Study on the Effective Process Parameters Influencing Styrene and Acrylonitrile Grafting onto Seeded Polybutadiene Latex

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ABSTRACT: A series of experiments were designed and conducted to determine the significance of process parameters in the grafting of styrene and acrylonitrile onto polybutadiene seeds in a semicontinuous emulsion copolymerization system. The significances of the parameters were obtained by comparing the variance ratios, or F values, with F-distributions. The significance level of each test (α-value) was obtained by variance analysis. The important process parameters in industrial polymerization processes are usually monomer-to-polymer ratio, initiator type and concentration, chain-transfer agent, and reaction temperature. The target responses were final monomer conversion, grafting degree, grafting efficiency, gel percent, and viscosity-average molecular weight of free styrene-acrylonitrile (SAN). The analysis of variance indicated that cumene hydroperoxide as the initiator and reaction temperature had strong effects on the graft structure. Moreover, free SAN molecular weight was significantly affected by the monomer/polymer ratio and cumene hydroperoxide and n-dodecyl mercaptan as chain-transfer agents. The raspberry-like morphology of grafted acrylonitrile-butadiene-styrene (ABS) particles and phase separation within the particles were confirmed by transmission electron microscopy. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 1752–1761, 2011

Key words: emulsion copolymerization; graft ABS; experimental design; graft density; graft efficiency

INTRODUCTION

Acrylonitrile-butadiene-styrene (ABS) is a member of a family of high-impact composite materials based on a thermoplastic matrix and a particulate rubber phase. The most significant advantage gained by the incorporation of the rubber is the transformation of a brittle polymer into a ductile thermoplastic with high impact strength. Three main processes are employed for the manufacture of rubber-reinforced thermoplastics: mechanical blending, bulk copolymerization, and emulsion grafting, with the third method being the most popular synthetic route for ABS. While the mechanical blending technique relies on a degree of compatibility between the rubber and matrix to provide adhesion between the two phases, grafting is necessary in both the bulk copolymerization and emulsion procedures. Grafting may occur by a chain-transfer mechanism. The radical sites may be formed by abstraction of reactive hydrogen atoms by initiator radicals or growing polymer chains, or by addition across the double bond.[1] Gesner provided evidence that grafting occurs primarily by direct interaction with initiator radicals.[2] This was supported by the fact that, for polybutadiene (PB)/styrene-acrylonitrile (SAN) graft terpolymers, the molecular weight of the grafted SAN copolymer was similar to that of the free copolymer, as shown by Dinges and Schuster.[3] Hayes and Futamura suggested a mechanism for the grafting copolymerization reaction. They found that the hydrogen abstraction mechanism does not occur in grafting.[4] Chern and Poehlein proposed that grafting reactions would take place when free radicals attack the carbon–carbon double bonds or when a chain-transfer process occurs for the hydrogen atoms in the allyl position.[5] In emulsion-grafted ABS, the structure depends to a large extent on the particle size and gel structure of the base PB latex. The particle sizes usually ranges from 0.1 to 1 μm, with the majority of particles found at around 0.3 μm.

Danials et al. studied the effects of hydroperoxide initiators on polymerization kinetics and grafting efficiency. They concluded that there were no significant differences between t-butyl and cumene hydroperoxides.[6] They also found that the type of emulsifier, monomer/polymer ratio, initiator amount, reaction temperature, and rubber particle size affect the kinetics and morphology of seeded emulsion copolymerization of styrene and acrylonitrile. As the grafting is an

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interfacial process, the grafting efficiency increased with decreasing particle size of the PB seed latex and with decreasing monomer/polymer ratio.

Okaniwa and Suzuki described the emulsion grafting of styrene and acrylonitrile onto 60–70 wt % PB in the presence or absence of *tert*-dodecanetriol as a chain-transfer agent. The absence of *tert*-dodecanetriol resulted in a reduction in toughness of ABS.[7]

Hu et al. reported the synthesis and characterization of PB-based core/shell latex particles with controlled particle size and crosslinking density of the core.[8] Increasing the initiator concentration favored uniform shell formation. The use of different gel fractions led to similar particle morphologies for the core/shell particles. The shell thickness was controlled by verifying the core polymer/shell monomer weight ratio. The crosslinking density of the core had little effect on the glass transitions of the core and shell polymers. Sohn et al. investigated the influences of initiator, reaction temperature, reaction time, polymer/grafting monomer ratio, and monomer-dropping frequency on the graft copolymerization reaction.[9] When core/shell rubber particles were used in epoxy toughening, the particle dispersion characteristics were affected mainly by the epoxy matrix–shell interaction. They concluded that the solubility parameter of the core/shell rubber particles depends on the AN content of the shell.

Sun et al. studied the effects of cumene hydroperoxide and *tert*-dodecyl mercaptan (TDM) on the grafting properties. Increasing initiator concentration and decreasing chain-transfer agent concentration caused the grafting degree and grafting efficiency of SAN on PB rubber particles to decrease.[10] Xu et al. prepared a series of PB-g-SAN impact modifiers with different ratios of PB to SAN.[11]

Hipps et al. employed an experimental program to determine the feasibility of graft polymerizing styrene and acrylonitrile onto PB seeds in a continuous-emulsion polymerization system. A wide variety of graft morphologies, ranging from perfect core/shell to phase-separated structures, were achievable by varying the reaction conditions. The observed graft structures were strongly affected by the potassium persulfate initiator level. The anchor effect caused by the affinity of polar end groups on the particle surface was evident in the higher initiator levels, which resulted in a more ordered core/shell morphology. Decreasing monomer concentration also contributed to core/shell formation. Higher monomer levels generally resulted in greater phase separation due to the higher chain mobility afforded by lower particle viscosity.[12]

The focus of this work was to investigate the main influences and contributions of the process parameters, such as monomer-to-rubber ratio, amount of initiator and chain-transfer agent used in the secondary polymerization, and polymerization temperature, on

the graft copolymerization of styrene and acrylonitrile in presence of seed PB latex in a semicontinuous system. Several target variables, such as the grafting degree (GD), grafting efficiency (GE), gel percent, and molecular weight of the free SAN were studied.

EXPERIMENTAL

Materials

PB latex (PBL), with 51% solid content, 300-nm average particle size, and 80% gel, commercial-grade graft monomers (styrene (St), > 99.65 wt % purity and acrylonitrile (AN), > 99.6 wt % purity) were supplied by Tabriz Petrochemical Company (TPC, Tabriz, Iran). The redox initiator system consisting of cumene hydroperoxide (CUH), > 81 wt % purity, and a complex catalyst containing tetrasodium pyrophosphate, > 99 wt % purity, ferrous sulfate (TSF), and dextrose (DEX), > 99 wt % purity were utilized as reducing agents. The chain-transfer agent, TDM, > 97.5 wt % purity, the nonionic emulsifier, naphthalene sulfonate soda formaldehyde (NSS), the ionic emulsifier, disproportionated rosin (DPR), the antioxidant for the prevention of rubber-chain degradation, 2,2 methylene-bis(4-methyl-6-tertiary-butyl-phenol), the buffer solution, sodium hydroxide (NaOH), and the graft ABS latex coagulation agent, 1.5% by weight of a sulfuric acid/water solution, were purchased from Tabriz Petrochemical Company (TPC, Tabriz, Iran). The polymerization terminator, hydroquinone 1% water solution, the solvent for determination of molecular weight of free SAN, dimethyl formaldehyde (DMF), the stain for double bond of rubber chains, osmium tetroxide (OsO_4), acetone and cyclohexane were purchased from Merck (Darmstadt, Germany).

Seeded emulsion graft copolymerization

The graft polymerization was conducted in a 1-L four-necked glass reactor, equipped with a double-curved-blade impeller, condenser, and thermometer. A dropping funnel was used for the semibatch process. Reaction temperature was controlled by adjusting the temperature of the surrounding water bath. PBL and other additives, such as a 25% water solution of DPR (10 g) at pH 11, a 21% water solution of NSS (1.65 g), and a 35% water solution of DEX (2 g) were loaded into the reactor. Then CUH, TDM, and 50% of the total grafting monomers were added to the reactor. A 72/28 ratio of styrene to acrylonitrile comonomers was provided to ensure the presence of an excess amount of acrylonitrile relative to the azeotropic ratio of 76/24, to compensate for the loss of acrylonitrile to the aqueous phase due to its water-solubility. Then the system was heated to the required temperature before addition of the complex catalyst. After 1 h, the remaining 50% of

TABLE I
Compositions of Seeded-Emulsion Graft Copolymerization Trials

Factor	A	B	C	D
	Monomer/ PB[a]	CUH (phr)[b]	TDM (phr)[b]	Temp (°C)
Level				
1	40/60	0.2	0.15	60
2	50/50	0.4	0.3	70
3	60/40	0.6	0.45	–
4	70/30	0.8	0.6	–

[a] By weight.
[b] All of the relative proportions are based on solid content weight.

the comonomer, CUH, and TDM mixture was added drop-wise to the preheated reaction mixture over 1 h. After 5 h, 0.5 g of antioxidant was added and mixing continued for about 30 min. The seeded polymerization was performed at the stirring speed of 400 rpm and the desired temperature for 6 h. The product latex was discharged into 90°C distilled water containing 1.5% by weight sulfuric acid and the particulate product precipitated. The product was washed several times with deionized water and dried in a vacuum oven for 48 h. The formulations for the graft polymerizations in the experimental design are included in Table I. Scheme 1 shows the temperature–time program used in seeded graft emulsion copolymerization.

An experimental design was employed to study the main effects of monomer-to-polymer ratio, initiator level, chain-transfer agent, and temperature levels. Table II shows 16 experiments designed by the Taguchi method. The Taguchi statistical method is well-suited to the study of process containing multiple factors that need to be evaluated at several levels. An L_{16} ($3^4 \times 1^2$) orthogonal array of experiments was chosen

TABLE II
### L16 Orthogonal Taguchi Array[a]

	A	B	C	D
Run	Monomer (total)/PB	CUH	TDM	Temp (°C)
1	1	1	1	1
2	1	2	2	1
3	1	3	3	2
4	1	4	4	2
5	2	1	2	2
6	2	2	1	2
7	2	3	4	1
8	2	4	3	1
9	3	1	3	1
10	3	2	4	1
11	3	3	1	2
12	3	4	2	2
13	4	1	4	2
14	4	2	3	2
15	4	3	2	1
16	4	4	1	1

[a] The numbers represent the levels used in Table I.

to reduce the total number of experiments; a fractional factorial design was employed. This L_{16} array can be used, in principle, to examine the effects of three variables at four levels and one variable at two levels on several target variables (conversion and molecular weight of free SAN) in only 16 experiments.[13]

Grafting analysis

To determine final conversion data, ~ 1 g of latex was accurately weighed in an aluminum weighing pan. One drop of hydroquinone solution was added to stop the polymerization. The samples were dried in a vacuum oven at 50°C for at least 24 h and then weighed to determine the solid percentages, corrected
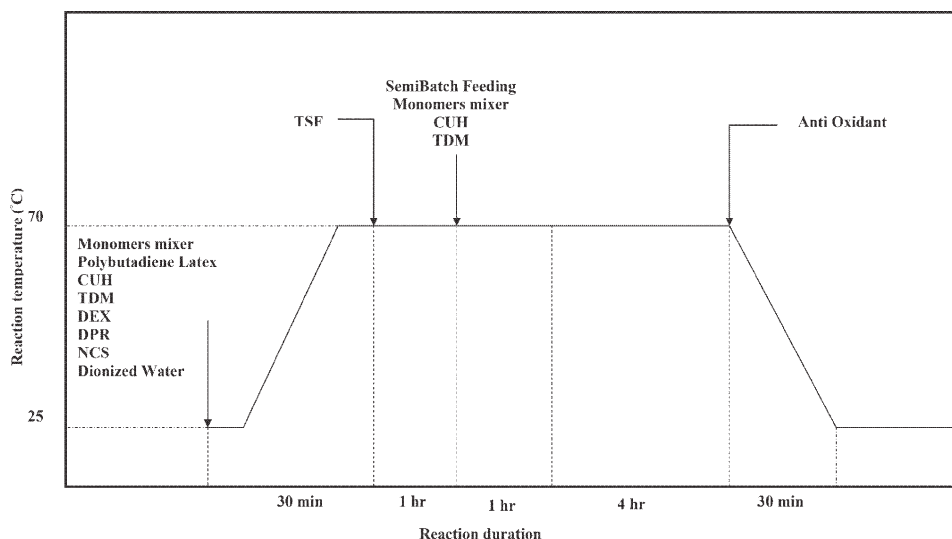
Scheme 1 The temperature-time program used for seeded-emulsion graft copolymerization.

for the fraction of the PB and the emulsifier. To analyze grafting,[14] samples of the coagulated rubber particles were oven-dried at 50°C for at least 24 h. To swell the rubber and dissolve the ungrafted PB, products were immersed in cyclohexane and held at the boiling point for at least 3 h. Then the product gels, containing free SAN and PB-g-SAN, were separated from the cyclohexane solution of PB by filtration through a Buchner funnel and dried for 72 h. To dissolve free SAN, insoluble polymer was added to cold acetone for 3 h and the insoluble polymer/acetone slurry was fully transferred to a plastic centrifuge tube and centrifuged at 10,000 rpm and 0°C for 1 h in a Beckman Avanti J-25 (USA). The acetone containing the free SAN was transferred into glass vials and dried, first at room temperature and then at 100°C for 1 h, to completely evaporate the acetone and then the samples were weighed. The grafting degree, grafting efficiency, and gel percentage were calculated from a material balance between the ungrafted PB and free SAN and PB-g-SAN. Replicate determinations were carried out for each latex recipe, and the grafting analyses were averaged. Scheme 2 shows the existence of various phases such as, PB-g-SAN, free SAN, and ungrafted PB.

The conversion, grafting degree, grafting efficiency, and gel percentage were calculated using the following relationships:

$$\text{Final conversion} = \frac{\text{weight of sythesized SAN}}{\text{weight of initial monomer}} \quad (1)$$

$$\text{Grafting degree} = \frac{\text{weight of grafted SAN}}{\text{weight of polybutadiene}} \quad (2)$$

$$\text{Grafting efficiency} = \frac{\text{weight of grafted SAN}}{\text{weight of synthesized SAN}} \quad (3)$$

$$\text{Gel percent} = \frac{\text{weight of PB} - \text{graft} - \text{SAN}}{\text{weight of graft} - \text{ABS}} \quad (4)$$

The viscosity-average molecular weight M_v, was measured using a Cannon-Fenske viscometer (S-50 model, France) at 30°C (based on ASTM D446); dimethyl formaldehyde was employed as a solvent for SAN. The relationship between viscosity-average molecular weight and intrinsic viscosity is given by the following equation.[15]

$$\eta = 17.2(M_v)^{0.73} \quad (5)$$

Morphology

The sample was prepared by diluting one drop of latex with $\sim$ 200 mL of deionized water. Two drops of 2% osmium tetroxide solution were added to the
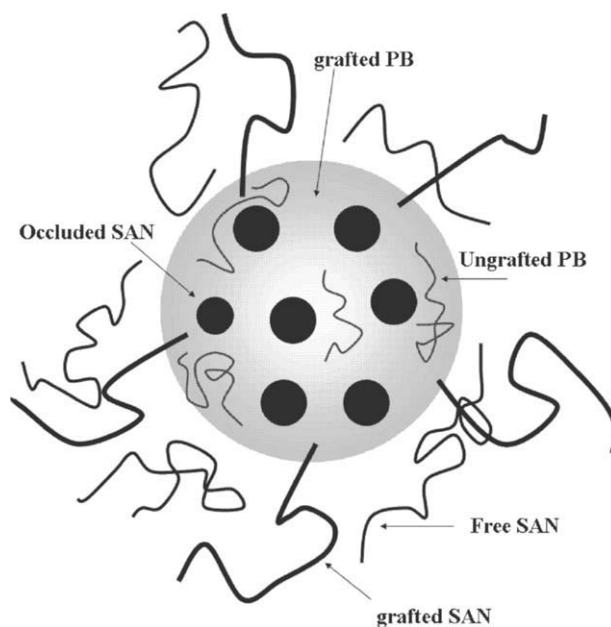
Scheme 2 Existence of various phases in emulsion-graft ABS.

dilute latex and allowed to react for at least 12 h. Osmium tetroxide attacks the residual double bonds in the PB. The carbon-film sides of the TEM grids were covered with the stained latex and allowed to dry in a desiccator overnight. The morphology was examined using a Zeiss CEM 9021(Germany) microscope.

Nuclear magnetic resonance and Fourier-transform infrared spectroscopy

The ^{1}H nuclear magnetic resonance (NMR) spectra were recorded in CDCl$_3$ on a Bruker Spectro Spin-400 MHz spectrometer (Germany).

Fourier-transform infrared (FTIR) spectroscopy was carried out with a Unicam Matson 1000 spectrometer (England), in the wave number range of 400–4000 cm^{-1}.

RESULTS AND DISCUSSION

Grafting copolymerization

The graft-ABS (G-ABS) consists of three phases: free SAN, ungrafted PB (ungr-PB), and PB-g-SAN. Free SAN and ungr-PB are the acetone- and cyclohexane-soluble fractions, respectively. The other fraction is insoluble and is called the gel fraction. To determine the presence of graft copolymer, extracted products were analyzed by FTIR. As shown in Figure 1, the FTIR spectra of the free SAN, ungr-PB, PB-g-SAN, and G-ABS show characteristic peaks attributed to styrene, acrylonitrile, and butadiene. The absorbance bands of butadiene, stretching of the benzene ring of
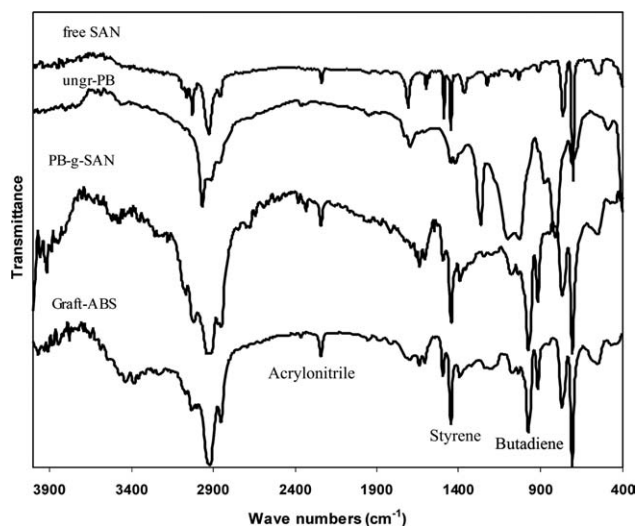
Figure 1 FTIR spectra of G-ABS, PB-*g*-SAN, ungr-PB, and free SAN.

TABLE III
Graft Analysis and Viscosity-Average Molecular Weight of Free SAN for Repared G-ABS Polymers

Run	Final conversion	Grafting degree	Grafting efficiency	Gel percent	M_v (g mole^{-1})
1	36	5	21	41	32,000
2	46	7	23	33	31,000
3	81	26	48	67	40,000
4	90	25	42	63	35,000
5	57	23	42	54	34,000
6	68	29	43	57	32,000
7	61	10	15	31	30,000
8	77	23	30	39	39,000
9	38	16	25	44	32,000
10	43	17	27	43	30,000
11	86	60	47	56	54,000
12	97	36	25	41	40,000
13	34	9	11	31	33,000
14	75	21	12	34	43,000
15	74	52	30	31	45,000
16	93	77	36	45	67,000

styrene, and nitrile-bond stretching in acrylonitrile appear at about 970, 1493, and 2236 cm^{-1}, respectively. These results confirmed that the PB was grafted with the SAN copolymer and the separation was done successfully.

Figure 2 illustrates the NMR spectrum of the free SAN fraction of the G-ABS that was soluble in acetone. The peaks at 1–3 ppm are assigned to the aliphatic proton content in copolymer chain. The signal at 6–7 ppm is attributed to the phenyl group of styrene. Using the characteristic peaks attributable to each group, the styrene-to-acrylonitrile ratio was determined to be about 70/30 wt/wt.

Grafting analysis

The main effects of the process parameters (monomer-to-polymer ratio, initiator level, chain-transfer agent, and temperature) on target variables were investigated. The target variables were final conversion, grafting degree, grafting efficiency, and molecular weight of free SAN.

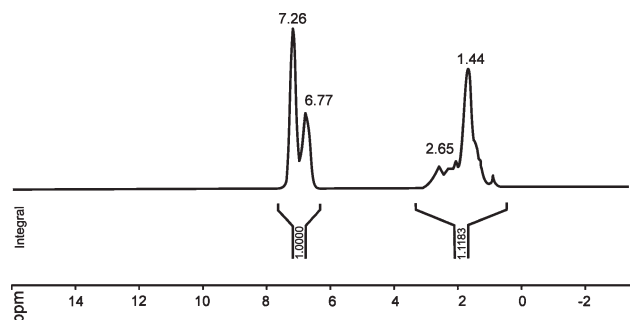The grafting efficiency (GE) and the grafting degree (GD) were calculated from the gel percentages and

conversion data for each experiment, which are given in Table III. A statistical analysis of the results was carried out to identify the effect of individual variables. Using information from the *F*-distribution table, the probability α value, often called the significance level of the test, can be obtained.[15] As shown in Table IV, the statistical analysis of the results shows that, within the selected range of variables, CUH as the initiator and temperature have the greatest effects on monomer conversion and grafting. The equations used for the analysis of variance (ANOVA) were recently presented by Hadi and Babaluo.[16]

The other target variable, viscosity-average molecular weight, is included in Table III. The results of ANOVA for this target variable were different from those for final conversion. The effect of each process parameter on the viscosity-average molecular weight was determined. As shown in Table V, the monomer-to-polymer ratio, initiator, and chain-transfer agent were significant parameters effecting viscosity-average molecular weight, but reaction temperature is not significant. The substantiations of the main effects on this target response are discussed in the following sections.

Effect of monomer-to-polymer ratio

The effect of the monomer-to-polymer ratio on the conversion is shown in Figure 3(a). The conversion increased slightly with increasing monomer-to-polymer ratio. Increasing the initial monomer concentration results in increase in monomer concentration at reaction loci inside seeded particles. This enhances diffusion of monomer and macroradicals through the seeded particles, and therefore growth reactions become more probable due to reduced viscosity. Further increasing the conversion causes the shell

Figure 2 Proton NMR spectrum of free SAN.

TABLE IV
Analysis of Variance (ANOVA) for Final Conversion

Factor	Freedom degree	Sum of square	Variance	Variance ratio	α value	Significance level
Monomer/polymer	3	0.006258	0.002086	0.39	>0.1	No significant
Initiator	3	0.522501	0.174167	39.36	<0.001	Highly significant
Chain transfer agent	3	0.042645	0.014215	2.64	0.01<α<0.1	Significant
Temperature	1	0.093303	0.093302	17.34	<0.001	Highly significant
Error	5	0.026911	0.005382	–	–	–
Total	15	0.691162	–	–	–	–

thickness and the local viscosity at grafting loci to increase, decreasing diffusion of monomeric radicals into the seeded particles. There are two possible anomalous occurrences that may cause the attenuation of the contribution of this parameter in the system.

With an increasing monomer-to-polymer ratio, secondary nucleation may occur because of the presence of a small amount of anionic emulsifier. This results in an increased polymerization rate and increased conversion. On the other hand, since the main loci of reaction are the seeded particles, increasing the monomer/polymer ratio decreases the number of seeded particles, which results in a decrease in the graft polymerization rate. This decrease in polymerization rate balances the increased rate caused by secondary particle formation.

The molecular weight of the resulting polymer also plays an important role in polymer reorganization toward the final graft structure. Chains with lower molecular weights have higher diffusivities. In Figure 3(a), it is observed that increasing the monomer-to-polymer ratio caused an increase in molecular weight of free SAN copolymer. The classical Smith-Ewart theory postulates that the rate of polymerization per particle depends on the monomer concentration within the particle, and the molecular weight of the growing polymer depends in turn on the rate of polymerization per particle, which accelerates the Trommsdorff gel effect in each particle. In fact, the Trommsdorff gel effect, caused by higher viscosities at the reaction sites at higher conversions, restricts chain mobility in seed particles. It is thought that these two effects increase the significance of the monomer-to-polymer ratio effects.

Figure 3(b) shows the effect of monomer-to-polymer ratio on GD and GE. Increasing the monomer-to-polymer ratio is seen to be the most suitable method for changing shell thickness. The GE values decrease with increasing monomer-to-polymer ratio. This result may be explained by the lower monomer amount within the particles and the lower probability for hydrogen abstraction than for propagation. On the other hand, the decreasing GE can also be explained by secondary nucleation; this means that secondary nucleation produces free SAN rather than grafted SAN. Merkel et al. hypothesized that grafting is a surface-controlled process and suggested that this process involves initiation either in the aqueous phase or, more likely, in the adsorbed emulsifier layer, followed by capture of the growing radicals by existing monomer-swollen particles.[17] As grafting proceeds and a certain shell thickness is reached, formation of the PB-g-SAN terpolymer becomes less probable due to the reduced availability of PB. Also, systems with lower monomer-to-rubber ratios have higher viscosities at the reaction site. This high viscosity restricts the mobility of both free radicals and monomers, increasing the probability for chain transfer to the PB. GD increases with increasing monomer-to-polymer ratio as a result of increasing monomer concentration at the reaction loci inside the particles and the proportion of monomer to polymer.[6,9]

Effect of initiator concentration

The effect of initiator on final conversion is shown in Figure 4(a). With an increase of initiator concentration, the final conversion increased. This is due to the increase in radical concentration, which causes

TABLE V
Analysis of Variance (ANOVA) for Viscosity-Average Molecular Weight

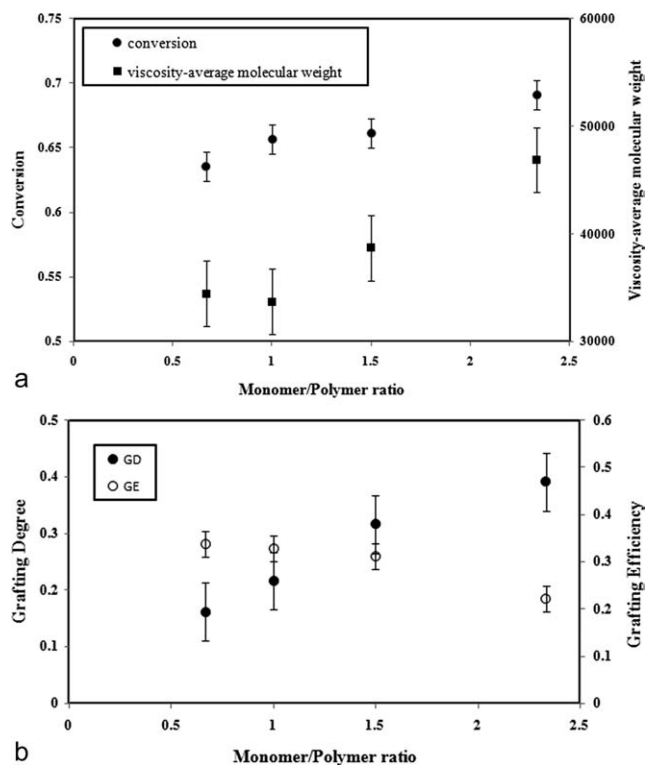| Factor	Freedom degree	Sum of square	Variance	Variance ratio	α value	Significance level
Monomer/polymer	3	17.05	5.68	4.41	0.01<α<0.1	Significant
Initiator	3	18.97	6.32	4.91	0.01<α<0.1	Significant
Chain transfer agent	3	15.92	5.31	4.11	0.01<α<0.1	Significant
Temperature	1	0.43	0.43	0.33	0.1<	No significant
Error	5	6.44	1.29			
Total	15	58.81	3.92			

Figure 3 Effect of monomer-to-polymer ratio on (a) final conversion and the molecular weight of free SAN, and (b) GD and GE.

the rate of polymerization and monomer consumption to increase. It should be noted that initiator concentration showed the strongest influence on seeded-grafting copolymerization.

The influence of radical initiator concentration on the molecular weight of free SAN copolymer is shown in Figure 4(a). The molecular weight of free SAN was also positively correlated to the amount of the initiator charged to the reactor. This trend can be explained by the fact that the seed latex particles of PB are crosslinked prior to and during polymerization of St and AN within particles during reaction, which is enhanced by increasing the initiator concentration, thus resulting in an increase in viscosity at reaction loci. The motion of macroradicals within particles is affected by increased viscosity, thus, occurrence of the Trommsdorff gel effect in rubber particles becomes likely when increasing the initiator concentration. The Trommsdorff gel effect increases the proportion of the propagation rate with respect to the termination rate.

Figure 4(b) shows the proportion of the SAN copolymer grafted onto the crosslinked rubber matrix (GD) and the grafted portion of total synthesized SAN (GE) versus the concentration of initiator used in the seeded emulsion polymerization. These results indicate that the GE and GD both increased as the concentration of initiator increased, up to 0.6 phr, after which point both GE and GD decreased with a

further increase in the initiator concentration. This may result from the instantaneous formation of higher amounts of radicals. These radicals might act as radical scavengers, resulting in a decrease in the initiator concentration.[18] This would result in a lower initiator efficiency that, however, fails to produce both the resultant ungrafted and grafted copolymers. The excess free polymer radicals may react with each other to form free copolymers rather than grafting onto the PB chain, and decrease the chain length of the grafts. Therefore, the production of free polymer would be encouraged more at higher initiator concentrations. In contrast, the rate of chain transfer of free polymer radicals to the PB rubber backbone may be less than the rate of termination of free polymer radicals, supporting the termination process of copolymers over the chain-transfer process.

Effect of chain-transfer agent concentration

The monomer conversion was decreased by increasing the chain-transfer agent concentration, as shown in Figure 5(a). Increasing the chain-transfer agent increases the rate of reaction of monomer radicals with chain-transfer agent molecules present inside particle. Therefore the rate of radical entry into the rubber particles decreases, which causes a decrease
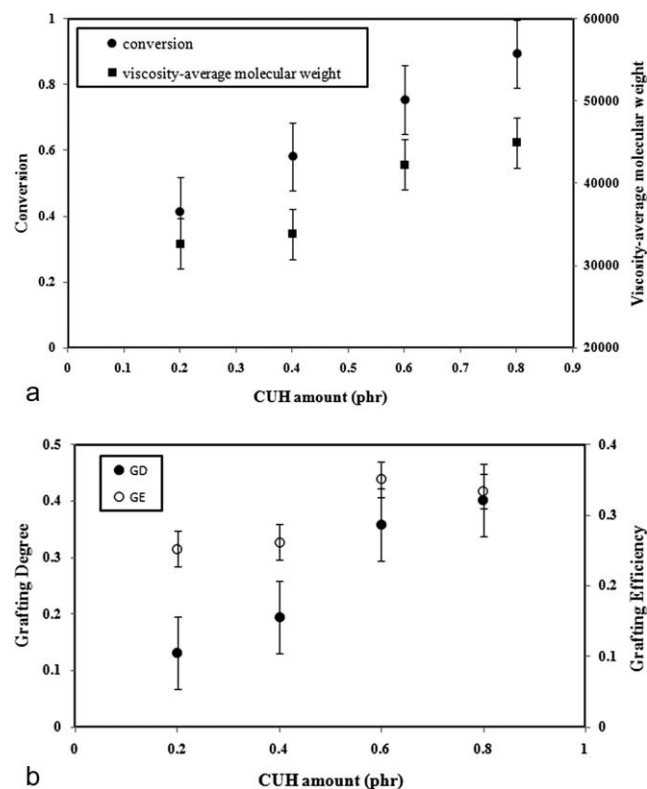

Figure 4 Effect of initiator level on (a) final conversion and the molecular weight of free SAN copolymer, and (b) GD and GE.
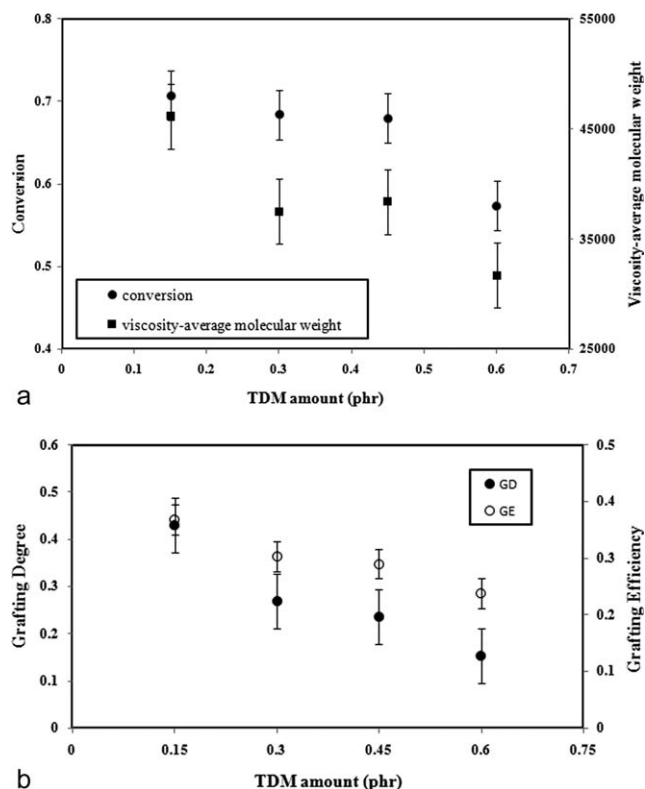
Figure 5 Effect of chain-transfer agent level on (a) final conversion and the molecular weight of free SAN copolymer, and (b) GD and GE.

in the radical concentration and polymerization rate in particles.

The effect of the amount of the chain-transfer agent *n*-dodecyl mercaptan on the molecular weight of free SAN is shown in Figure 5(a). Aliphatic mercaptans are widely used in polymerization to reduce the polymer chain length to within the range required for the growth rate of polymer particles in emulsion polymerization. The percent of the graft chains could be controlled by use of chain-transfer agents. Increasing the chain-transfer agent loading can progressively decrease the chain length per particle.

Figure 5(b) displays the influence of chain-transfer agent concentration on the GD and GE. As the amount of chain-transfer agent increased, the grafting degree and grafting efficiency of SAN onto PB rubber particles decreased. The increase of chain-transfer agent content in the reactive system causes propagating free macroradicals to transfer to chain-transfer agent molecules, which induces the decrease in grafting degree and grafting efficiency of SAN onto PB particles. As previously indicated, this parameter has a significant effect on a grafting system. As the rate of chain-transfer reaction of free radicals to mercaptan is increased, a decrease occurs in macroradical formation, thereby decreasing the grafting and free copolymerization. When the concentration

of chain-transfer agent was increased, the percentage of graft copolymers and free copolymers was shifted to a lower level.

Effect of temperature

The rate of decomposition of the initiator depends on the reaction temperature. With an increase in reaction temperature, more alkoxy radicals are produced. The effect of initiator concentration on final conversion is shown in Figure 6(a). An increase in the amount of alkoxy radicals led to a higher copolymerization rate and final conversion.

As the decomposition energy of the redox initiator system is rather low, the graft polymerization occurs at low temperatures. Thus, it appears that chain growth is independent of temperature. The molecular weight of free SAN increased slightly with the temperature, as shown in Figure 6(a). The results of the ANOVA, included in Table V, show that the effect of temperature on molecular weight is not significant. Also, the higher temperatures will give an increase in penetration of free radicals from the aqueous phase. This should promote a large number of graft sites at the expense of shorter chains. Despite this fact, the rate of chain growth increased at higher temperatures, while for viscosity it had the opposite effect. It is thought that increasing
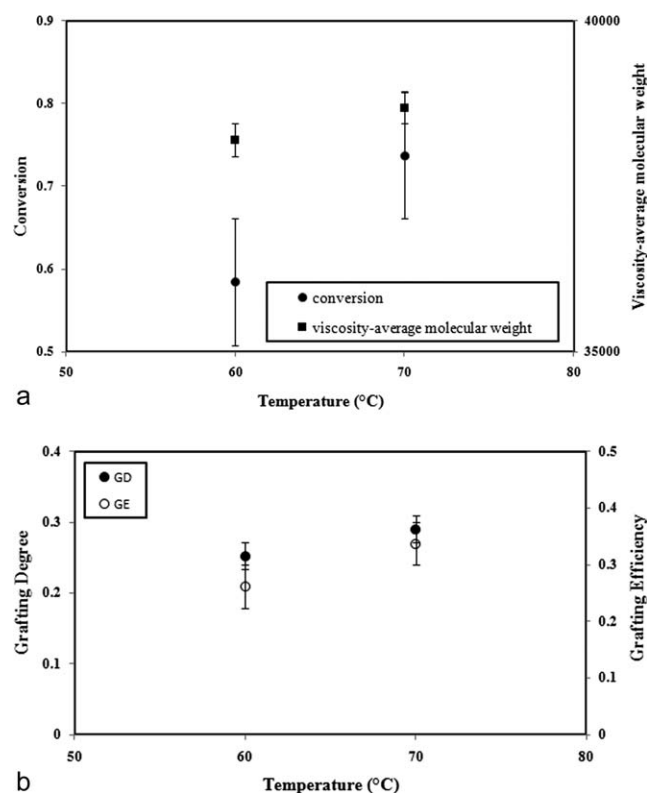

Figure 6 Effect of temperature level on (a) final conversion and the molecular weight of free SAN copolymer, and (b) GD and GE.
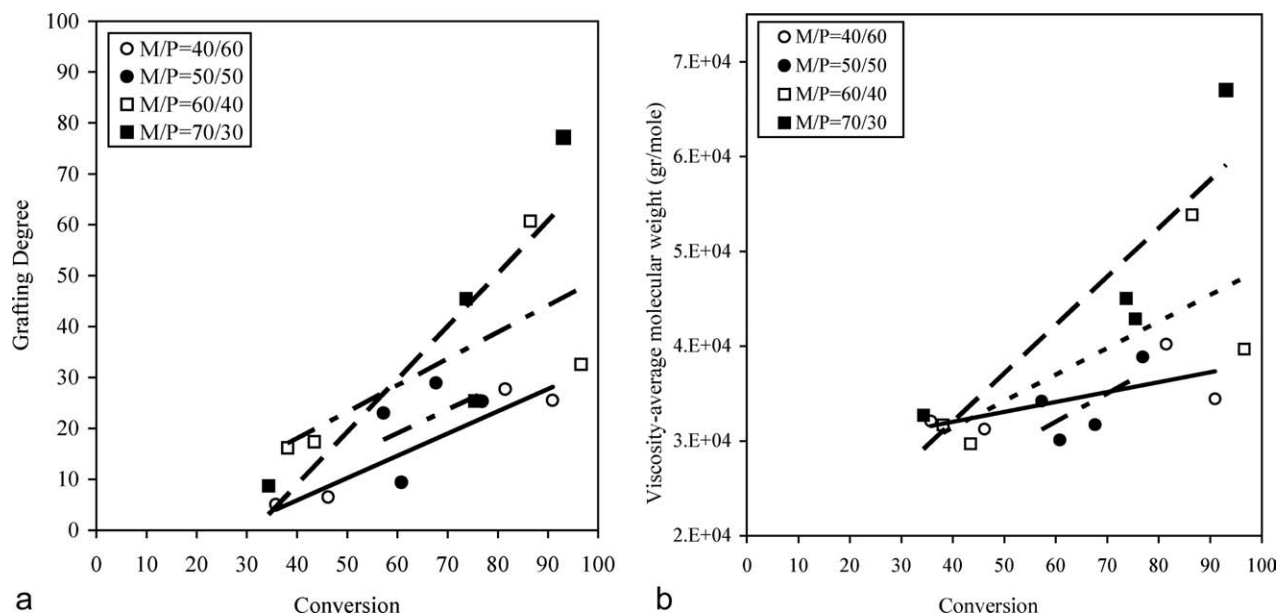
Figure 7 (a) Grafting degree, and (b) molecular weight of free SAN versus final conversion.

temperature lowers the viscosity and provides higher penetration of monomer molecules through the crosslinked PB particles, which enhances the diffusion of macroradicals into the particles and increases termination of macroradicals.

The grafting efficiency and degree of grafting increased as the polymerization temperature increased, as shown in Figure 6(b). Increasing the temperature increased the rate of initiation and produced more alkoxy radicals. On the other hand, the transfer of alkoxy radicals to the rubber chains produced graft polymers. This would increase the probability of chain transfer of monomeric and polymeric radials to the PB backbone, so initiating more graft sites, in turn leading to higher GE and GD values.

In Figure 7(a), the dependencies of GD on conversion are shown for different monomer-to-polymer ratios. A steady increase of GD was observed over the whole final conversion range. There is significant scatter in the data, because the final conversion is a measured response and not a true design factor. An increase in the slope of grafting degree versus conversion is clearly observed, which could be due to an increase in the grafting rate along with the polymerization rate. It must be noted that the experiments listed under each monomer-to-polymer ratio level did not have the same reaction compositions and are thus difficult to compare.

As observed in Figure 7(b), the positive correlation between total conversion and free SAN molecular
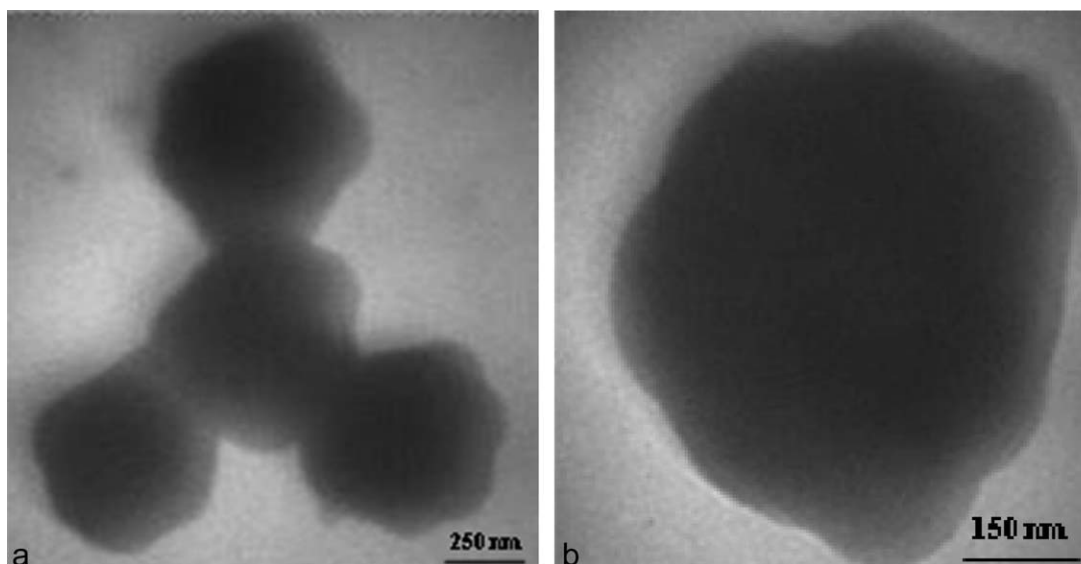

Figure 8 Transmission electron micrographs of G-ABS particles with different magnifications.

weight is manifested from the trends. The effects of increased monomer-to-polymer ratio levels comply with the expectation that the gel effect phenomenon is significant, particularly at high monomer conversion. According to the results obtained, it is obvious that ABS16 has the highest molecular weight and a relatively high final conversion (94%).

Morphology of G-ABS

Controlling the particle morphology in emulsion graft copolymerization processes is important for optimizing the properties of a latex system and those of the resulting polymer products for a given application. The final morphology in polymer micro-particles involves the movement of at least two molecular species under the influence of driving forces towards the formation of new interfaces (a change of the free energy), leading to rearrangement through phase separation.[19] The raspberry-like morphology of composite latex particles of g-ABS is shown in Figure 8.

CONCLUSIONS

In this study, an experimental design was used to establish important process parameters in grafting styrene and acrylonitrile onto PB seeds. It was found that the ANOVA method was able to determine the most effective process parameters with regard to their influence on graft microstructure. The main effects of each parameter, such as monomer-to-polymer ratio, initiator level, chain-transfer agent level, and temperature, were studied. The monomer-to-polymer ratio had no significant effect on conversion or grafting microstructure, but its effect on the molecular weight of free SAN was significant. This inconsistency might be due to viscosity effects at reaction loci. The conversion and molecular weight of free SAN increased with increasing initiator concentration, suggesting a large amount of free radicals, thus increasing the polymerization rate and the probability of a Trommsdorff gel effect. It was found that grafting yield peaked at 0.6 phr of initiator. This can be attributed to an increased recombination rate of higher free radicals within the particles, therefore decreasing the available grafting sites on the PB backbone. The target responses were significantly affected by initiator changes.

It can be concluded that increasing chain-transfer agent concentrations decreases the monomeric radi-

cal concentration and the initiation rate, and so decreases the conversion. When the amount of chain-transfer agent added to a system is increased, macroradicals react with chain-transfer agent molecules and produce shorter chains. On the other hand, radicals produced on PB also react with these molecules, which results in a higher grafting yield. Furthermore, this parameter had a significant effect on conversion and the molecular weight of free SAN. The experimental results revealed that conversion and grafting yield were positively correlated to the reaction temperature, confirming the increase in grafting sites and polymerization rate. The ANOVA performed indicates that these parameters were considerably affected by temperature. It was found that both GD and molecular weight increased with final conversion. This dependency was more pronounced at higher monomer-to-polymer ratios.

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