 36 g of MMA, and the other chemicals mentioned in the previous section. Figure 2 shows the rela-

TABLE I
DPNR or HA Latex and MMA Used in the Graft Reaction

DPNR or HA latex[a]/MMA (mol %)	Weight (g)	
	Latex	MMA
95/5	321	15
90/10	304	30
80/20	270	60
70/30	236	90
60/40	202	120

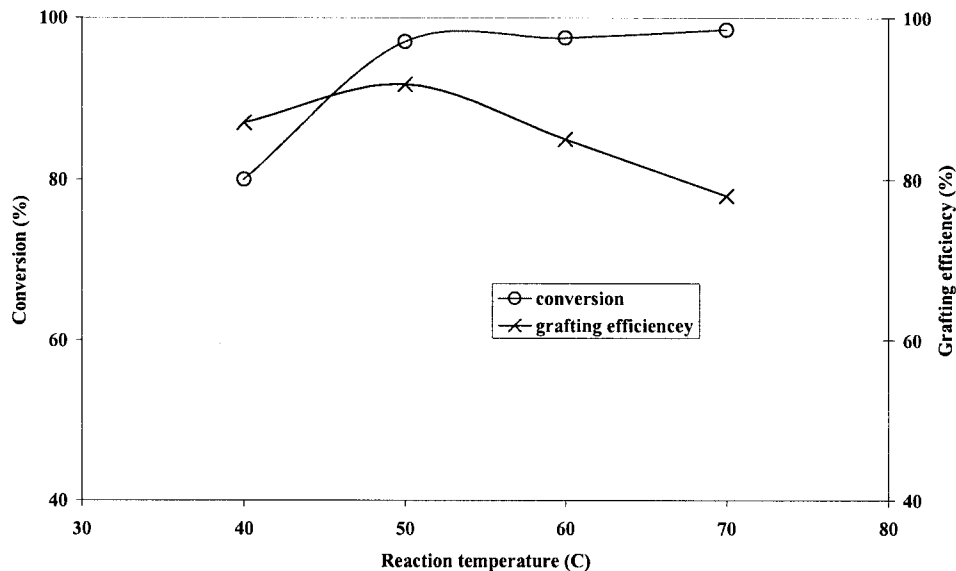[a] Moles of NR calculated based on the molecular weight of an isoprene unit.

Figure 2 Effect of the reaction temperature on the graft copolymerization (DPNR, 300 g; MMA, 36 g; TEPA, 2.12 g; *tert*-BuHP, 2.57 g).

tionship between the monomer conversion and grafting efficiency with the reaction temperature. A higher temperature caused a higher conversion. This may be attributed to the increasing trend of the initiator decomposition. Therefore, an increased number of radicals and rate of polymerization occurred. The highest grafting efficiency was observed at a reaction temperature of 50°C. An increase in the reaction temperature beyond 50°C caused a decreasing trend in the grafting efficiency. This may be attributed to radical recombination and other side reactions, such as the homopolymerization of MMA and NR.

Effect of the reaction time

Figure 3 shows the effect of the reaction time on the grafting of MMA onto the DPNR latex at 50°C. We found that as the reaction time increased, there was an increase in the conversion and grafting efficiency in the lower reaction time range. The highest gradient of the relationship between the conversion and grafting efficiency with time was found for reaction times of 1–3 h. At the reaction time of 3 h, the conversion and grafting efficiency reached a maximum value; there-
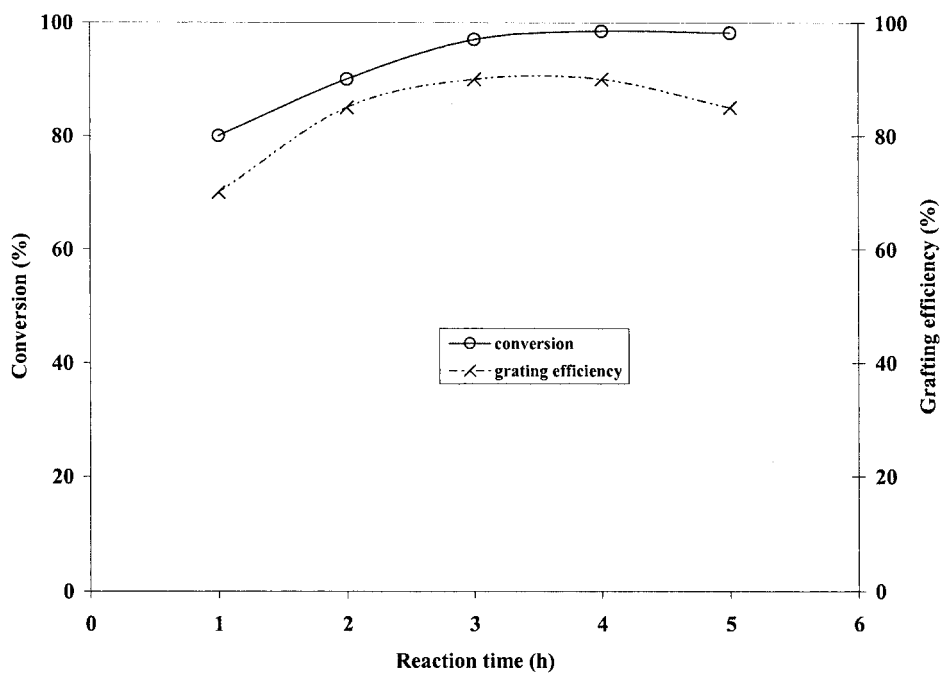

Figure 3 Effect of the reaction time on the graft copolymerization (DPNR, 300 g; MMA, 36 g; TEPA, 2.12 g; *tert*-BuHP, 2.57 g).
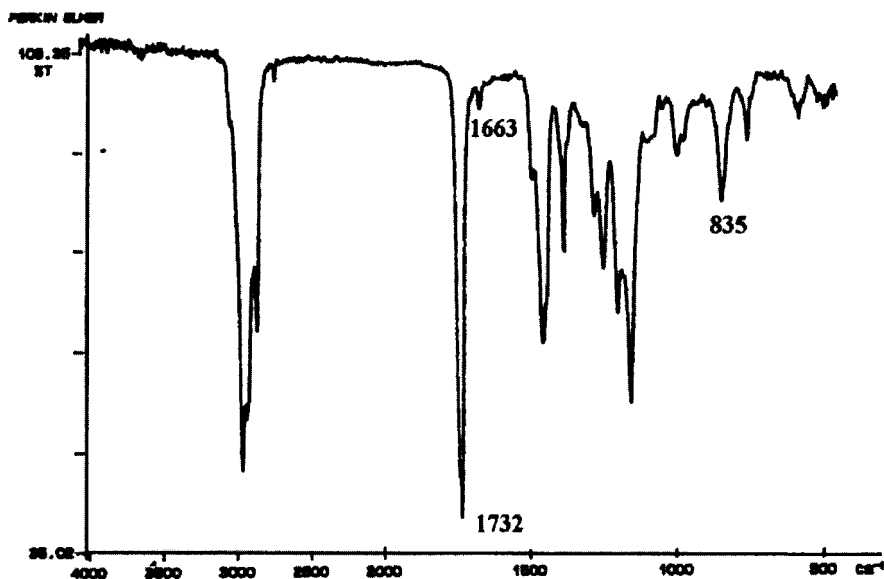
Figure 4 IR spectrum of the graft copolymer prepared with an NR/MMA molar ratio of 60/40.

after, the grafting efficiency decreased slightly. At a long reaction time, there were no new generated active grafting sites on the rubber molecules. Therefore, the PMMA homopolymer was formed more readily than the graft copolymer. The appropriate conditions for the preparation of the graft copolymer were found to be a reaction temperature of 50°C for 3 h, which led to a high conversion and a high grafting efficiency.

Characterization of the NR graft copolymer with fourier transform infrared

Figure 4 shows a representative IR spectrum of DPNR-*g*-PMMA with the molar percentage ratio of DPNR to MMA at 60/40. We found the transmission peak at 1732 cm^{-1} in the graft copolymer. This indi-

cates the presence of —C=O stretching in the graft copolymer molecules. The quantification of the PMMA level in the graft copolymer was performed with the absorbance ratio of the peaks at 1732 to 835 cm^{-1} (=C—H, cis-1,4), as shown in Figure 5. The level of grafted PMMA increased with increasing quantities of MMA in the graft reaction. Furthermore, the DPNR latex gave a higher absorbance ratio than the HA latices. That is, at the same level of the molar percentage ratio of NR to MMA, a higher quantity of grafted PMMA was found in DPNR-*g*-PMMA. The difference between the levels of grafted PMMA in DPNR and untreated HA latices might be due to the removal of proteins. It is believed that proteins in the latices act as free-radical scavengers. They terminate the activity of
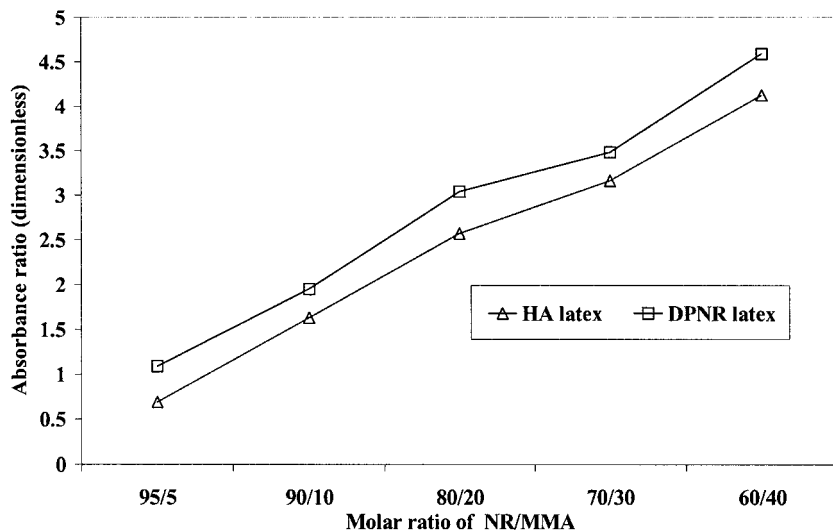

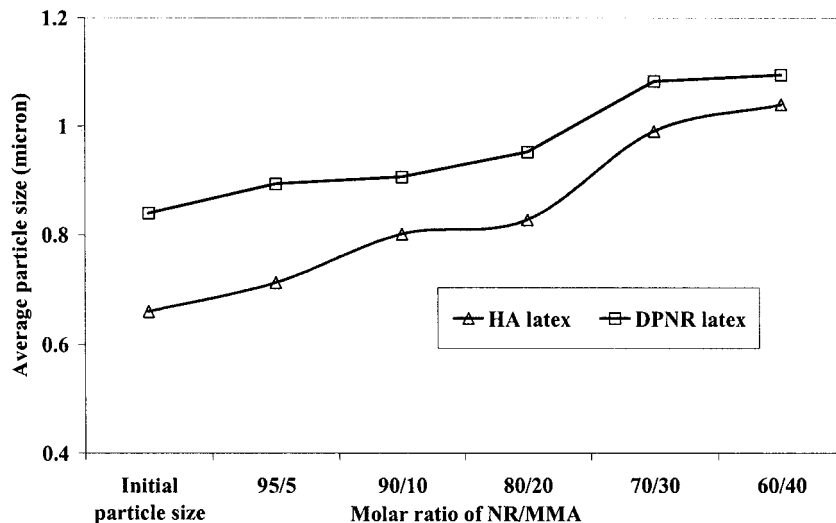**Figure 5** Absorbance ratio of the graft copolymers at various molar percentage ratios of NR to MMA.

Figure 6 Average particle size of the initial and graft copolymer latices.

free radicals during the initiating and propagating processes of graft copolymerization.[17] As a result, higher levels of grafted PMMA were observed in the DPNR molecules.

Effect of the molar percentage ratio of NR to MMA on the particle size distribution

The average particle sizes of the NR (initial particle size) and the graft copolymer latices are compared in Figure 6. The average particle sizes for both types of graft copolymers increased with increasing concentrations of MMA in the grafting reaction. At the same level of the molar percentage ratio of NR to MMA, a larger particle size was observed for DPNR-g-PMMA. This may be attributed to the larger initial particle size of DPNR. Also, the higher level of PMMA-grafted sites in the DPNR molecule caused the expansion of the latex particle.
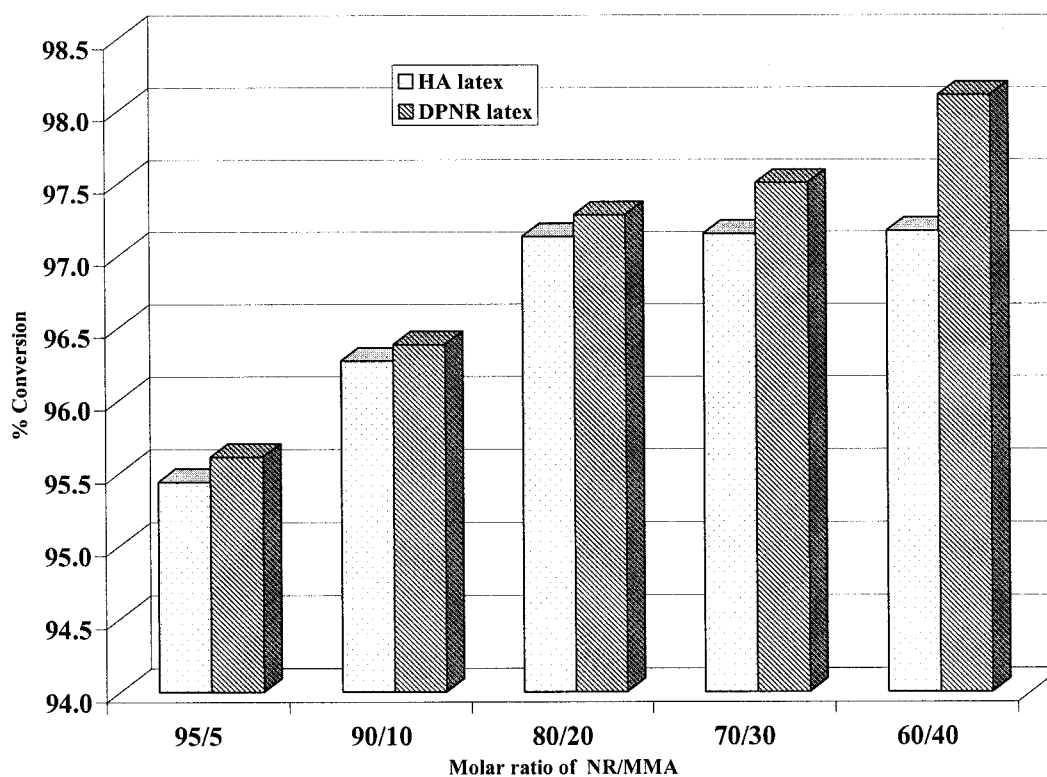

Figure 7 Conversion percentage at various molar percentage ratios of NR to MMA.
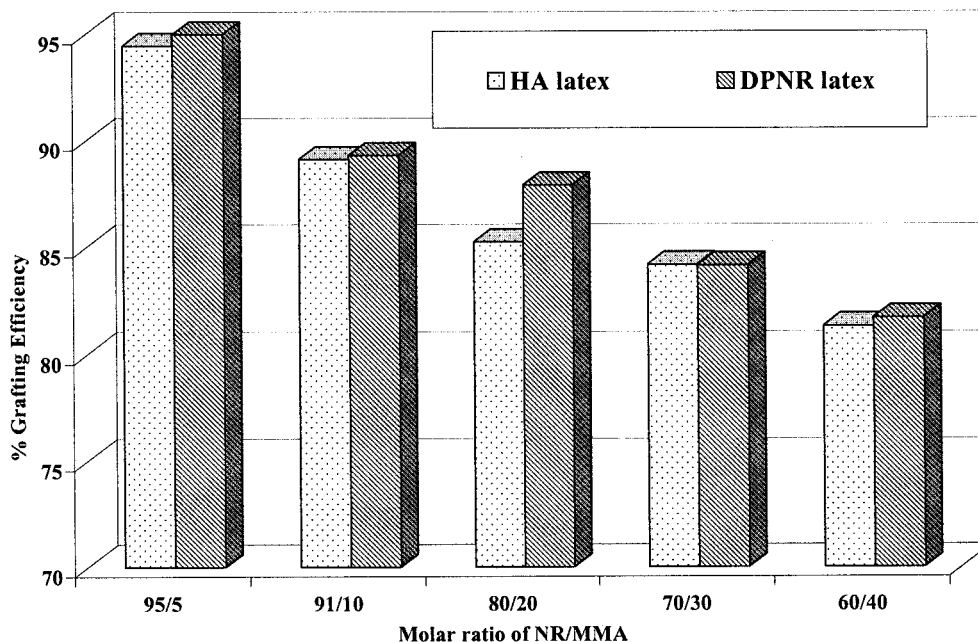
Figure 8   Grafting efficiency of the graft copolymerization at various molar percentage ratios of NR to MMA.

Effect of the molar percentage ratio of NR to MMA on the conversion percentage and grafting efficiency

Figure 7 shows the conversion percentage of the graft copolymerization of the DPNR and HA latices with MMA. With the concentration of MMA increasing, a higher conversion percentage was observed. Furthermore, at the same molar ratio of NR to MMA, a higher conversion percentage was found in the graft reaction of the DPNR latex. Therefore, the removal of proteins in the DPNR latex had an effect not only on the levels of grafted PMMA and the average particle size of the latex but also on the conversion. That is, the initiation and propagation processes of the graft copolymerization were facilitated under a lower concentration of proteins. Therefore, a higher conversion percentage was observed.

The grafting efficiency was calculated as the ratio of the amount of the graft copolymer to the amount of the coagulum product.[5] The grafting efficiency decreased with increasing monomer concentration, as shown in Figure 8. However, the grafting effi-
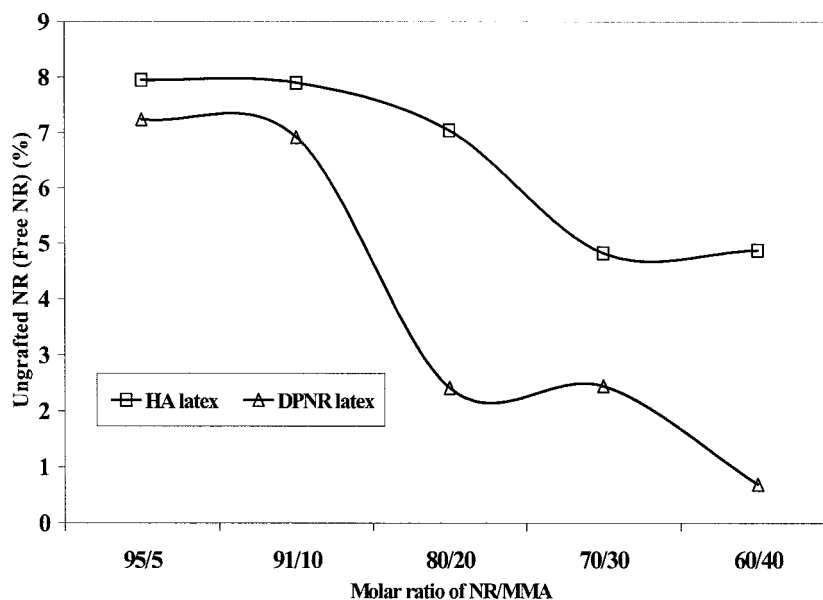

Figure 9   Quantity of ungrafted NR (free NR) at various molar percentage ratios of NR to MMA.
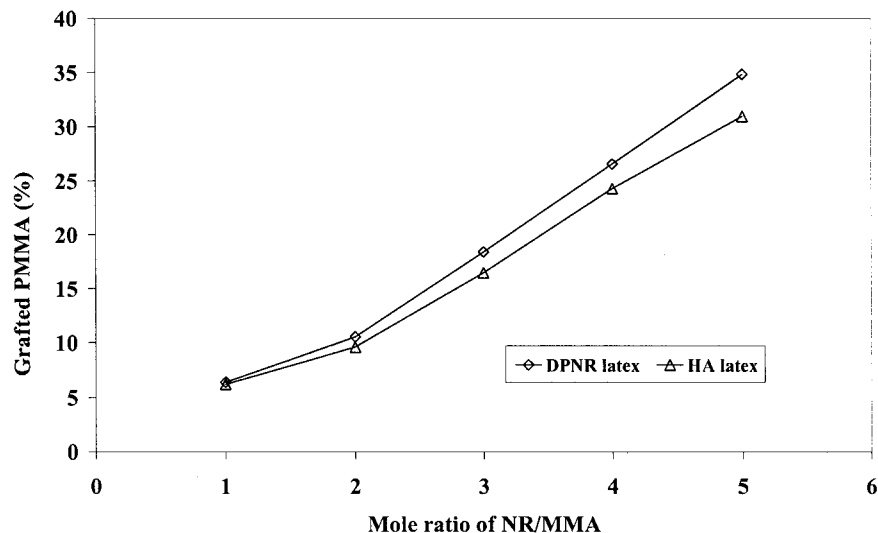
Figure 10   Quantity of grafted PMMA on NR molecules at various molar percentage ratios of NR to MMA.

ciency of the graft reaction with the DPNR latex was slightly higher. At higher monomer concentrations, there were many reactions that probably competed with the graft copolymerization. Therefore, homopolymerization was more pronounced than graft copolymerization at higher monomer concentrations. Moreover, there were no new active sites on the rubber molecules for the newly arriving active monomers. This was because of the limitation of the cis-1,4-configuration: the grafting sites on the cis positions might not be available after a certain percentage of grafting took place. Also, the molecules sterically hindered with respect to growth prevented the reaction of the newly arriving monomer molecules.[15]

The free NR (i.e., NR molecules without grafted PMMA) was reduced with the MMA concentration increasing, as shown in Figure 9. This means that the higher monomer concentrations provided a greater possibility for NR molecules to react with the active species. Moreover, the free NR molecules for the graft reaction of the DPNR latex were fewer in number than those of the HA latex. Therefore, the removal of proteins also affected the decreasing levels of the free NR molecule. That is, the reaction of DPNR was more pronounced than that of HA at the same monomer concentration.

The quantity of grafted PMMA was calculated with the conversion percentage and the quantities of free NR and free PMMA, as shown in Figure 10. Despite the decreasing trend in the grafting efficiency, an increasing trend of grafted PMMA was observed. Furthermore, the grafted PMMA for the system with DPNR latices was greater than that for the system with HA latices.

CONCLUSIONS

DPNR with a very low nitrogen content (0.07 wt %) was successfully prepared. Both DPNR and HA latices were successfully used to prepare graft copolymers with MMA. IR spectra for both types of graft copolymers showed a transmission peak at 1732 cm^{-1} (—C═O stretch). The conversion percentage, grafting efficiency, and levels of grafted PMMA for the graft copolymer obtained from DPNR were higher than those of the graft copolymer of HA. Furthermore, a larger average particle size and a lower free rubber content were observed in the graft copolymer of DPNR. The removal of proteins from the DPNR latex was the main reason for the different characteristics of the graft copolymers. It is believed that proteins play a significant role in free-radical polymerization. That is, the free-radical species may be terminated by proteins during graft copolymerization.

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