

From a Laboratory to a Pilot Scale Production of Natural Rubber Grafted with PMMA

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ABSTRACT: Graft copolymers of natural rubber and poly(methyl methacrylate) (NR-g-PMMA) were prepared in a laboratory scale, and then extended to a pilot scale production. Reaction conditions were first assessed based on a preparation in the laboratory scale with a reactor capacity of 1.5 l. An optimum grafting efficiency was obtained when cumene hydroperoxide/tetraethylenepentamine (CHP/TEPA) redox initiator was used at the reaction temperature and time of 50°C and 3 h, respectively. MMA monomer was used without purification in the polymerization process comparing with the purified one by means of extraction. It was found that only a slight decrease of grafting efficiency was observed when the nonpurified monomer was used in the reaction. The nonpurified monomer was therefore used to prepare the NR-g-PMMA in a pilot scale production with a reactor

capacity of 260 L. Various weight ratios of NR/MMA at 50/50, 60/40, 70/30, and 85/15 were studied. The resulting graft copolymers were characterized by FTIR and ¹H-NMR techniques. It was found that increasing concentration of MMA caused an increase of free PMMA (i.e., homopolymer) but a decrease of free NR (i.e., ungrafted NR) and grafting efficiency. Quantity of grafted PMMA on the NR backbone was estimated using the integrated peak areas of ¹H-NMR spectra and quantitative analysis by extraction method. The results were found to be in good agreement. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 587–597, 2009

Key words: natural rubber; poly(methyl methacrylate); graft copolymer; pilot scale production; grafted PMMA

INTRODUCTION

Natural rubber (NR) is a renewable and sustainable material, which gives various good properties, such as high tensile strength, high elongation, and outstanding resilience, lending itself to be used in various applications. NR is an unsaturated rubber that consists of mainly *cis*-1, 4-polyisoprene.¹ It is therefore holding some drawbacks such as poor oil resistance due to its nonpolar nature; high sensitivity to heat, oxygen, and ozone due to its reactive double bonds. A variety of synthetic counterparts are made to meet some specific requirements such as for high temperature applications or for oil-in contact products. However, these synthetic rubbers are mostly manufactured from nonrenewable oil-based resource. Under an increasing awareness of environmental issue and fuel shortage in the future, natural rubber and other renewable and sustainable resources are undoubtedly back into play.

The nonpolar and highly unsaturated nature of NR limits its use in some industries including adhesives and sealants for polar substrates. To extend the use of NR, a variety of modification methods can be used to partly or completely alter the NR structure to enhance its properties to meet some specific requirements.² The modification of NR via graft copolymerization is probably the most common method used to prepare a product that has some better properties than those of unmodified one. Graft copolymers of NR with various types of vinyl monomers, e.g., styrene,^{3–5} acrylonitrile,⁶ dimethylaminoethyl methacrylate,^{7,8} and methyl methacrylate (MMA)^{9–21} have been investigated. Graft copolymerization of MMA onto NR molecule has been performed by free radical polymerization either in solution or in latex states using various initiator systems including thermal initiators, such as benzoyl peroxide,¹⁰ potassium persulfate,¹³ and redox initiators,^{11,12,14,16–21} e.g. cumene hydroperoxide/tetraethylene pentamine (CHP/TEPA), *tert*-butyl hydroperoxide/tetraethylene pentamine (*tert*-BuHP/TEPA), or potassium persulfate/sodium thiosulfate (K₂S₂O₈/Na₂S₂O₃). The CHP/TEPA was found to be the most effective redox initiating system¹⁸ and has been widely applied to prepare the graft copolymers of NR and MMA.^{16,19,21} The graft copolymer of NR and MMA exhibits the

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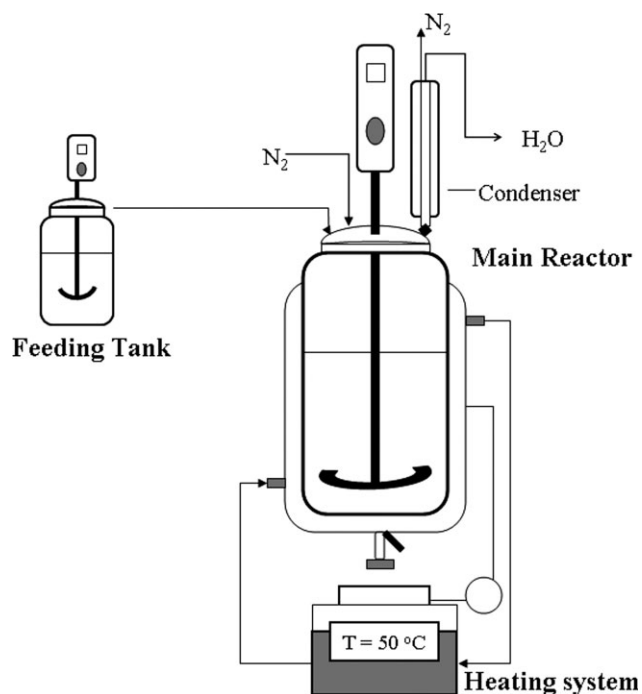


Figure 1 Laboratory scale apparatus used to prepare NR-g-PMMA.

improved polarity, hardness, toughness, and oxidation resistance.^{13,15,18} Therefore, it could be widely applied for adhesives, binders, surface modified agents, and hardness modifier. The NR-g-PMMA latex blended with normal concentrated natural rubber latex gives films with improved modulus, hardness, and tear resistance.¹

The investigations of NR-g-PMMA in various aspects are normally carried out using the products obtained from a laboratory scale production.^{9–21} Even though this material is commercialized, such as by Akrochem (USA) and Regitex (Japan), the open discussion on a pilot scale production is very limited. Being the largest NR producer since 1991, a value added to NR is very important to boost Thailand economics. Therefore, in this work, we are interested to investigate the preparation of graft copolymer in a pilot scale in order to extend its use in various industries. This work started from a laboratory scale production to screen for the most suitable parameters, and hence extended to a pilot scale preparation. The graft copolymer of NR and MMA was prepared by a semibatch emulsion polymerization technique using CHP/TEPA as a redox initiator. A behavior of the mixtures with varying weight percentage ratios of NR to MMA during polymerization in a pilot scale production was observed in terms of temperature profiles. The resulting products were characterized by FTIR and proton NMR techniques. In addition, the characteristics of pilot scale produced graft copolymers were evaluated in compari-

son with those prepared in a common laboratory scale.

EXPERIMENTAL

Materials

The natural rubber latex used for graft copolymerization was high ammonia (HA) concentrated latex containing 60.7% dried rubber content. It was manufactured and kindly supplied by the Rubber Estate Organization (Nakorn Sri Thammarat, Thailand). Methyl methacrylate (MMA) monomer with purity > 99.8% and 15 ppm of 2, 4-dimethyl-6-*tert*-butylphenol (Topanol A) inhibitor was produced by Thai MMA Co., Ltd. (Thailand). Cumene hydroperoxide (CHP) and tetraethylene pentamine (TEPA), manufactured by Fluka (Steinheim, Switzerland), were used as redox initiator. The 37% potassium laurate used to stabilize the latex was prepared from a reaction of lauric acid (manufactured by S.O.C Co., Ltd, Indonesia) and potassium hydroxide (manufactured by Unid Co., Ltd., Korea). Purification of MMA monomer was performed by washing with a 10% aqueous solution of NaOH and then with deionized water until neutral.

Polymerization reactors

The laboratory and pilot scale apparatus used for the preparation of NR-g-PMMA are schematically illustrated in Figures 1 and 2, respectively. The laboratory scale reactor consists of a jacket glass reactor of 1.5 L equipped with two-paddle impeller, condenser, thermometer, and nitrogen gas system. The pilot scale reactor consists of a jacket polypropylene-

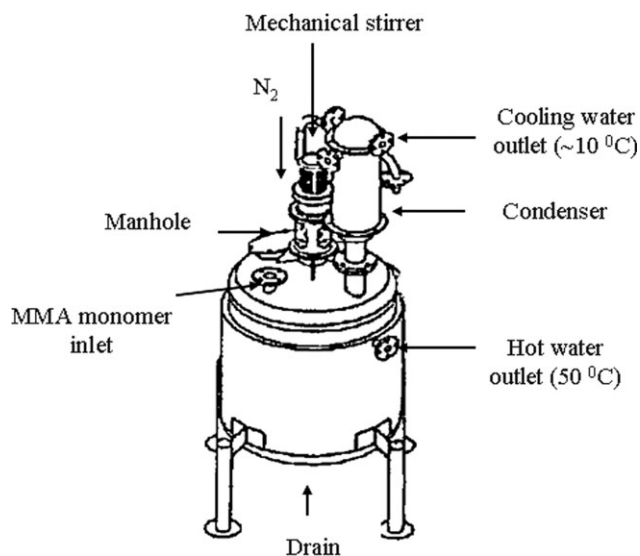


Figure 2 Pilot scale apparatus used to prepare NR-g-PMMA.

TABLE I
Dimensions and Agitation Conditions of the
Laboratory and Pilot Scale Reactor Systems Used to
Prepare NR-g-PMMA

Dimension and agitation condition	Lab scale	Pilot scale
Reactor capacity (L)	1.5	260
Reactor internal diameter (m)	0.10	0.71
Reactor height (m)	0.23	0.86
Reaction mixture height (m)	0.08	0.43
Volume of reaction mixture (L)	0.5	100
Impeller diameter (m)	0.08	0.66
Impeller type	Paddle	Propeller
Stirring rate (rpm)	120	60
Reynolds number ($\times 10^{-4}$)	0.02	0.75

coated aluminum reactor of 260 liters equipped with propeller typed impeller, condenser, thermometer, and nitrogen gas system.

Dimensions of the main reactors in which the polymerization takes place are summarized in Table I. The flow regime for each polymerization system was determined according to the Reynolds number (Re), which was calculated from the following equation²²:

$$Re = \frac{\rho N D_a^2}{\eta}$$

where N is a stirring rate (rps), D_a is an impeller diameter (m), ρ is a density of latex ($=0.92 \text{ kg/dm}^3$), and η is a viscosity of latex ($=58 \text{ mPa s}$).

Calculated Reynolds numbers are reported in Table I. Even though most of the emulsions should be prepared under a turbulent flow regime ($Re > 10^4$),²³ the graft copolymerization involving natural rubber latex should keep the Re below 10^4 to retain latex stability. The excessive shear force obtained by mechanical stirring under a turbulent flow could result in a coagulation of NR latex during the polymerization. It was found that a use of the same stirring rate in the pilot scale reactor as that of the laboratory scale reactor (i.e., 120 rpm) caused a flocculation of latex. Therefore, the stirring rate in the pilot scale reactor was reduced to 60 rpm, as reported in Table I.

Preparation of NR-g-PMMA

The CHP/TEPA redox initiation system has been reported to be the most efficient redox initiating system for preparing the NR-g-PMMA,¹⁸ and hence, they are selected for this study. The NR-g-PMMA was prepared using a semibatch emulsion polymerization technique in the laboratory and pilot scale reactors following the formulations given in Table II.

Laboratory scale preparation of NR-g-PMMA: effect of reaction temperatures, reaction times, and purity of monomer

To determine the reaction conditions for the pilot scale preparation, the laboratory scale experiments were first implemented by varying the reaction temperatures and times. An amount of MMA monomer used for this initial investigation was fixed at 20 phr, i.e., a weight ratio of NR/MMA was equal to 83/17, and the TSC was 50%. Other ingredients are as listed in Table II. The reaction temperatures were first varied at 50, 60, and 70°C ($\pm 5^\circ\text{C}$), whereas the reaction time after the completion of monomer addition was fixed at 3 h. Then, the reaction temperature was fixed at 50°C, and the reaction times were varied from 0 to 9 h. For both reaction temperature and time studies, the purified monomer was used. After that, the graft copolymerization was carried out using nonpurified monomer under the suitable temperature and time, in order to compare with the purified one.

The HA latex, TEPA (85 wt %), potassium laurate (37 wt %), and water were initially added into the main reactor according the formulation shown in Table II. The mixture was then thoroughly stirred under a nitrogen atmosphere for 30 min at the required temperature ($\pm 5^\circ\text{C}$), which was controlled by the temperature of water circulating through the jacket glass reactor. The monomer (MMA) and CHP (80 wt %) were then incorporated into a feeding tank and subsequently added drop-wise into the main reactor. The monomer feeding for the laboratory scale reactor took approximately 0.5 h. The mixture was then left to react for the required times. For characterization purpose, the graft copolymers obtained under different reaction conditions were coagulated with a 10% aqueous solution of calcium chloride (CaCl_2), washed with deionized water, and finally dried at 40°C for 24 h.

TABLE II
Formulation Used in Grafting Reaction at Various
Weight Percentage Ratios of NR and MMA

Chemical	Laboratory scale	Pilot scale
Chemicals in a main reactor		
HA latex	100 phr (83 g)	50, 60, 70, and 85 (g)
TEPA	1.0 phr	1.0 phr
Potassium laurate	1.5 phr	1.5 phr
Water	To adjust TSC equaling to 50%	
Chemicals in a feeding tank		
MMA	20 phr (17 g)	50, 40, 30 and 15 (g)
CHP	1.0 phr	1.0 phr

Comparison of the laboratory and pilot scale production of NR-g-PMMA

The graft copolymers were prepared using a weight ratio of NR/MMA equal to 60/40. The reaction mixture volumes in the laboratory and pilot scale reactors were 0.5 and 100 L, respectively. The reaction temperature was $50^{\circ}\text{C} \pm 5^{\circ}\text{C}$, and the reaction time after the end of monomer charging was 3 h. The reaction was carried out following the same procedures as described previously for the laboratory scale preparation using the nonpurified monomer. For the pilot scale reactor, the addition of MMA monomer into the reactor was started when the temperature reached 40°C , and this step took approximately 2.5 h. After the completion of grafting reaction, small amount of graft copolymer latex was coagulated with a 10% aqueous solution of CaCl_2 , washed with deionized water, and finally dried at 40°C for 24 h before analysis.

Pilot scale production of NR-g-PMMA at various weight ratios of NR to MMA

Under the suitable conditions determined from the laboratory scale preparation, a series of NR-g-PMMA were produced in a pilot scale reactor using different weight ratios of NR/MMA, i.e., 50/50, 60/40, 70/30, and 85/15, as formulations given in Table II. The grafting reaction was carried out at $50^{\circ}\text{C} \pm 5^{\circ}\text{C}$ for 3 h after the completion of monomer charging, using nonpurified monomer. The procedures for grafting reaction and product work-up are as previously described.

Determination of conversion, free NR, free PMMA, and grafting efficiency of the graft copolymer

Conversion

A known weight of graft copolymer latex was dried to a constant weight at 80°C for approximately 24 h. The dried weight was then used to calculate a percentage of monomer conversion into polymer using the following equation:

$$\text{Conversion (CV, \%)} = \frac{M_2 - M_1}{M_0} \times 100 \quad (1)$$

where M_0 is the mass of initial monomer (g), M_1 is the mass of solid NR plus other chemicals excluding monomer (g), and M_2 is the mass of dried sample (g).

Free NR, free PMMA, and grafting efficiency

The solid samples of graft copolymers for the analysis of free homopolymers (free NR and free PMMA) and grafting efficiently were obtained by coagulating

the graft copolymer latex with 10% CaCl_2 , washing with deionized water until neutral, and finally drying in a hot air oven at 40°C for 24 h. Soxhlet extraction method, which has been widely applied to determine the ungrafted NR and PMMA,^{11,18,21} was used in this work. The Soxhlet extraction of pure NR, which was coagulated from the concentrated NR latex before being used for graft copolymerization, by using light petroleum ether revealed that the NR molecules were completely soluble, i.e., no residue left after the extraction. Acetone is also known as a good solvent for PMMA and can completely dissolve PMMA. In this work, the free NR was first extracted in a Soxhlet extractor by light petroleum ether for 24 h. The residue was dried to a constant weight in an oven at 40°C . The free PMMA was later extracted by acetone for 24 h and then dried at 40°C . The free NR and free PMMA were then calculated based on a weight difference before and after each extraction interval, as shown in eqs. (2) and (3). The weight difference between the initial weight and the final weight of sample after extracting both free NR and free PMMA was then used to calculate grafting efficiency (GE) according to eq. (4). The analyses were repeated two times for each sample and average values were reported in this work.

$$\text{Free NR (\%)} = \frac{(M_3 - M_4)}{M_3} \times 100 \quad (2)$$

$$\text{Free PMMA (\%)} = \frac{(M_4 - M_5)}{M_4} \times 100 \quad (3)$$

Grafting efficiency (GE, %)

$$= \frac{\text{Weight of grafted copolymer}}{\text{Weight of polymer formed}} \times 100 \quad (4)$$

where M_3 is the mass of sample before extraction (g), M_4 is the mass of residue after extraction by light petroleum ether (g), and M_5 is the mass of residue after extraction by acetone (g).

FTIR and $^1\text{H-NMR}$ characterization

After extracting the homopolymers (free NR and free PMMA), the resulting graft copolymers were analyzed by using FTIR and $^1\text{H-NMR}$ techniques. For the FTIR analysis, the graft copolymers were dissolved in a mixed solvent of toluene and methyl ethyl ketone (50/50 wt/wt), and later cast on KBr cell. The infrared spectra were acquired by using the Omnic ESP Magna-IR 560 spectrophotometer in a range of $4000\text{--}400\text{ cm}^{-1}$. For the $^1\text{H-NMR}$ characterization, the graft copolymers were dissolved in CDCl_3 and then characterized by the 500 MHz NMR spectrometer (Varian, Germany). The mole and

TABLE III
Effect of Reaction Temperature on the Graft copolymer

Reaction temperature (°C)	Conversion (%)	Free NR (%)	Free PMMA (%)	Grafting efficiency (%)
50	95.5	1.3	2.6	96.1
60	95.7	2.7	2.7	94.7
70	95.9	2.9	2.2	95.0

weight percentages of grafted PMMA on NR molecules were calculated using the integrated peak areas assigned to methoxy protons ($-\text{OCH}_3$) of grafted PMMA and olefinic proton ($=\text{CH}-$) of NR, using the following relationships¹⁶:

% mole of PMMA in the copolymer

$$= \frac{I_{3.5}/3}{(I_{3.5}/3) + (I_{5.1})} \times 100 \quad (5)$$

% weight of PMMA in the copolymer

$$= \frac{C_{\text{PMMA}} \times M_{\text{PMMA}}}{(C_{\text{PMMA}} \times M_{\text{PMMA}}) + (C_{\text{NR}} \times M_{\text{NR}})} \times 100 \quad (6)$$

where $I_{3.5}$ = integrated peak area of the methoxy proton of PMMA at 3.5 ppm; $I_{5.1}$ = integrated peak area of the olefinic proton of NR at 5.1 ppm; C_{PMMA} = % mole of PMMA in the copolymer; M_{PMMA} = molecular mass of repeating unit in PMMA; C_{NR} = % mole of NR in the copolymer; M_{NR} = molecular mass of repeating unit in NR.

Testing of NR-g-PMMA latices

The NR-g-PMMA latices containing different levels of grafted PMMA from the pilot scale production were tested for their total solid content (TSC), alkalinity in NH_3 form, pH, viscosity, mechanical stability time (MST), and surface tension according to American Society for Testing Materials (ASTM) D 1076-02. Determination of pH was done using pH meter Delta Model 320 (Mettler-Toledo, England). The viscosity was measured using Brookfield viscometer model DV-11 (Brookfield Engineering Lab, USA). The MST was tested at the speed of 14,000 rpm using Klaxon MST machine (Klaxon, England), and the surface tension was measured using Du Nouy surface tension apparatus (Du Nouy, USA). All measurements were performed at room temperature.

RESULTS AND DISCUSSION

Laboratory scale preparation of NR-g-PMMA: effects of reaction temperatures, reaction times, and purity of monomer

This preliminary parameter screening process was executed using the laboratory scale reactor, and the

graft copolymer was prepared using a weight ratio of NR/MMA at 83/17, i.e., the amount of MMA monomer was equal to 20 phr. For the temperature investigation, the reaction time was fixed at 3 h, and the reaction temperatures were varied at 50, 60, and 70°C. On the other hand, for the time assessment, the reaction temperature was fixed at 50°C, and the reaction times after a completion of monomer feeding were varied from 0 to 9 h. The results of conversion, %free NR, %free PMMA, and grafting efficiency are summarized in Tables III and IV.

The effect of reaction temperatures on the grafting reaction is shown in Table III. The %conversion and grafting efficiency were found to be more or less constant at about 95%. This indicates that the use of redox initiators at which the initiation reaction can occur at low temperature could readily give the reactive radicals under the range of temperatures studied. However, the highest grafting efficiency was observed at a reaction temperature of 50°C. This is in agreement with the previous work¹⁵ based on the use of deprotonized natural rubber (DPNR) and HA latices. Kochthongrasamee et al.¹⁸ also suggested the reaction temperature in a range of 30–60°C, and found that the raise of reaction temperature beyond 60°C resulted in a decrease of grafting efficiency.

In Table IV, it is seen that as the reaction time after the monomer addition increased from 0 to 3 h, there was a slight increase of the % conversion. However, there was no further increase when the reaction time exceeded 3 h. Therefore, the high conversion was readily obtained after a completion of monomer feeding, indicating that the reaction occurred simultaneously while adding the monomer and CHP initiator. However, the increase of reaction time from 0 to 3 h showed an increase of grafting efficiency to a maximum value. A further increase of reaction time caused a slight decrease of the grafting efficiency. This behavior was also observed in the previous works.^{13,15} At a long reaction time, there were no new generated active sites on the rubber molecules, and the PMMA homopolymer was formed more readily than the graft copolymer. The reaction temperature of 50 °C and the reaction time of 3 h were therefore selected as the appropriate

TABLE IV
Effect of Reaction Time on the Graft copolymer

Reaction time ^a (h)	Conversion (%)	Free NR (%)	Free PMMA (%)	Grafting efficiency (%)
0	93.4	4.2	5.2	90.8
1	94.5	2.1	4.1	93.1
3	95.5	1.3	2.6	96.4
5	95.5	1.1	2.6	96.1
9	95.6	2.4	3.6	94.1

^a Reaction time after a completion of monomer addition.

TABLE V
Effect of the Purified and Nonpurified Monomers on the Graft Copolymer

Monomer type	Conversion (%)	Free NR (%)	Free PMMA (%)	Grafting efficiency (%)
Purified	95.0	1.3	2.1	96.6
Nonpurified	95.6	2.7	3.1	94.3

conditions for the preparation of the graft copolymer in the pilot scale.

For storage stability, inhibitors are generally added to vinyl monomers. It is a norm procedure for polymerization process that these inhibitors are to be removed before being used for polymerization. Purification can be done by using either liquid or solid extraction media. This purification process increases both time and cost. For a pilot scale production that involves a large quantity of monomer, nonpurified monomer is therefore a preferred choice. To investigate an effect of monomer purity, the graft copolymerization of NR/MMA at the weight ratio of 83/17 (i.e., MMA = 20 phr) was carried out using a reaction temperature at 50°C and reaction time of 3 h, using both purified and nonpurified monomers. The purified monomer was obtained after extraction by using 10% NaOH. The results showed that the graft copolymer obtaining from the nonpurified monomer exhibited a slight increase of free homopolymer and hence a slight decrease of grafting efficiency, as shown in Table V. It is seen that the use of both purified and nonpurified monomers gave similar results. Even though a presence of the inhibitors should hinder active free radicals and active sites on the NR molecules, and hence, less grafting sites are available, the effect of inhibitor was not significantly observed in this work. This is possible due to a high concentration of inhibitor (1.0 phr or $\times 10^{-2}$ 6.6 $\times 10^{-2}$ mmol/1 g of rubber). Arayaprane and Rempel²¹ reported an increase in GE with increasing the amount of initiator from $\times 10^{-2}$ 1.7 $\times 10^{-2}$ to $\times 10^{-2}$ 5.0 $\times 10^{-2}$ mmol/1 g of rubber. The increase of initiator amount over $\times 10^{-2}$ 5.0 $\times 10^{-2}$ mmol/1 g of rubber resulted in a decrease of GE. Kochthongrasamee et al.¹⁸ was also observed the highest GE at the concentration of CHP/TEPA of 0.5 phr. In this work, the small amount of inhibitor (15 ppm) was therefore consumed by the excessive amount of initiator, so that, the nonpurified monomer could be used without a significant deterioration in conversion and GE.

Comparison of the laboratory and pilot scale production of NR-g-PMMA

The graft copolymers were prepared using NR/MMA at a weight ratio of 60/40 in both laboratory

and pilot scale reactors. The reaction mixture volumes in the laboratory and pilot reactors were 0.5 and 100 L, respectively. The temperatures of the latex during and after monomer feeding were monitored, and the temperature profiles are shown in Figure 3. It is clear that the reaction mixtures in both laboratory and pilot scale reactors displayed similar pattern during the graft copolymerization, despite the reactor vessels are made of different materials. As depicted in Figure 3, the temperatures increased gradually while adding the MMA monomer due to an exothermic reaction of polymerization. Because the redox initiators were used, so the polymerization could immediately take place when the monomer and redox initiator were presented in the system. For this graft copolymerization, the monomer was slowly added into the latex to maintain the latex stability. Because a pH of the MMA monomer is in a range of 3–5, too fast addition of MMA into NR latex could therefore lead to a latex coagulation. It was found that the reaction temperatures increased upon the addition of monomer and reached the maximum values at 55 and 59°C for the laboratory and pilot scale preparation, respectively. The temperature differences between the initial and maximum temperatures in the laboratory and pilot scale reactors were found to be 12 and 18°C, respectively, as shown in Figure 4. The higher temperature increase in the large reactor is simply attributed to a slower heat transfer in the larger volume of latex. However, the temperature differences in the two very different production scales were found to be not that much difference. It is clearly demonstrated that the pilot scale preparation of the graft copolymer could be carried out without a need of extensive cooling system.

The graft copolymer products obtained from the laboratory and pilot scale production were investigated by the extraction method in order to

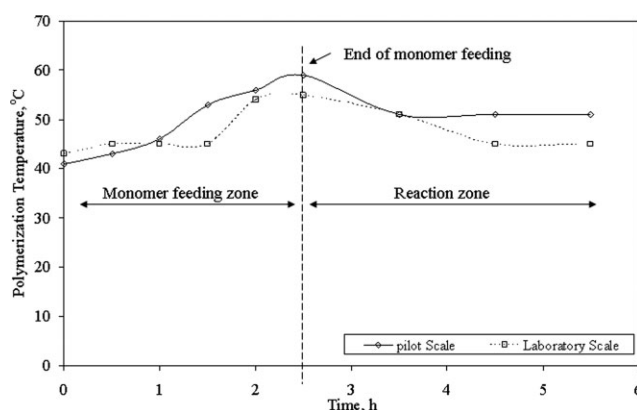


Figure 3 Temperature profiles of the reaction mixtures during graft copolymerization in the laboratory and pilot scale reactors.

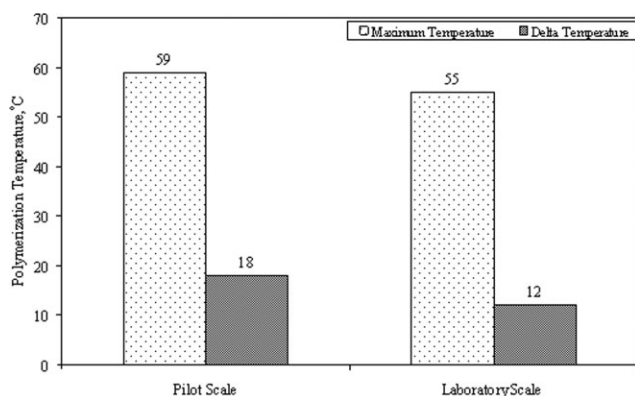


Figure 4 Maximum and delta temperatures during polymerization in the laboratory and large scale production.

determine the grafting efficiency. The NR-g-PMMA was also analyzed using the $^1\text{H-NMR}$ method. The percentages of conversion, free NR, free PMMA, grafting efficiency, and grafted PMMA are summarized in Table VI. The pilot scale production gave lower monomer conversion when compared with the small scale production. However, the final products displayed similar weight percentages of grafted PMMA on the NR molecules. In addition, the grafting efficiency of the copolymer prepared in large volume was slightly higher than that of the copolymer prepared in the small reactor. It has been clearly demonstrated in this work that the NR-g-PMMA can be prepared to have similar grafted PMMA content, providing that the formulation used is the same even though the reactor sizes used are different.

Pilot scale production of NR-g-PMMA at various weight ratios of NR to MMA

The pilot scale production of NR-g-PMMA was prepared using various weight percentage ratios of NR to MMA. The reaction mixture volume was 100 L. The temperature profiles of the latex during the graft copolymerization reaction were observed and shown in Figure 5. We started to add monomer at 40°C and the monomer addition took 2.5 h. The temperature gradually increased as soon as the monomer was added and reached a maximum at more or less the

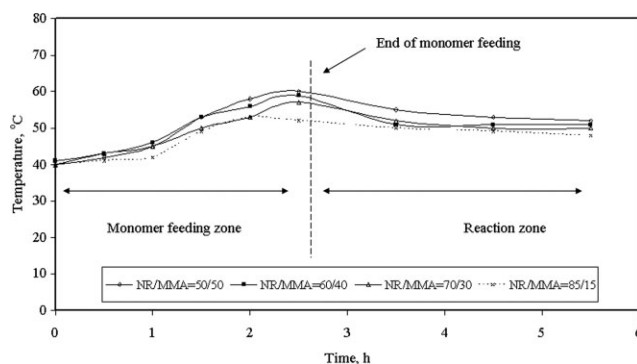


Figure 5 Temperature profiles during polymerization of the reaction mixtures containing different weight ratios of NR to MMA.

same time at the finish of monomer addition. After that the temperature gradually decreased to equilibrium at the set temperature of $50 \pm 5^\circ\text{C}$ within 3 h. All the graft copolymers prepared using different weight percentage ratios of NR to MMA displayed similar pattern, and the maximum temperatures were found to increase with increasing the amount of MMA added. The higher the concentration of the monomer the higher the rate of polymerization, and hence, more heat was generated. The maximum temperatures observed during the polymerization, and the differences of temperatures at the maximum and the beginning of monomer feeding are illustrated in Figure 6.

The graft copolymers with varying wt % ratios of NR to MMA, which were prepared in the pilot scale reactor were first analyzed for the percentages of monomer conversion, free NR, free PMMA, and grafting efficiency. The grafting efficiency was calculated from the weight ratio of extracted graft copolymer and unextracted sample. The unextracted sample composed of free NR, free PMMA, and NR-g-PMMA. The Soxhlet extraction of ungrafted NR and PMMA using light petroleum ether and acetone, respectively, resulted in the sole NR-g-PMMA. The results are summarized in Table VII. By using the same reaction time, an increase of the monomer concentration resulted in a decrease of conversion and grafting efficiency. In addition, quantities of free NR and free PMMA presented in the products produced

TABLE VI
Comparison of Conversion, Free NR, Free PMMA, Grafting Efficiency and Grafted PMMA of the Copolymers Obtained from the Laboratory and Pilot Scale Production

Production scale	Conversion (%)	Free NR (%)	Free PMMA (%)	Grafting efficiency (%)	Grafted PMMA (wt %)
Lab scale	98.2	4.6	10.9	85.3	34.0
Pilot scale	92.4	3.9	8.5	87.6	32.9

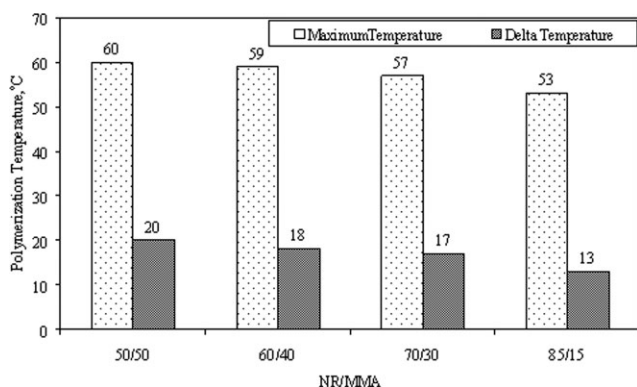


Figure 6 Maximum and delta temperatures during polymerization at various weight ratios of NR to MMA.

using different wt % ratios of NR/MMA are shown in Figure 7. It can be clearly seen that the ungrafted NR molecules decreased, whereas the PMMA homopolymer increased with increasing concentration of MMA in the reaction. The reduction of initiator concentration with an increase of monomer content resulted in a decrease of active radicals and hence a decrease of reaction sites on the NR molecules. In addition, the graft copolymer occurs on the surface of the latex particles and the grafting mechanism involves a surface-controlled process.^{13,21} Once the PMMA shell was formed to a certain thickness, the graft copolymerization was more difficult to occur.

It is well known that the grafting of MMA onto NR particles occurs mainly at the interface and the particle sizes of NR increase after grafting.^{16,21,24} The investigation of NR-g-PMMA particles by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) clearly showed a core-shell structure, where NR was the core and PMMA was the shell.^{19,21} The recent observation of NR-g-PMMA using scanning transmission electron microscopy also showed small nodules of PMMA grafted inside NR particles with an average size of these nodules about 25–30 nm, and the amount of nodules in the particles was found to increase with the monomer content.²⁵ Therefore, an increase in monomer concentration and

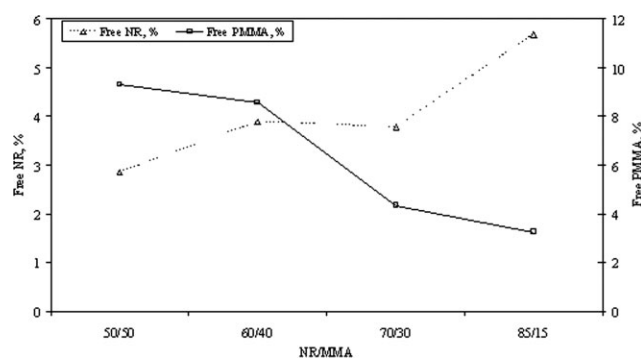


Figure 7 Percentages of free NR and free PMMA in the graft copolymers at various loading levels of MMA monomer.

hence a decrease of initiator concentration in combination with a surface-controlled grafting mechanism resulted in a reduction of conversion and grafting efficiency but a substantial increase of PMMA homopolymer. From the results obtained, it indicated that homopolymerization is more pronounced at higher monomer concentrations. Furthermore, the *cis*-1, 4 configuration of NR should also play a role because the grafting sites on the *cis* positions might not be available after a certain percentage of grafting had taken place. The grafted chains sterically hindered the initiator and the newly arriving monomers to react on the NR molecular chains. Homopolymerization was then favored at high monomer concentrations. The decrease of grafting efficiently with increasing monomer contents was also reported by George et al.¹⁹ and Arayaprane and Rempel.²¹

Characterization of NR-g-PMMA obtained from the pilot scale production

The functional groups of NR-g-PMMA, which had been prepared using various weight percentage ratios of NR and MMA were characterized by FTIR technique. The spectra, as shown in Figure 8, demonstrated the absorption peaks at the wave numbers of 1732 and 1140 cm^{-1} in the graft copolymer. This indicates the presence of C=O and C–O stretching in the graft copolymer molecules, respectively. The higher concentration of MMA monomer added into the reaction, the stronger the characteristic absorption peaks of grafted PMMA was observed. To compare the levels of grafted PMMA on the NR molecules, the absorbance ratios of peaks at 1732 cm^{-1} to 835 cm^{-1} were calculated, and the results are shown in Figure 9. The 1732 cm^{-1} peak corresponds to the C=O stretching of grafted PMMA, whereas the 835 cm^{-1} peak arises from the =C–H out of plane bending of *cis*-1, 4 polyisoprene. The result clearly shows an increase of levels of grafted PMMA with increasing quantities of MMA in the grafting reaction.

TABLE VII
Conversion, Free NR, Free PMMA, and Grafting Efficiency of the Graft Copolymerization at Various NR/MMA Weight Ratios

NR/MMA (by wt)	Properties (%)			
	Conversion	Free NR	Free PMMA	Grafting efficiency
50/50	88.2	2.9	9.3	87.8
60/40	92.4	3.9	8.5	87.6
70/30	93.5	3.8	4.4	91.9
85/15	94.8	5.7	3.3	91.1

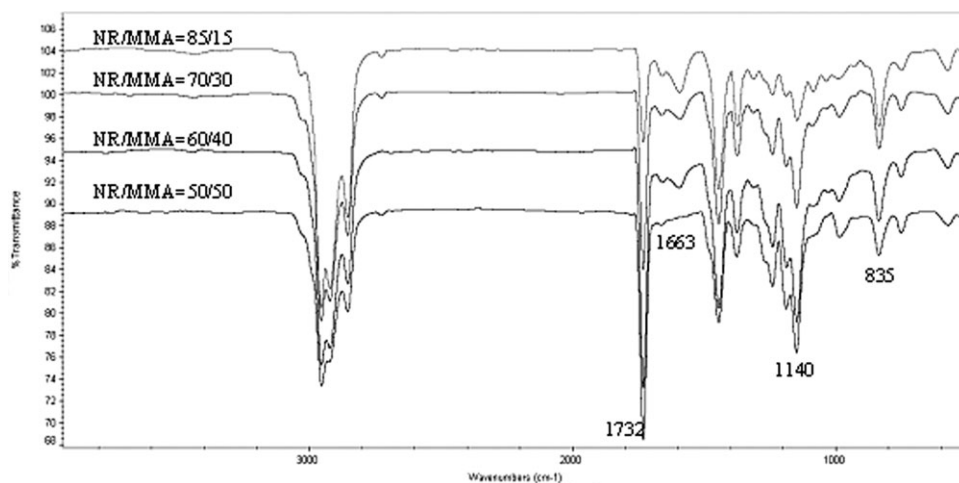


Figure 8 FTIR spectra of the graft copolymers prepared using various weight percentage ratios of NR and MMA.

The graft copolymers were also characterized by ¹H-NMR spectroscopy, and the NMR spectra are shown in Figure 10. The absorption bands at the chemical shifts of 3.5 and 5.1 ppm, which indicate the signals of -OCH₃ proton of PMMA and =CH proton of polyisoprene, respectively, were clearly observed. This confirms the occurrence of grafted PMMA on the NR structure in the graft copolymers which were prepared in the pilot scale reactor.

To quantify the amount of PMMA grafted onto the NR molecules in terms of weight and mole percentages, the integrated peak areas of methoxy- and olefinic protons of PMMA and NR in the ¹H-NMR spectra were used for calculation according to the eqs. (5) and (6). The calculated results from ¹H-NMR spectra are presented in Table VIII, in comparison with the weight percentages of grafted PMMA, which were estimated by extraction method. From the extraction technique, the amount of grafted PMMA was calculated by relating the percentage of grafting efficiency obtained to the initial monomer content employed.

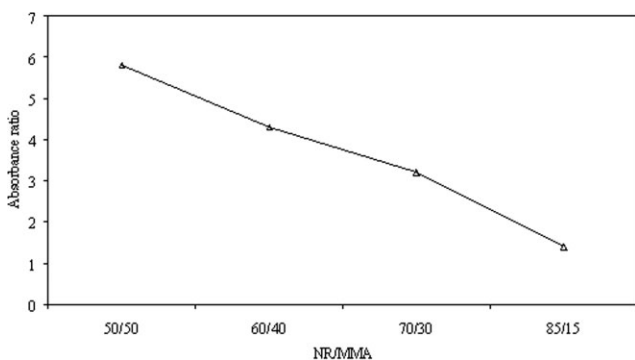


Figure 9 Absorbance ratios of FTIR peaks at 1732 and 835 cm⁻¹ of NR-g-PMMA at various weight ratios of NR and MMA.

Even though the ¹H-NMR technique should provide more accurate results than the extraction technique, we found that both techniques gave similar results in terms of wt % of grafted PMMA onto NR, as exhibited in Table VIII. The grafted PMMA increased with increasing MMA contents used for the graft copolymerization. However, because of the incomplete conversion and occurrence of homopolymer, the amount of final grafted PMMA was then less than the amount of initial monomer used.

The characterization results from both FTIR and ¹H-NMR techniques agreed well, and it is clearly demonstrated that the graft copolymers with various grafted PMMA contents were successfully prepared using our pilot scale reactor. The suitable conditions

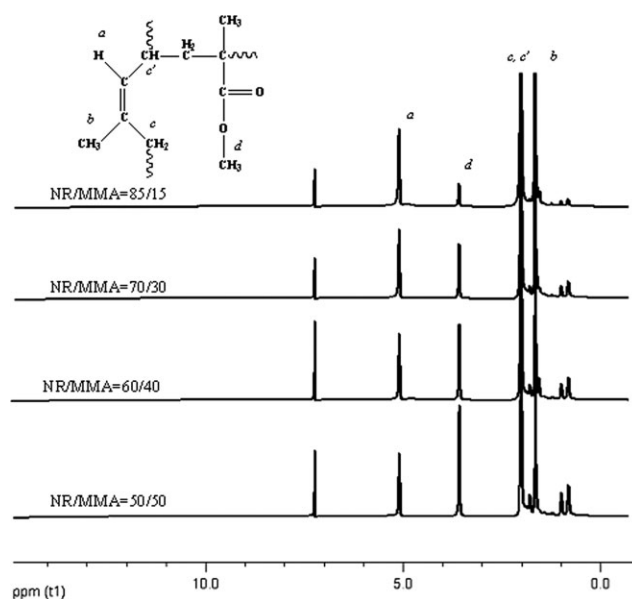


Figure 10 ¹H-NMR spectra of the graft copolymers prepared using various weight percentage ratios of NR and MMA.

TABLE VIII
Comparison of Percentages of Grafted PMMA Analyzed
by Extraction and $^1\text{H-NMR}$ Methods

NR/MMA (by wt)	Initial MMA (wt %)	Percentage of grafted PMMA		
		Extraction method	$^1\text{H-NMR}$ method	
			wt %	mol %
50/50	50.0	43.9	33.9	43.0
60/40	40.0	35.0	25.0	32.9
70/30	30.0	27.6	19.1	25.8
85/15	15.0	13.7	8.3	11.7

from laboratory scale production could be easily extended to the pilot scale production. The NR-g-PMMA product can then be wider applied in industry level for various applications either in the latex state or in the solid state.

Properties of NR-g-PMMA latices

The graft copolymers are intended to use initially for adhesive applications, so the latex properties are important. The graft copolymers were prepared at the volume of 100 L in the 260 L reactor, and the latex was tested without any further purification. This means that the graft copolymer latex contains both grafted and ungrafted PMMA, including the unreacted MMA monomer. The initial total solid content (TSC) calculated was 50%. The results, as summarized in Table IX, showed that the final TSC of the latex was lower than the initial TSC, and increasing of MMA contents decreased the TSC of the final product. This is in agreement with the percentages of monomer conversions reported in Table V; the higher monomer concentration, the lower the conversion, and hence, the lower TSC of the graft copolymer latex. The alkalinity and pH of the latex were also reduced with the increase of MMA content due to the acidic nature of MMA and a loss of NH_3 during the reaction. The latex viscosity decreased with increasing the MMA content because

the portion of natural rubber, which has higher viscosity was reduced. The resulting graft copolymer showed very high stability toward a high shear, as the mechanical stability time (MST) was very much higher than that of the NR latex. The lower surface tension of this graft copolymer when compared with the NR latex shall also enhance a wetting ability toward substrates. According to the test results, the properties of the NR-g-PMMA latex indicate a beneficial influence on the adhesion property.

CONCLUSION

Graft copolymers of natural rubber and poly (methyl methacrylate) (i.e., NR-g-PMMA) with different levels of grafted PMMA were successfully prepared in a pilot scale production, utilizing the suitable conditions found for the laboratory scale reactor. The pilot scale production gives lower conversion but similar grafting efficiency and percentage of grafted PMMA, when compared with the laboratory scale preparation. The NR-g-PMMA prepared using different wt % ratios of NR/MMA; 50/50, 60/40, 70/30, and 85/15, exhibited similar temperature profiles of the reaction mixtures during the polymerization, but the temperature rise increased with increasing the MMA concentrations. It was found that the percentages of conversion and grafting efficiency decreased with increasing concentrations of MMA. The structure of NR-g-PMMA prepared on the pilot scale production was confirmed by FTIR and $^1\text{H-NMR}$ techniques. The FTIR spectra showed the characteristic absorption peak of $-\text{C}=\text{O}$ stretching of grafted PMMA at 1732 cm^{-1} , whereas the $^1\text{H-NMR}$ spectra exhibited the peak associated with the resonance of methoxy protons in the grafted PMMA at 3.5 ppm. The wt % of grafted PMMA calculated from the NMR spectra is in good agreement with the value calculated based on the extraction method. The grafted PMMA increased with the increasing of MMA concentration. In addition, the properties of the graft copolymer

TABLE IX
Properties of the Graft Copolymer Latices at Various Weight Percentage
Ratios of NR to MMA

Properties	NR	NR/MMA (by wt)			
		50/50	60/40	70/30	85/15
Grafted PMMA (wt %)	–	43.0	32.9	25.8	11.7
TSC (%)	61.4	47.7	49.7	48.8	50.0
Alkalinity (in NH_3 form), %	0.6	0.2	0.3	0.3	0.4
pH	10.3	9.5	9.9	10.1	10.1
Viscosity (centipoises)	57.7	20.1	22.1	28.5	36.5
Spindle no. 1 at 60 rpm					
MST (s)	826	>1800	>1800	>1800	>1800
Surface tension (dyne/cm)	38	35	35	34	33

lattices were tested, and the results are beneficial to the use for adhesive applications.

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