Factorial Experimental Design for Graft Copolymerization of Styrene and Methyl Methacrylate onto Styrene–Butadiene Rubber

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ABSTRACT: The graft copolymerization of styrene (ST) and methyl methacrylate (MMA) onto styrene–butadiene rubber (SBR) latex prepared by seeded emulsion polymerization has been studied under various reaction conditions using cumene hydroperoxide redox initiator. The mechanism of graft copolymerization has been investigated. The synthesized graft copolymers were purified and then characterized by proton nuclear magnetic resonance (^{1}H NMR) analysis. A 2 2^{6-2}_{IV} fractional factorial experimental design was applied to study the effects of the process variables such as the amount of initiator and emulsifier, the presence or absence of chain-transfer agent, ST to MMA ratio, monomer to rubber ratio, and reaction temperature on the grafting efficiency. The analysis of the results from the design showed the sequence of the main effect on the observed response of the grafting of ST and MMA onto SBR and that the amount of chain-transfer agent had a significant effect. Transmission electron microscopy was used to study the morphology of the graft copolymers. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 2867–2874, 2006

Key words: experimental design; styrene–butadiene rubber; styrene; methyl methacrylate; grafting

INTRODUCTION

Grafting reactions provide a potential route for significantly altering the physical and mechanical properties of a substrate polymer for specific end used. Chemical modification of diene polymers, e.g., natural rubber (NR),[1–4] polybutadiene (PB),[5–8] polybutyl acrylate (PBA),[9,10] and styrene–butadiene rubber (SBR),[11] via vinyl graft copolymerization constitutes a powerful means of improving the polymer properties, thereby enlarging the range of their utilization. Graft copolymers with a soft core and a hard shell are used as impact modifiers,[12] plastic tougheners,[13] and compatibilizers for polymer blends.[14,15] The core–shell emulsion copolymerization is achieved by grafting the monomer in the second stage polymerization onto the preformed polymer. Usually, diene polymers are chosen as the soft core component, whereas the polymers of methyl methacrylate (MMA), styrene (ST), and so on are chosen as the hard shell component. Primarily, free-radical initiated processes are used to produce graft copolymers. Emphasis is placed on radiation[16–18] and redox systems.[19–23] Among the redox initiators, hydroperoxides were found to be particularly susceptible to activation by polyalkylenepolyamines.[24–26] Whitby et al.[24] studied the polyamines used as activators in the cumene hydroperoxide (CHPO)-catalyzed emulsion polymerization of a 70 : 30 mixture of butadiene:styrene. They reported that with triethylenetetraamine, tetraethylenetetraamine, and pentaethylenetetraamine, the inclusion of caustic alkali had a favorable effect on the rate of polymerization.

Many authors have noted the influence of various process variables on grafting reactions, mainly focusing on the grafting of vinyl monomer onto rubber. Brydon et al.[27,28] studied the grafting of ST onto PB in benzene solution at 60°C, with benzoyl peroxide as initiator. They found that the rate coefficient for the primary radical attacking a monomer molecule was slightly greater than that for a primary radical attacking the backbone of the polymer. Cameron and Qureshi[29] studied the grafting of ST onto polyisoprene and found that the proportion of polystyrene incorporated as graft was not affected by the initiator (benzoyl peroxide) concentration. Sundberg et al.,[30] investigating the graft copolymerization of ST onto PB latex, has

determined that the grafting efficiencies are due to various factors, i.e., monomer/polymer ratio, initiator level, degree of conversion, and concentration of chain-transfer agent. Enyiegbulam and Aloka[31] investigated the grafting of MMA onto NR in methyl ethyl ketone (MEK)/toluene solution initiated by benzoyl peroxide. An increase in the concentration of MMA decreased the grafting efficiency. However, the grafting efficiency was weakly affected by the concentration of benzoyl peroxide initiator. Gasperowicz et al.[10] investigated the grafting of ST onto PBA in emulsion form. The parameters investigated in relation to the grafting efficiency of ST onto PBA were time, temperature, the concentration of initiator and emulsifier, and the monomer/polymer ratio. The grafting efficiency decreased with increasing time of reaction, the monomer/polymer ratio, and emulsifier and initiator concentration. The grafting efficiency was weakly affected by the temperature of polymerization.

The effects of process variables on the grafting involve a complicated investigation, in view of the great number of variables involved, among which are type and concentration of initiator, monomer concentration, type and concentration of emulsifier, rubber latex concentration, chain-transfer agent concentration, reaction time, and reaction temperature. Factorial designs are very useful in identifying the effects of process variables on grafting. Factorial designs require 2^N experiments if N factors have to be investigated. In our case, with six variables, this would lead to 64 experiments, which is still a large number. The number of experiments can be reduced by using only part of the factorial design (fractional factorial design) without loss of information about the main effects.[32] We chose to do 1/4 of the 64 experiments, giving 16 experiments.

In previous grafting studies,[3] we used NR as the backbone polymer and ST and MMA as the shell monomers in the seeded emulsion process, with further investigates of the effects of process variables on the grafting efficiency. Therefore, in this work, we switched the backbone polymer to NR, since we had used SBR earlier. The aim of this work is to highlight the effects of process variables on the grafting reaction of ST and MMA onto SBR through a statistically based experimental design. The influences of process variables, including the amount of initiator, emulsifier, the ST to MMA (ST/MMA) ratio, monomer to rubber (M/R) ratio, the reaction temperature, and chain-transfer agent, were investigated by using a two level fractional factorial design.

EXPERIMENTAL

Materials

The SBR latex with a solid content of ~21.7% was provided by the Bayer Inc. The SBR latex is composed of 27% ST composition. Reagent grade ST (Aldrich, purity ~99%) and MMA (Aldrich, purity ~99%) monomer are made free of inhibitor by applying a 10% aqueous solution of NaOH, followed by deionized water and by distillation under reduced pressure. It was then stored in a refrigerator until required. The chain-transfer agent n-dodecyl mercaptan (Aldrich), the emulsifier sodium dodecylsulfate (Aldrich, purity ~98%), the stabilizer isopropanol, the buffer potassium hydroxide (Aldrich), the initiators, redox initiator system, cumene hydroperoxide ($C_9H_{12}O_2$, CHPO, Aldrich, purity ~80%), and the activator agent tetraethylenepentamine ($HN(CH_2CH_2NHCH_2CH_2NH_2)_2$, TEPA, Aldrich) were used as received. Deionized water was used throughout the work.

Preparation of grafted SBR

The graft polymerizations were carried out using a 300 mL Parr reactor, equipped with a condenser. SBR latex and an aqueous solution of additive 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, while 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 TEPA was added. The SBR seed latex was swollen with the monomer mixture for 1 h at reaction temperature before adding the initiator. The redox initiation system, consisting of CHPO and TEPA with a ratio of 1:1, was used. The polymerization reaction was performed at a stirring speed of 200 rpm and the desired temperature for 8 h. The polymerization temperature was maintained at a constant temperature for all polymerization runs. Samples were taken at intervals to establish, gravimetrically, the degree of conversion of monomer to polymer. The post treatment included the coagulation of polymer latex and washing with deionized water. The gross polymers were recovered and dried to constant mass in a vacuum oven at 40°C. The recipes used in the synthesis of graft copolymers are listed in Table I and variable design factors for the graft copolymerization are shown in Table II, verifying the effect of process variables on the grafting efficiency, which is the response or dependent variable to describe the influence of process variables. Process variables were varied according a 2 2_{IV}^{6-2} design, resolution R = (IV). For each process variable, the low level coded as −1 and the high level of each design factor coded as +1 were chosen in the range to be studied (Table II). Each combination of − and + levels represented an experiment.

The conversion, a measure of how much monomer is converted into polymer, was calculated using:

TABLE I
Standard Recipes used for Graft Copolymerization

Ingredients	SBR (21.7% DRC) quantities
Latex (g)	138.2
Water (g)	61.8
Stabilizer amount (g)	3
Buffer amount (g)	0.12
Redox initiator amount, CHPO : TEPA = 1 : 1	Variable
Emulsifier amount	Variable
Chain-transfer agent	Variable
Styrene amount	Variable
Methyl methacrylate amount	Variable

Conversion (%)

$$= \frac{\text{weight of monomers polymerized}}{\text{weight of monomers initially charged}}$$
$$\times 100 \quad (1)$$

In the graft copolymerization, not all of the monomers added to the SBR seed latex will become grafted onto the SBR backbone (ST/MMA-g), but part of it will polymerize without being chemically bonded onto the backbone, called free copolymers (ST/MMA-f). A 60–80°C boiling point fraction of petroleum ether and a MEK/acetone (50 : 50 v/v) mixture were used for extracting free rubber and free copolymers (ST/MMA-f), over a 24 h period, respectively. The weight difference between the initial sample and extracted samples provides a measure of grafting efficiency (GE) calculated using the following relationship:

Grafting efficiency (GE, %)

$$= \frac{\text{total weight of monomers grafted (ST/MMA−g)}}{\text{total weight of monomers polymerized}}$$
$$\times 100 \quad (2)$$

^{1}H NMR spectra were obtained on a A Bruker AC 250 MHz NMR spectrometer, which was found to provide accuracy and reproducibility (±2 wt %) with ease of analysis. Analysis was carried out using a 5–10% (w/v) solution in deuterated chloroform (CDCl$_3$).

The morphology was examined by using a JEM-200CX transmission electron microscope (TEM) at 120 kV. The grafted latex was diluted 400 times with deionized water to a concentration of 0.025 wt %. To this solution, 1 mL of a 2% aqueous OsO$_4$ solution was added and allowed to stain the rubber in the graft copolymers overnight.

Experimental designs

The large number of independent variables involved in graft copolymerization processes lead to a thorough experimental study. The grafting efficiency was determined gravimetrically, with the responses or dependent variables to be measured for each run. In this work, six process variables, which are expected to have an effect on the grafting efficiency, were considered. These variables include the concentrations of initiator, emulsifier, and chain-transfer agent, the reaction temperature, the ST/MMA ratio, and the M/R ratio. The effects are complex and may include many interactions. When using two level fractional factorial design, the number of experiments can be reduced without loss of information about the main effects. However, some information about interaction effects will be lost. In this case, a two level fractional factorial design was chosen, since the higher-order interactions were expected to be negligible. Process variables were varied according a 2 2_{IV}^{6-2} design, resolution R = (IV). For each process variable, a "−level," "+level" were chosen in the range to be studied (Table II). The low level coded as −1 and the high level of each design factor coded as +1 were also defined for each independent variable. The independent variables are listed in the first column of Table II and represent the amount of initiator (INT), emulsifier (EMUL), ST to MMA ratio (ST/MMA), monomer to rubber ratio (M/R), reaction temperature (TEMP), and chain-transfer agent (CTA). The experiments (a total of 16 runs) are listed in Table III using the coding scheme shown in Table II.

TABLE II
Graft Copolymerization Runs: Low and High Level of Design Variables

Ingredient	Name	Amount (low = −1)	Amount (high = +1)
INT (phr)	Cumene hydroperoxide	1	2
EMUL (phr)	Sodium dodecylsulfate	1	2
ST/MMA	Styrene/methyl methacrylate	0.75	1.0
M/R	Monomer/rubber ratio	1.0	1.25
TEMP (°C)	Reaction temperature	50	70
CTA (phr)	n-dodecyl mercaptan	0	0.5

TABLE III
The Experimental Results of Graft Copolymerization

Experiment	Design factor						GE (%)
	INT	TEMP	EMUL	CTA	ST/MMA	M/R	
GSBR01	−1	−1	−1	−1	−1	−1	71.8
GSBR02	+1	−1	−1	−1	+1	−1	72.4
GSBR03	−1	+1	−1	−1	+1	+1	77.3
GSBR04	+1	+1	−1	−1	−1	+1	81.1
GSBR05	−1	−1	+1	−1	+1	+1	68.0
GSBR06	+1	−1	+1	−1	−1	+1	68.9
GSBR07	−1	+1	+1	−1	−1	−1	86.6
GSBR08	+1	+1	+1	−1	+1	−1	84.1
GSBR09	−1	−1	−1	+1	−1	+1	59.0
GSBR10	+1	−1	−1	+1	+1	+1	51.2
GSBR11	−1	+1	−1	+1	+1	−1	69.4
GSBR12	+1	+1	−1	+1	−1	−1	60.0
GSBR13	−1	−1	+1	+1	+1	−1	48.3
GSBR14	+1	−1	+1	+1	−1	−1	57.2
GSBR15	−1	+1	+1	+1	−1	+1	45.5
GSBR16	+1	+1	+1	+1	+1	+1	57.1

The grafting efficiency was analyzed using analysis of variance (ANOVA). To ensure that the assumptions of normality and constant variance were met, the response variable (grafting efficiency) was calculated. The F test was used to evaluate if a variable has a significant effect ($F > 18.5$). The data processing and calculations were carried out with the help of the Statistica (Version 5) programs.

RESULTS AND DISCUSSION

Mechanism of grafting

For the graft copolymerization process using the redox initiator couple CHPO/TEPA, most of the free radicals are produced at the monomer swollen particle/water interface, taking into account the fact that the peroxide is soluble in the organic phase, whereas the activator TEPA is water-soluble. The CHPOs in the dilute aqueous solution decomposes to yield alkoxy radicals. During the formation of the graft copolymers, the surface of latex particles became the loci of polymerization. The alkoxy radical might interact with the monomer or the rubber molecule producing macroradical, which initiates grafting. The alkoxy radicals not only add to double bonds or attack the α-hydrogen atoms to produce rubber radicals, which initiate monomers to form the graft copolymers, but also initiate monomers to form free polymer radicals, which combine with rubber radicals to terminate or transfer to rubber to form graft copolymers. Furthermore, some of the free polymer radicals still terminate to form free copolymers on the surfaces of the latex particles.

To demonstrate the presence of the graft copolymers, the products were extracted by petroleum ether

and a mixture of acetone and MEK, respectively. After the solvent extraction, graft copolymers were analyzed by ^{1}H NMR. Figure 1 illustrates the ^{1}H NMR spectrum of the residues (the graft copolymers) and the SBR. The peaks at 5.4 ppm are assigned to the olefinic proton content in the SBR. The signals at 6.5–7.5 ppm are attributed to the phenyl group of PST. The peaks observed at 3.5–3.7 ppm are attributed to the methoxy group of PMMA. It would be expected that the signals at 6.5–7.5 ppm of the phenyl group should change with the amount of grafting. However, this is not quantitatively reflected, since SBR predominately
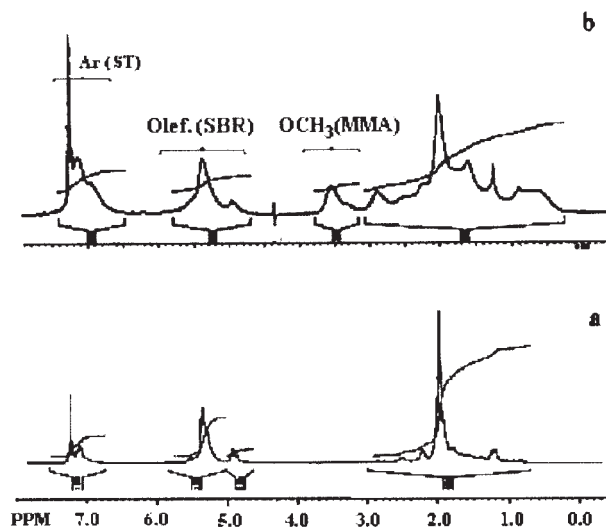

Figure 1 ^{1}H NMR spectra (250 MHz) of polymers. (a) SBR and (b) graft copolymers. Ar(ST) represents the aromatic protons of the ST unit, Olef(PB) represents the olefinic protons of the SBR unit, and OCH3(MMA) represents the resonance of the methoxy protons.
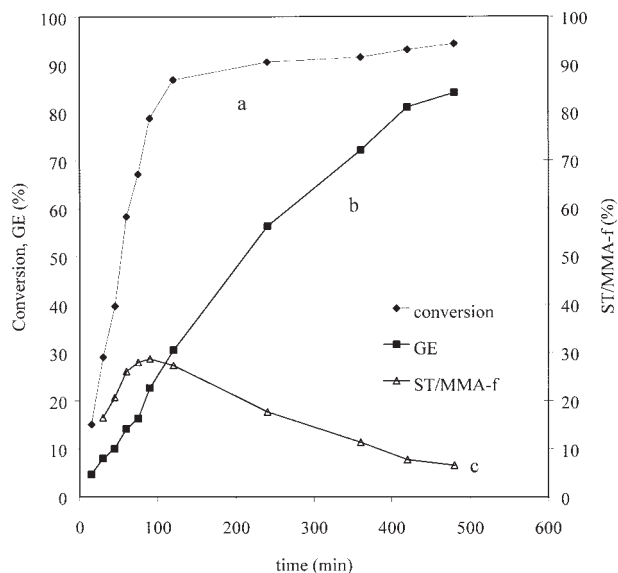
Figure 2 Effect of time on conversion, grafting efficiency, and the percentage of PST/MMA-f for GSBR08.

contains the phenyl group in its structure, as evident from trace a. in Figure 1. These ^{1}H NMR analyses confirm that the ST and MMA were grafted onto SBR during graft copolymerization.

Rate of polymerization

Figure 2(a) shows the plot for the conversion versus reaction time for experiment GSBR08. The shape of conversion versus time curve indicates that the polymerization rate was extremely rapid during the initial period (<2 h). After the first 2–3 h, conversion of vinyl monomer in the reactor reached a maximum value and remained constant.

The grafting efficiency of ST and MMA onto SBR latex as a function of reaction time was investigated from graft copolymerization reactions [Fig. 2(b)]. The grafting efficiency increased gradually at the beginning period and thereafter increased only slightly. The formation of graft copolymers is shown by competition between the free copolymers and the graft copolymers. The free copolymers showed gradual rise at the beginning and then decreased [Fig. 2(c)]. This suggests that the conversion at the beginning increased rapidly, since most of the ST and MMA monomers were polymerized in the aqueous phase to form new polymeric radicals until the monomers were nearly consumed. Then, the growing free copolymer chains are terminated by recombination with rubber radicals, thus forming graft copolymers, leading to a decrease in free copolymer amount with increasing reaction time. Aerdts et al.[33,34], who studied the grafting of ST and MMA onto PB latex using either a water soluble

or an oil soluble initiator, had found a similar observation for the grafting reaction.

The influence of process variables

The experiments of a 2 2_{IV}^{6-2} factorial experimental design (a total of 16 runs) are listed in Table III. Within this framework, the effect of process variables was investigated including the amount of initiator, emulsifier, ST/MMA ratio, M/R ratio, reaction temperature, and chain-transfer agent. Statistical analysis was used to study the influence of each process variable irrespective of and in combination with the other process variables on the grafting efficiency. The grafting efficiency was analyzed using ANOVA. Since a factorial design was used to organize the experiments, analysis of the results is facilitated with ANOVA. The values obtained for grafting efficiency for the 16 experiments of the 2 2_{IV}^{6-2} factorial design are shown in column 8 of Table III. From these results, the highest grafting efficiency was (86.6%) obtained in experiment GSBR07. To ensure that the assumptions of normality and constant variance were met, the response variable, grafting efficiency, was calculated. The importance of these effects may be confirmed with the ANOVA. The total sum of squares (SS$_{total}$) is calculated as

$$SS_{total} = \sum_{i=1}^{n} y_i^2 - (\sum_{i=1}^{n} y_i)^2/n$$

where y_i is the response and n the number of experiments. The sum of squares (SS) for any main and interaction effect is SS$_{effect}$ = 2^{N-2-2}(effect)^2, where N is known as the number of effects. The error sum of square (SS$_{error}$) is a result of the differences between the total sum of square and the sum over all the SS$_{main\ effect}$ and SS$_{interaction\ effect}$. The degrees of freedom for the main effects are the total number of levels less one. The main effect has (2–1) degrees of freedom, while the interaction effect has (2–1) (2–1) degrees of freedom. Therefore, there are 16 (the total number of experiments) − 13 (the sum over all the number of main and interaction effects) −1 = 2 degrees of freedom for error. If we divide each of the sum of squares by the corresponding number of degrees of freedom, we obtain the mean squares (MS) for the effect, the interaction, and error. According to F statistics for testing the significance of main and interaction effects, the F test is calculated by dividing the mean squares for each effect by the mean squares for error. The 95% confidence interval ($F_{1,2}$ = 18.5) provides a test to decide whether the variance due to an observed response is significant or not. If the F test is smaller than 18.5, the variance due to the observed response is not significant. If the observed F test is larger than 18.5, the

TABLE IV
Results for Main Effects and Two-factor Interactions for Response and the Analysis of Variance of Percentage GE for Grafting of ST and MMA onto SBR

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

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

observed response is probably significant. Results for main effects and two-factor interactions are identified in Table IV, showing the F test of effects of the process variables on grafting efficiency. In this design, only one significant effect with respect to grafting efficiency was CTA. All interactions could be eliminated because of no significance (see in Table IV).

According to the definition, the main effect of the controlled independent variable is the mean of the difference between the values at the high level (+) and the values at low level (−). Figure 3 shows the mean grafting efficiency of grafting of ST and MMA onto SBR latex as a response to the six variables investigated.

The effect of initiator level on the grafting is shown in Figure 3(a). It is noticed that increasing initiator level from low to high level caused a slight increment in the GE. This behavior may be interpreted as the comprehensive result of two competing reactions, in which the monomer is consumed, i.e., free copolymerization and graft copolymerization. The radicals transferred to either rubber or monomer, producing macroradicals, which was enhanced on increasing the initiator level. When the concentrations of initiator used in the seeded emulsion polymerization are higher, they increase both rubber radical and free polymer radical simultaneously. The free polymer radical preferred to combine with rubber radicals to terminate or transfer to rubber to form graft copolymers. The increase of grafting efficiency at a higher level of initiator arose from the predominance of grafting over free copolymerization. The experimental results are in agreement with the reports of Enyiegbulam and Aloka.[31]

Figure 3(b) shows the effect of the amount of emulsifier on the grafting, which decreased with increasing emulsifier level. The result seems to indicate that the amount of emulsifier had little effect on the grafting efficiency in the absence of coagulation or renucleation. It is suggested that the emulsifier charged covered mainly the SBR latex seed particles and kept the emulsion system stable. At a high level of emulsifier, more free micelles exited in the water phase, which, in turn, caused the formation of a new crop of particles. So there would be less monomer left for grafting. The grafting efficiency decreased with increasing emulsifier amount, which is in agreement with the results of Zhao et al.[11]

The grafting efficiency is essentially unchanged with increasing ST/MMA ratio [Fig. 3(c)]. The result obtained shows that the grafting efficiency was not affected by ST/MMA ratio. In the previous work,[3] we investigated the graft copolymerization of ST and MMA onto NR and found that the grafting efficiency increased with increasing ST/MMA ratio. The SBR backbone shows a quite different grafting behavior when compared with the NR backbone, and this may be due to the presence of polystyrene segments in the
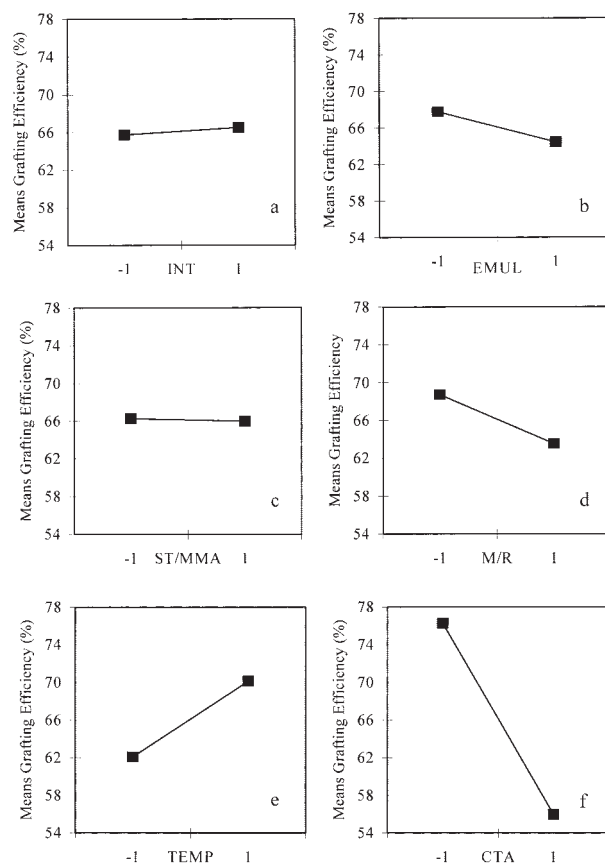

Figure 3 Effect of (a) the amount of initiator, (b) the amount of emulsifier, (c) ST/MMA ratio, (d) M/R ratio, (e) reaction temperature, and (f) the amount of chain-transfer agent on grafting efficiency.

copolymer. Because of the presence of polystyrene segments in the copolymer, the chemical structure of the backbone polymer was changed. The attack of primary radical on SBR backbone would generate a radical that ought to compete effectively with the poly(methyl methacrylate) radical. Thus, the grafting efficiency was not significantly affected by ST/MMA ratio.

Figure 3(d) shows the relationship between the graft efficiency and M/R ratio in the two-stage emulsion polymerization. The graft efficiency decreased with increasing M/R ratio. This demonstrates that the graft reactions occurred mainly in the shell of the particles. When the M/R ratio increased, the contact area between monomers and SBR decreased gradually. As grafting proceeded and a certain shell thickness of grafted material is reached, grafting decreased because of the reduced availability of the polymer backbone. Therefore, more free copolymers were produced than graft copolymers. As a result, the graft efficiency decreases with increasing M/R ratio. A similar observation was recorded by Merkel et al.,[35] studying the emulsion polymerization of MMA onto PB latex. They found that the amount of graft copolymer decreased concurrently with increasing M/R ratio.

The effect of the reaction temperature was studied by changing the reaction temperature from 50 to 70°C. The results obtained are presented in Figure 3(e). The grafting efficiency increased with the increase of temperature. According to the Arrhenius relation, in radical polymerization started by thermal decomposition of an initiator, as temperature was increased, the rate of polymerization is strongly enhanced. On the other hand, when temperature was raised, the diffusion rate of vinyl monomers into the SBR was enhanced, thus resulting in a higher grafting efficiency. Lenka et al.[21] found similar results when they studied the graft copolymerization of MMA onto rubber.

Figure 3(f) shows that the grafting efficiency was detrimentally affected by adding chain-transfer agent, indicating that the grafting efficiency is significantly reduced as the level of chain-transfer agent is increased. This can be ascribed to the increase in rate of chain-transfer reaction of radicals to mercaptan, which resulted in a decrease of radical formation, thereby decreasing the grafting and free copolymerization. The amount of mercaptans significantly affected the grafting efficiency, which was in agreement with the results of Sundberg et al.[30] investigating the grafting mechanism of ST onto a PB rubber latex.

The morphology

The grafting of ST and MMA onto the SBR is a core–shell type, emulsion copolymerization. The grafted SBR particles consist of the SBR core and the compatibilized PST/MMA shell. The morphology of the graft
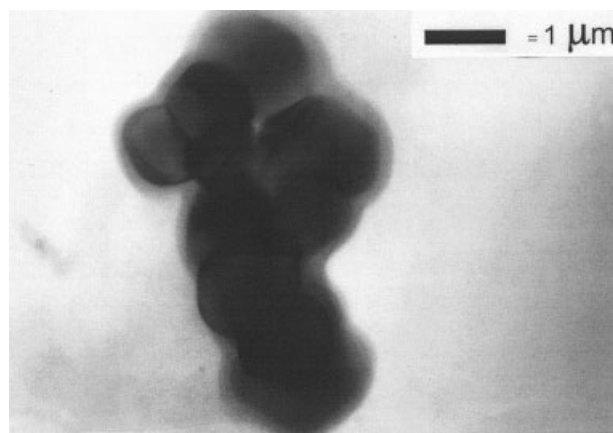

Figure 4 Transmission electron micrographs of graft copolymers of ST and MMA onto SBR (×150,000).

copolymer is shown in Figure 4. The darker areas represent the SBR core regions, while the lighter areas are P(ST/MMA) film as shell. The 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 ST and MMA polymerized in the aqueous phase to form secondary particles, which then flocculate with the SBR seed particles, thus enhancing the encapsulation of the core and then fusing to give a shell layer with a smooth surface.

CONCLUSIONS

The sequence of the main effects of the process variables on grafting efficiency for graft copolymerizing ST and MMA onto SBR latex, by using a 22_{IV}^{6-2} experimental design, in ascending order, is amount of chain-transfer agent > temperature > M/R ratio > amount of emulsifier > initiator > ST/MMA ratio. The two-factor interaction effects are not significantly related to the grafting efficiency. The grafting efficiency appeared to be strongly influenced by the presence of the amount of chain-transfer agent as a result of radical scavengers limiting propagation. The increase in grafting efficiency with increasing temperature and the amount of initiator results in more alkoxy radicals being produced, which brought about an increase in grafting efficiency. The grafting efficiency decreased with increasing M/R ratio. This suggests that the grafting reactions occurred mainly on the surface of the seed latex particles. The grafting efficiency decreased with increasing the amount of emulsifier serving to enhance the particle stability. The ST/MMA ratio did not influence the grafting as a variable over the range investigated. Characterization of the graft copolymers by ^{1}H NMR and TEM indi-

cates the occurrence of grafting on the rubber backbone in the core–shell latex particles.

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