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Synthesis of Poly (Butadiene –g–Styrene) Core-Shell Latex for Use in Cement Modifying

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Abstract. Polybutadiene-graft –polystyrene (PB-g -PS) latex with different ratios of polybutadiene to polystyrene were prepared via emulsion graft copolymerization method through grafting styrene onto polybutadiene latex using a redox initiator system. The PB macroradicals reacted with styrene to form graft copolymers. The effect of initiator concentration, reaction temperature, grafting monomer /polybutadiene weight ratios, and monomer dropping time on the conversion, grafting efficiency, degree of grafting, and mean particle diameter of graft copolymerization reaction were investigated. The grafting efficiency of PB-g-PS was determined by a solvent-extraction technique. Fourier transform infrared spectroscopy and nuclear magnetic resonance technique were used to confirm structure of the synthesized copolymers. Transmission electron micrographs verified that the synthesized latex particles had a core –shell structure, which can be incorporated into cement as modifier.

1. Introduction

The properties of the core-shell structure polymers, such as particle size, morphology, composition, and crosslinking density of core, can be controlled separately during latex particle preparation by emulsion polymerization [1-3]. Polymers with a soft core and a hard shell have been used as impact modifier. To toughen plastics and thermosetting resins. It is well know that the cement also has the same weakness as plastics and thermosetting resins. Which shows lower tensile strength, bending strength flexible modulus and impact toughness. Core-shell structured polymer latex particles have lots of excellent performances than the irregular copolymer because of the existence of grafting between the core and shell, it can marked improve bearing water, bearing abrade, bearing climate, resistance dirt ,radiation protection , tensile strength and viscosity property of polymer, and can decrease temperature polymer becoming film, performance of becoming film, stability and mechanic properties are better. Therefore, the consideration is that core-shell structured polymer latex was incorporated into cement as the modifier of cement because of above reasons. Performance of the latex mainly depends on the process parameters used during emulsion polymerization. Thiraphattaraphun et al [4] studied the grafting of MMA monomer onto natural rubber using potassium persulfate as an initiator. The effects of the initiator concentration, reaction temperature, monomer concentration, and reaction time on the monomer conversion and grafting efficiency were investigated. Merkel et al^[5] studied the grafting of MMA onto polybutadiene latex by seeded emulsion polymerization method and the influence of the initiator concentration used in the secondary polymerization, monomer-to-polymer weight ratio, the specific surface area of the seed latex, and the degree of conversion onto core-shell grafting copolymerization reaction have been investigated. Kochthongrasamee et al [6] studied the effect of the three types of redox initiators on the grafting extend of MMA on natural rubber. Kangwansupamonkon et al [7] investigated the modification of NR by grafting with hydrophilic vinyl



monomers using three redox initiation systems. The influence of the grafting factors on the graft copolymerization was investigated. Sungkyun et al [8] investigated the effect of the main process parameters, such as initiator, reaction temperature, grafting monomer/polybutadiene ratio and monomer dropping time on graft polymerization reaction. In the present work, PB - g - PS core-shell structured polymer latex was synthesized by emulsion graft polymerization. The influence of various process parameters, such as initiator content, reaction temperature, core-shell ratio (w/w) and monomer dropping time, were investigated. The PB - g - PS core-shell structured polymer latex were confirmed by FTIR and ^1H -NMR analysis. The morphology of the resulting polymer latex was investigated by TEM. The basic data is necessary to develop appropriate latex as cement modifier.

2. Experimental

2.1. Materials

Polybutadiene latex was kindly supplied by Jilin Chemical Company, china. The effective diameter of PB latex is about 300nm, the polydispersity is 0.056, and gel content is 57%. Styrene was washed with 5% sodium hydroxide solution to remove the inhibitor. Cumene hydro-peroxide (CHP, Aldrich chemical), iron (II) sulfate (Aldrich Chemical), dextrose (DX, supplied by Beihai Starch Factory, China), sodium pyrophosphate (SPP, supplied by tianjin chemistry factory, china) were used as initiators.

2.2. Emulsion Grafting Copolymerization

Graft copolymers of styrene onto polybutadiene latex were prepared by emulsion graft copolymerization method. All the grafting experiments were carried out using a 2-L glass reactor equipped with a reflux condenser. (Table 1 shows the graft copolymerization recipes). Firstly, deionized water, polybutadiene latex, dextrose, tetrasodium pyrophosphate were charged into reactor, subsequently, ferrous sulfate was added. The reaction temperature was maintained at 50-80°C. The reaction medium was stirred at 250 rpm, and nitrogen gas was purged into reactor through the reaction. The solution of CHP and St was added in continuous feed manner to the reaction system, and then reaction was carried out for 2h. After 10g antioxidant solution was added, reactor temperature was decreased to 60°C, and the reaction was ended.

Table 1. Recipe for emulsion grafting polymerization used in the preparation of PB-g-PS

Ingredient	PB-g-PS
Deionized Water	1000mL
CHP	1.5mL
SPP	2.5g
DX	3.5g
FeSO ₄	0.05g
KOH	0.5g
Polybutadiene	(1000-100X)g
Styrene	100X(X=1,2,3,4,5,6,7)g

2.3. Conversion

The PB-g-PS latex was cast in an aluminum dish in a vacuum oven at 65°C, leached in distilled water, and dried again in vacuum oven. The degree of conversion was determined by the percentage increase in weight of PB-g-PS latex.

2.4. Grafting Properties

The grafting properties were determined by extracting the ungrafted or free Ps of the dried 0.5g PB-g-PS copolymer by 5ml methyl ethyl ketone (a solvent for PS but not for PB). After the methyl ethyl ketone solution of dried PB-g-PS powdery polymer particles were shaken for 24h at room temperature, the solutions were centrifuged at 10,000 rpm in a GL- 21M centrifugal machine for 40min with a

temperature of -5°C . The grafting efficiency and degree of grafting were calculated from the following equation [6, 9-11]:

$$\text{Grafting efficiency (\%)} = \frac{\text{weight of monomers grafted}}{\text{weight of monomers polymerized}} \times 100 \quad (1)$$

$$\text{Degree of grafting (\%)} = \frac{\text{weight of shell polymer grafted to core}}{\text{weight of core}} \times 100 \quad (2)$$

2.5. Characterization of PB-g-PS Latex

After the solvent extraction of PB-g-PS powder, it was analyzed for its functional groups by FTIR and ^1H -NMR techniques.

2.5.1. Fourier Transform Infrared Spectroscopy (FTIR). Functional groups of the PB and PB-g-PS were determined by Fourier transform infrared spectroscopy (FTS-BS). The FTIR spectra of the PB and PB-g-PS powder are presented in Figure 1.

2.5.2. Nuclear Magnetic Resonance Spectroscopy (^1H -NMR). The PB and PB-g-PS powdery was swollen with CDCl_3 , and measured by NMR spectrometers (Model UV-400). The ^1H -NMR chemical shifts are presented in Figure 2.

2.6. Morphology of the PB and PB-g-PS Latex Particles

PB and PB-g-PS latex were diluted 400 times with distilled water, then 1-2 drops of 2% aqueous solution of osmium tetroxide was used to stain the latex particles for 24h, and the diluted latex was placed on a carbon-coated Formvar film. The osmium tetroxide solution was used to stain the PB domain but the PS domain was not stained. The morphology of the PB and PB-g-PS latex particles was observed using transmission electron microscopy (Model Japan TEM-2000 EXL at 120KV).

2.7. Particle Size Analysis

The mean diameter and distribution of the particle diameter of polymer latex were important parameters. The particle sizes of synthesized polymers were analyzed by Brookhaven laser particle size analyzer (Model 90 PLUS).

3. Result and Discussions

3.1. FTIR Analysis

FTIR spectra of the PB and PB-g-PS were showed in Figure 1. Figure 1(a) is characterized by the presence of absorption peaks attributed to the unsaturated carbon-carbon double bonds associated with polybutadiene molecules as follows: Absorption peaks at 3070cm^{-1} corresponding C-H stretching vibration, 1640cm^{-1} for $\text{C}=\text{C}$ stretching vibration, 1420cm^{-1} and 920cm^{-1} for C-H bend vibration. The spectra of PB-g-PS (Figure 1 (b)-(e)) shows not only the characteristic polybutadiene peaks, but also additional absorption peaks for polystyrene. The aromatic structure of PS is pronounced clearly with the absorption peak at 3030cm^{-1} corresponding to aromatic C-H stretching vibration. The absorption peaks at 1600cm^{-1} is corresponding to aromatic backbone vibration, 760cm^{-1} and 694cm^{-1} are corresponding to aromatic C-H bend vibration, and a group of absorption peaks at 1600cm^{-1} – 2000cm^{-1} (1940cm^{-1} , 1870cm^{-1} , 1800cm^{-1} , 1740cm^{-1} , 1640cm^{-1}) verifies the single substitution of the benzene ring. Furthermore, the intensity of absorption peaks increases with the increases of M/P ratio, FTIR analysis shows that PB-g-PS copolymers contain PS chains.

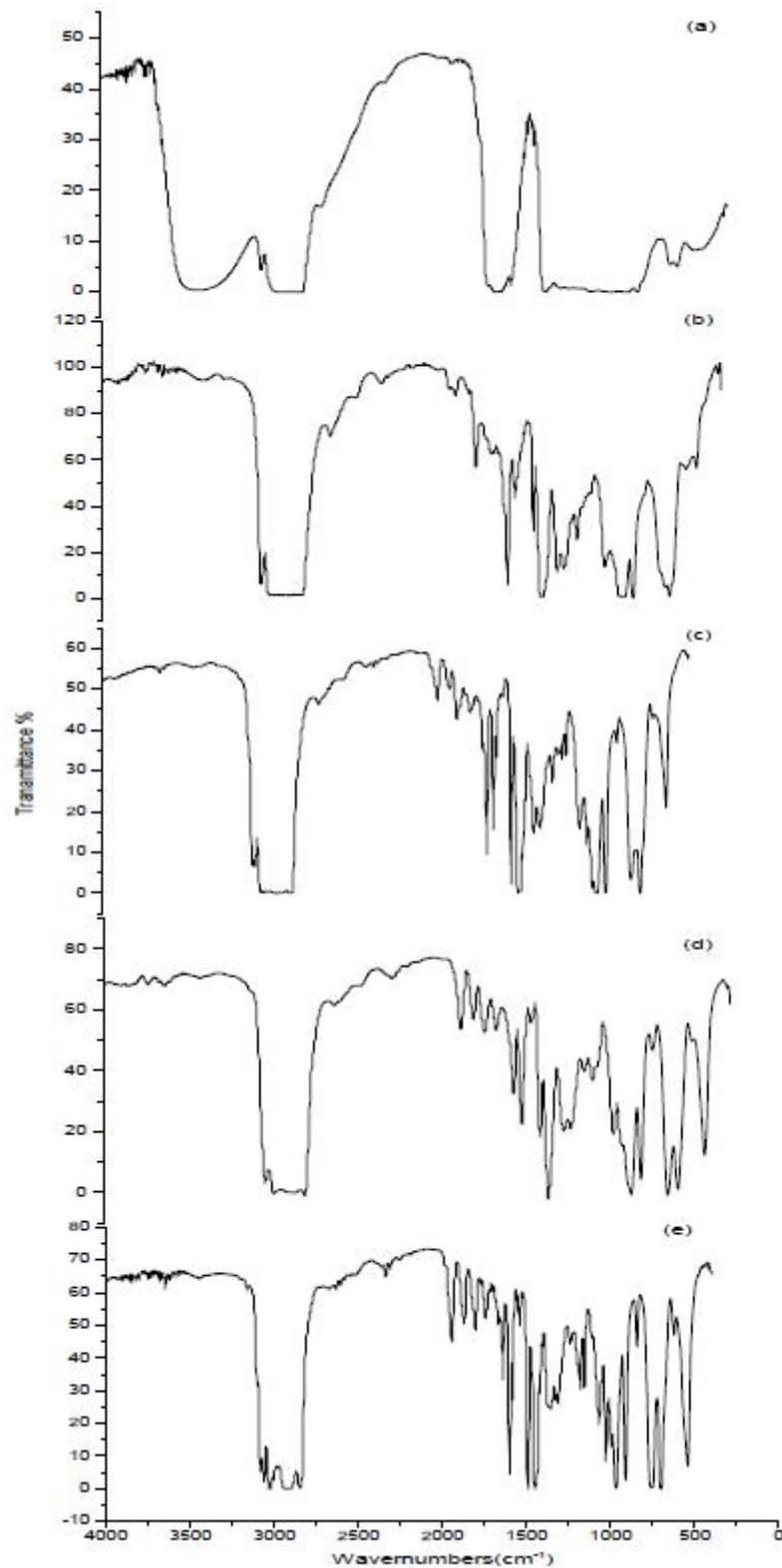


Figure 1. The FTIR spectra of (a) PB; (b) PB-g-PS (90/10 w/w); (c) PB-g-PS (70/30 w/w); (d) PB-g-PS (50/50 w/w); (e) PB-g-PS (30/70 w/w)

3.2. ^1H -NMR Analysis

The PB and PB-g-PS characterized with ^1H NMR is showed in Figure 2. Figure 2(a) is the ^1H -NMR spectra of PB which exhibits the signal of $\text{CH}=\text{CH}$ and $\text{CH}_2=\text{CH}$ protons of polybutadiene at about 5.41ppm and 4.96ppm, respectively, and the signal of aliphatic protons of the alkenes can be found at about 1-4ppm. Figure 2(b)-(e) are the ^1H -NMR spectra of PB-g-PS. the signal of $\text{CH}=\text{CH}$ and $\text{CH}_2=\text{CH}$ protons of polybutadiene were decreased along with the increase of M/P, Furthermore, the signal of aromatic protons at about 7.0ppm and CH_2 protons of polystyrene at about 1.56ppm increase with M/P ratio. This confirms the occurrence of grafting polymerization of styrene onto polybutadiene. The analytic results of the ^1H NMR are consistent with the FTIR results.

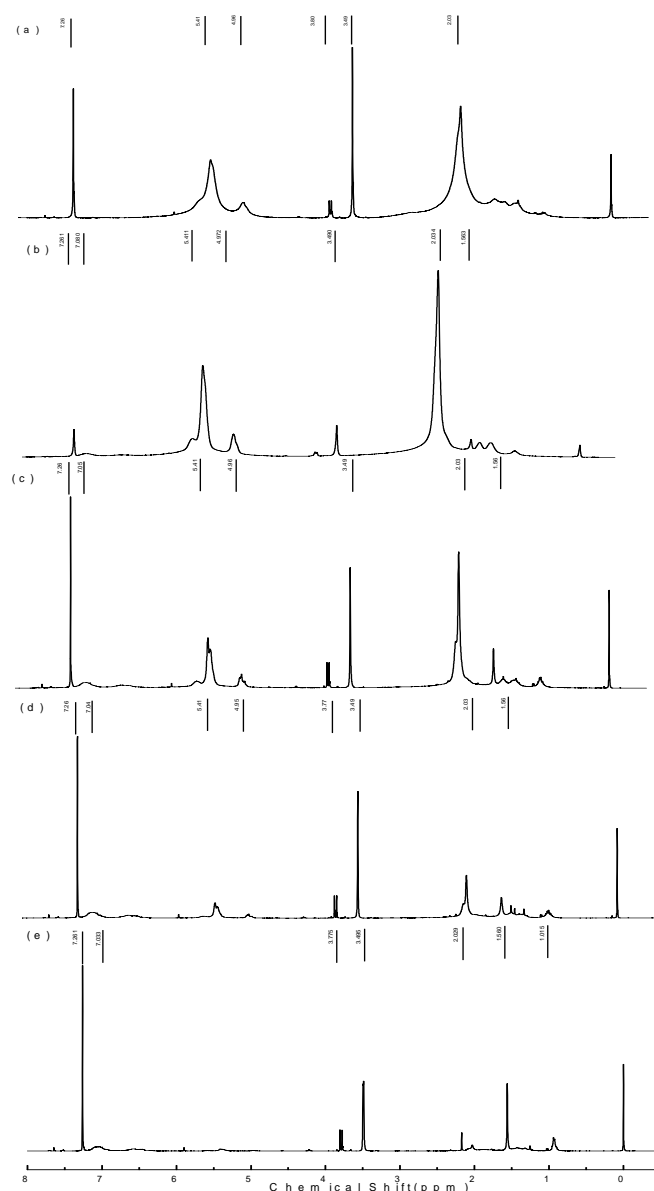


Figure 2. The ^1H -NMR spectra of (a) PB; (b) PB-g-PS (90/10 w/w); (c) PB-g-PS (70/30 w/w); (d) PB-g-PS (50/50 w/w); (e) PB-g-PS (30/70 w/w)

3.3. Reaction Mechanism of Emulsion Graft Copolymerization

The preparation of PB latex adopts batch emulsion polymerization method. Reaction mechanism accords with the Harkins [12-15] four stage models of the batch emulsion polymerization. PB latex does not contain butadiene monomers, micelles and initiators. Emulsifier has not been added to the system when the reaction beginning. The monomer was added in continuous feed manners to the reaction system. Monomer was scattered to liquid drop because of stirring and emulsifier in water was adsorbed to its surface to form monomer droplet. The number of monomer droplet was less than the batch process. After initiator addition, radicals mainly produce in water, and are absorbed to surface of latex particle, according to the Chern and Poehlein [16]. The primary radicals mainly attack double bond of polybutadiene, producing graft site in order to make the St grafting on the PB. Outside of the latex particle, some of the radicals may also react with monomer in water to make “ungrafted” homopolymers. Along with reaction process, the monomer was consumed gradually. The monomer was added in continuous feed manners to the reaction system producing new monomer droplet as complement, up to the monomer dropping was over. Monomer droplet decrease gradually until disappear. The emulsifier has not been added to the system when the reaction began. Along with grafting, more monomers are grafted to latex particle when core/shell ratio increases. Seed latex particle volume much bigger and its surface area also became bigger which needed to adsorb emulsifier molecule from water in order to cover new surface. Leading to lower emulsifier content, even some latex particle surfaces could not be covered completely, resulting in the increase of surface free energy of the latex system. So the latex stability decreased, resulting in latex breaking. For the sake of raising latex stability, and not producing new micelles, the emulsifier should be added to reaction system after monomer dropping was exhausted.

The polymer concentration is higher and higher in the evening of grafting reaction and the viscosity is higher and higher in the interior. Macromolecular tangled each other and the radicals' activity felled. The resistance of spreading together and terminating of two radicals is very big. The chain termination velocity descends and average life of radicals prolongs, resulting in reaction velocity more and more quickly until reaction equilibrium.

3.4. Effect of Reaction Conditions on Conversion

The effects of initiator concentration, monomer/Polymer weight ratio, reaction temperature and monomer dropping time on graft polymerization were investigated.

Table 2. Graft Polymerization Condition of Poly (butadiene-g-styrene)

Condition	Description
CHP amount (parts)	0.3, 0.6, 0.9, 1.2
Monomer/Polymer weight ratio	10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30
Reaction temperature (°C)	50, 60, 70, 80
Monomer dropping time (min)	60, 120, 180, 240

3.4.1. The Effects of the Initiator Concentration.

The effects initiator content on styrene grafted polybutadiene latex was investigated for the grafting characteristics of PS grafted PB over a range of approximately 0.3 to 1.2 phr. The optimum conditions of graft copolymerization reactions were obtained as follows: monomer /polymer weight ratio, 50/50; reaction temperature, 70°C; Dropping frequency of monomer, 1.25g/min. The grafting efficiency and degrees of grafting are shown in Figure 3. As the amount of initiator increase, more radicals are produced which increases the number of grafting sites, resulting in higher grafting efficiency.

The grafting efficiency was seen to increase with an increased in the amount of initiator from 0.3 to 0.9 phr. This trend can be explained by the fact that the radicals transfer to backbone of PB, producing macroradicals. Which are enhanced by increasing the initiator concentration. Hence, resulting in an increase in grafting. However, beyond 0.9phr, the grafting efficiency decreases, and the possible reasons as follows, firstly, excessive radicals react with each other at higher initiator concentration, leading to a faster rate of termination or primary termination. Secondly, the radical concentration

increase in the water phase as initiator concentration increase and velocity of diffusing into monomer droplet increases. It is more readily to initiate polymerization of monomer droplet. Finally, the probability for the rate of chain transfer for the free polymer radicals to PB backbone is less than the rate of termination of the free polymer radicals, favoring the termination of the free copolymers over the chain transfer process. Similar results were also reported by Lenka [17] et al and Arayapranee [18] et al. in the ease of grafting methyl methacrylate onto natural rubber.

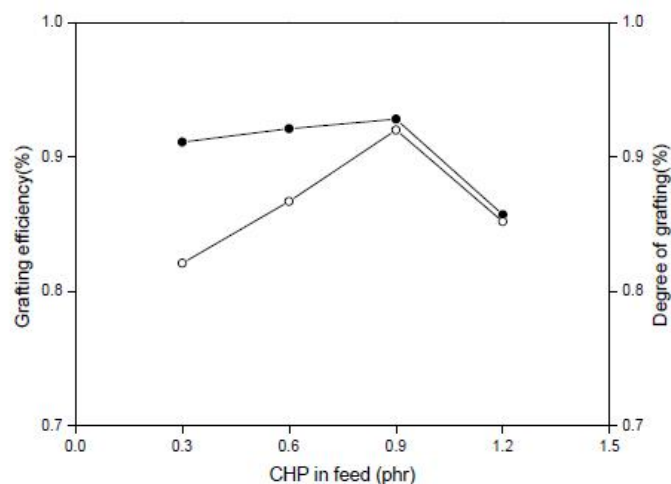


Figure 3. Effect of CHP amount on grafting efficiency and degree of grafting (M/P=50/50, 70°C, 1.25g/min): (●) Grafting efficiency; (○) Degree of grafting

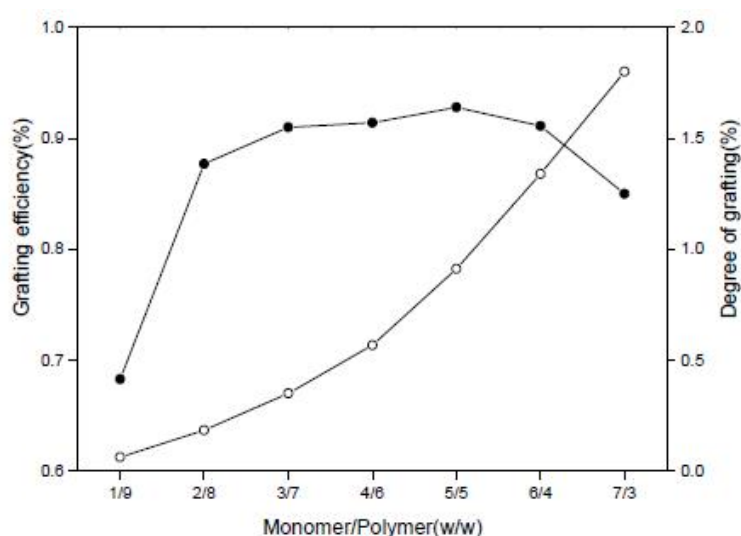
3.4.2. The Effect of Monomer/Polybutadiene(M/P)Weight Ratio.

The experiments aimed to explore the effect of core/shell ratio on grafting copolymerization. The effect of core/shell ratios on the percentage of conversion, grafting efficiency. And degree of grafting is shown in Table 3 under the following polymerization conditions. Grafting monomer/polybutadiene ratio was changed to 10/90, 20/80, 30/70, 40/60, 50/50, 60/40 and 70/30 varying the feed ratio in order to make particles with different shell thickness. The parameters of graft copolymerization were obtained as follows: reaction temperature, 70°C; Dropping frequency of monomer, 1.25g/min; initiator concentration, 0.9 phr of amount of monomer as M/P is 7/3. The PB-g-PS of the same amount was synthesized with different M/P. The size of the polybutadiene core is constant. It is reasonable that the degree of grafting and mean particle diameter increase with the M/P ratio. More monomer are fed with M/P increase, more grafting reactions are possible and the grafting efficiency is increased which reaches a maximum at 50/50 of M/P, and thereafter it decreases. The possible reason lies in the increase of monomer concentration in the water phase with the increase of M/P ratio, the diffusion of primary radicals into monomer droplet increase which initiate more readily polymerization of monomer droplet. Therefore, the diffusing velocity of the monomer from monomer droplet to one of reaction is increased. Furthermore, many side reactions, which probable competed with the grafting reaction, take place in the aqueous phase with the increase of M/P ratio, such as chain transfer to monomer. This means that homopolymerization is more pronounced than graft copolymerization at higher M/P ratio the results are illustrated in Figure 4.

Table 3. Effect of Initiator Concentration and Monomer/Polymer Weight Ratio on Graft Copolymerization

Sample	Initiator Concentration (phr)	Monomer/Polymer weight ratio	conversion	Mean particle diameter(nm)	Grafting Properties ^a	
					Grafting efficiency	degree of grafting
A	0.3	50/50	0.902	363	0.911	0.821
B	0.6	50/50	0.941	395	0.921	0.867
C	0.9	50/50	0.983	410	0.928	0.912
D	1.2	50/50	0.995	355	0.857	0.852
E	0.9	10/90	0.835	305	0.683	0.064
F	0.9	20/80	0.844	325	0.877	0.185
G	0.9	30/70	0.896	343	0.910	0.352
H	0.9	40/60	0.932	367	0.914	0.568
I	0.9	60/40	0.986	401	0.911	1.340
J	0.9	70/30	0.908	395	0.85	1.800

^a CHP same as M/P=7/3, St in the feed=100phr, Initiator=0.9phr; 70°C, 1.25g/min

**Figure 4.** Effect of the Monomer/Polymer weight ratios on grafting efficiency and degree of grafting (CHP same as M/P=7/3, 0.9phr, 70°C, 1.25g/min) (●) Grafting efficiency; (○) Degree of grafting

3.4.3. Effect of Reaction Temperature.

Since the decomposition energy of the CHP-Fe²⁺ redox system is rather low, the graft polymerization occurred at 50°C. The graft copolymerization of styrene were carried out at four reaction temperatures between 50°C to 80°C while keeping the other reaction parameters constant. The optimum condition of graft copolymerization were obtained as follow: M/P weight ratio, 50/50; initiator concentration, 0.9phr; dropping frequency of monomer, 1.25g/min. The PB-g-PS of the same amount was synthesized with different reaction temperature. In Table 4, it can be seen that a higher temperature results in a high conversion. Decomposition of the initiator increases with an increasing reaction temperature which causes an increase in both the number of free radicals and the rate of polymerization. Grafting efficiency and degree of grafting increase as the reaction temperature increase, as shown in Figure 5. However, it is thought that the thermally induced homopolymerization may take place at a higher reaction temperature. So 70°C was selected as the standard polymerization condition to achieve a sufficient degree of grafting in this study.

The very rapid decomposition of the initiator yields an instantaneously high radical concentration and radicals then might be act as radical scavengers, which result in the decrease of the amount of initiator. Thus, the result is lower initiator efficiency, however, fails to produce both the corresponding ungrafted homopolymers and graft copolymers.

Table 4. Effect of temperature and monomer dropping time on graft copolymerization

Sample	Monomer dropping		conversion	Mean particle diameter (nm)	Grafting Properties ^a	
	Temperature (°C)	Time (min)			Grafting efficiency	degree of grafting
K	50	240	0.491	305	0.882	0.433
L	60	240	0.982	391	0.916	0.90
C	70	240	0.983	410	0.928	0.912
M	80	240	0.973	383	0.935	0.910
N	70	60	0.904	330	0.891	0.805
O	70	120	0.934	365	0.901	0.842
P	70	180	0.949	360	0.915	0.868

^aM/P=50/50; St in the feed=100phr, Initiator=0.9phr

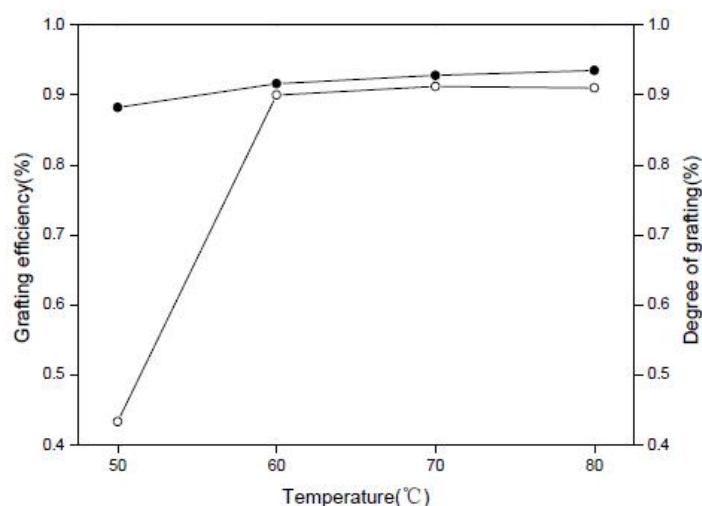


Figure 5. Effect of the reaction temperature on grafting efficiency and degree of grafting (M/P=50/50, CHP=0.9phr, 1.25g/min): (●) Grafting efficiency; (○) Degree of grafting

3.4.4. Monomer Dropping Time.

The effect of monomer dropping time on the grafting of styrene onto polybutadiene by redox initiator is shown in Table 4. The parameters for the graft copolymerization were as follows: M/P weight ratio, 50/50; initiator concentration, 0.9phr; reaction temperature, 70°C; the PB-g-PS of the same amount were synthesized with different monomer dropping time. According to Table 4, the percentage conversion, grafting efficiency and degree of grafting increase with increasing monomer dropping time.

As shown in Figure 6, it is possible that some of the grafting monomers may take part in homopolymerization at short monomer dropping times. It is thought that this results in a decrease of grafting efficiency and degree of grafting. With a long monomer dropping time, the PS is formed more readily than is the graft copolymer. Since there are only a few new acting grafting sites available. On the polybutadiene for higher graft copolymerization. In this study, 240 minutes was thought to be sufficient and was chosen as standard condition.

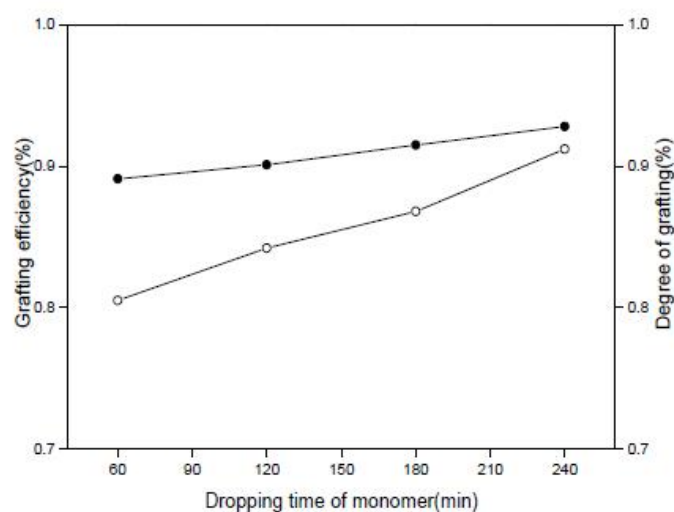


Figure 6. Effect of the monomer dropping time on grafting efficiency and degree of grafting (M/P=50/50, CHP=0.9phr, 70°C): (●) Grafting efficiency; (○) Degree of grafting

3.5. Morphological Observation

Figure 7 shows transmission electron microscopy of PB and PB-g-PS latex particles. These particles were stained with osmium tetroxide (OsO_4). OsO_4 can only stain polybutadiene region through reaction with the residual double bonds present in polybutadiene. Figure 7(a) shows TEM of the PB latex particle. We find that PB latex particles are spherical in nature with a smooth surface, and dark areas. Figure 7(b)-(e) shows TEM of the PB-g-PS latex particles. The darker areas indicate the PB core regions, while the lighter areas are for polystyrene as shell. The particles covered with polystyrene reveal irregular shapes which indicate that polystyrene is distributed continuously on the surface of the PB latex particles. This is due to the diffusion of radicals from the water phase to the surface of PB latex particles, which attacks the double bond of the polybutadiene on the particle surface, producing activated site. And initiating graft copolymerization. The surface viscosity of the particle increase with grafting reaction, resulting in the difficult diffusion of the radicals from the surface to center of the particles. Therefore, the radical concentration on the particle surfaces is higher than center, resulting in grafting reaction on the surface of the PB particles.

These phenomena are probably due to phase separation, that is, the PB rubber is immiscible with the second grafting polystyrene plastics. PB rubber and polystyrene are highly hydrophobic, furthermore, it has been demonstrated that the grafting of the second stage polymer onto the core particle producing heterogeneous structure of core-shell morphology, which could be formed by phase separation of immiscible polymers during polymerization. The shell thickness of the grafting copolymer on the seeded particles increases with the M/P ratio because the size of the polybutadiene core is constant. The polystyrene resides on the surface of the particles as a continuous shell and the seeded particles have a complete closed shell.

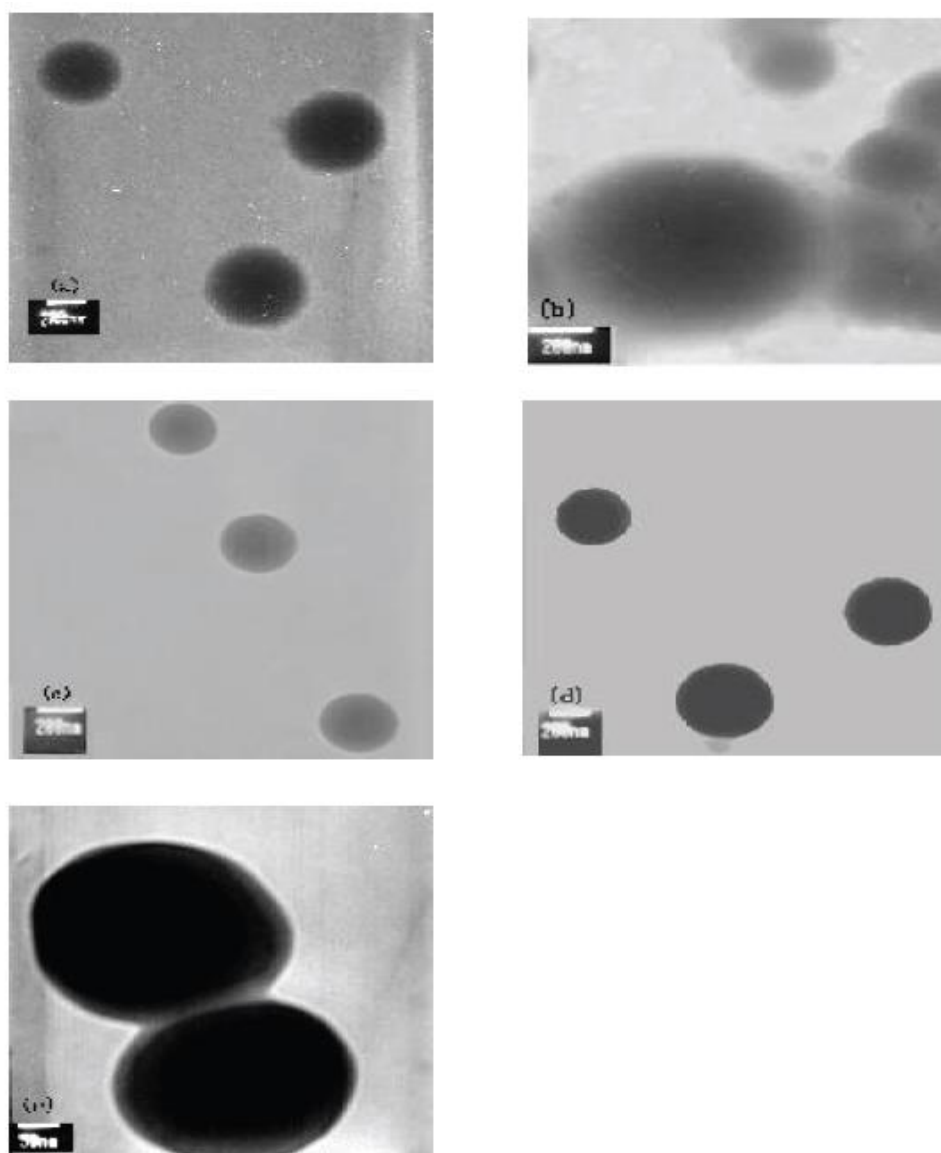


Figure 7. The transmission electrons micrographs of (a) PB, (b) PB-g-PS (90/10w/w), (c) PB-g-PS (70/30 w/w), (d) PB-g-PS (50/50 w/w), (e) PB-g-PS (30/70 w/w)

4. Conclusion

Core-shell PB-g-PS latex were synthesized by emulsion polymerization by grafting styrene onto PB latex particles using redox initiation systems. FTIR and $^1\text{H-NMR}$ spectroscopy shows that PB-g-PS has already formed. The influential factors such as the initiator concentration, reaction temperature, monomer to polymer weight ratios, and monomer dropping time were investigated. The grafting efficiency increased with increasing initiator concentration up to 0.9 phr, then, it decreased which indicated that further increase the initiator concentration favored homopolymerization rather than grafting. An increase of the M/P ratio increased the grafting efficiency until 50/50. The grafting efficiency decreased with an increase in temperature above 70°C . At 4h of the monomer dropping time is suitable for higher grafting efficiency. The PB-g-PS copolymers showed mainly a spherical morphology of a core-shell configuration with PB particles as the soft core and a thin PS film as a hard shell.

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