Synthesis and Application of Poly(butadiene-g-acrylonitrile–styrene) Core–Shell Rubber Particles for Use in Epoxy Resin Toughening. I. Synthesis of Poly(butadiene-g-acrylonitrile–styrene)

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SYNOPSIS

Graft copolymers of acrylonitrile (AN)–styrene (ST) onto polybutadiene were prepared via emulsion polymerization method using a redox initiator system, cumene hydroperoxide-tetrasodium pyrophosphate–ferrous sulfate–dextrose. The effects of initiator, reaction temperature, reaction time, polymer/grafting monomer ratio, and monomer dropping frequency on the graft copolymerization reaction were investigated. Transmission electron micrographs confirmed that the synthesized particles had a core–shell shaped structure. The powdery core–shell shaped poly(butadiene-g-AN–ST) particles with various AN contents in their shells and with different shell thicknesses were prepared, which can be incorporated into brittle epoxy resin as impact modifier. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The properties of structured core–shell polymer particles, such as size, morphology, composition, and crosslink density of the core, can be controlled separately during particle preparation by emulsion polymerization.[1–3] Polymers with a soft core and a hard shell are used as impact modifiers, toughened plastics, etc. For these reasons, current research has focused not only on the enhancement of various properties of conventional core–shell-polymer-incorporated thermoplastics such as ABS or MBS, but also on their applications as impact modifiers for thermosetting resins, such as epoxy. It is known that core–shell rubber particle modified epoxies show better fracture toughness than rubber- or thermoplastic-modified epoxies when the same amount of toughener is incorporated.[4] In this article, the influences of the main process parameters such as initiator, reaction temperature, grafting monomer/polymer ratio, and monomer dropping time on graft polymerization reaction were investigated using polybutadiene as the soft-core and acrylonitrile (AN) and styrene (ST) as the hard-shell monomers.

EXPERIMENTAL

Materials

Polybutadiene latex (Cheil Industries, Cheon Nam 555-210, Korea) was used as received. According to the manufacturer's literature, the average particle size and gel content of the polybutadiene latex were 300 nm and 80%, respectively. AN (Junsei Chemical, Tokyo) and ST (Aldrich Chemical, Milwaykee, WI) were purified by washing with 5% sodium hydroxide solution to remove the inhibitor. After this treatment, the monomers were washed with distilled water and dried on anhydrous calcium chloride for 24 h. The monomers were then distilled under reduced pressure in nitrogen and stored in a refrigerator. Sodium lauryl sulphate (Aldrich Chemical) used as emulsifier, ferrous sulfate (Kanto Chemical, Tokyo), dextrose (Junsei Chemical), tetrasodium pyrophosphate (TSPP, Aldrich Chemical), cumene hydroperoxide (CHP, Aldrich Chemical) used as initiator, and divinyl benzene (DVB, Aldrich Chemical) used
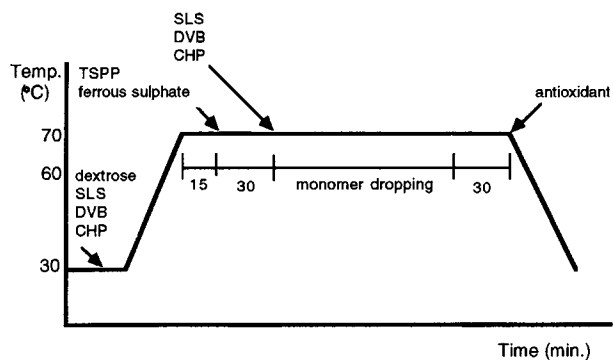
Scheme 1 Polymerization profile.

as crosslinking agent were used as received without further purification.

Graft Copolymerization

In this study, a semibatch process was used for the graft copolymerization. The reaction condition is shown in Scheme 1. Deionized water (360 g), polybutadiene latex (50 wt % solid content in water, 300 g), dextrose (1.05 g), and 10% water solution of emulsifier (21 g) were charged into a 1-L reactor equipped with a mechanical stirrer, temperature controller, and nitrogen inlet tube. Then 0.9 g of CHP, 0.45 g of DVB, and 25% of the total grafting monomers to be used were added into the reactor. The reaction medium was stirred at 250 rpm and nitrogen gas was purged into the reactor throughout the reaction. Ten minutes after the reactor was heated to the required temperature, the solution of TSPP–ferrous sulfate was added to initiate the reaction. After 30 min, 2.7 g of CHP and 1.35 g of DVB were added and the remaining monomers were prepared. The remaining 75% of the monomers were added by delayed addition over periods of 30/60/90/120 min. The reactor temperature was maintained at 70°C. After 5 g of antioxidant solution was added, reactor temperature was decreased to 40°C and the reaction was ended. In this study, shell thickness

was controlled by polybutadiene/grafting monomer feed ratio. Feed ratios of polybutadiene and grafting monomers were varied as 70/30, 60/40, 50/50, 40/60, and 30/70 (wt %/wt %). In order to make core–shell rubber particles with different shell compositions, feed ratios of AN and ST were also varied as 35/65, 25/75, 15/85, 5/95, and 0/100 (AN/ST, wt %), keeping the polybutadiene/monomer feed ratio as 50/50 (wt %/wt %). Table I contains the polymerization conditions.

Coagulation and Posttreatments

The synthesized polymer latex was filtered by 100-gauge wire mesh to remove the coagulum. Then the latex was coagulated by the addition of 5 parts (part/total solids) of calcium chloride at 65°C for 5 min, and for another 5 min at 80°C. The coagulated polymer particles were then washed five times with abundant amounts of distilled water to remove any possible residual additives. The resultant polymer particles were dried in a vacuum drying oven for 24 h.

Grafting Efficiency and Degree of Grafting

A solution of 2 g of powdery polymer particles in acetone was stirred with reflux at 65°C for 2 h. This solution was centrifuged and the precipitated "grafted" parts were sampled, followed by drying in a vacuum drying oven at 85°C for 2 h. Grafting efficiency and degree of grafting were calculated from the following equations:

$$\text{Grafting efficiency (\%)} = \frac{\text{wt of monomer grafted}}{\text{wt of fed monomer}}$$

$$\text{Degree of grafting (\%)} = \frac{\text{wt of monomer grafted}}{\text{wt of polybutadiene}}$$

$$= \frac{\begin{array}{c}\text{wt of grafted polymer}\\\text{after centrifuge}\\-\text{wt of polybutadiene}\end{array}}{\text{wt of polybutadiene}}$$

Table I Graft Polymerization Conditions of Poly(butadiene-g-AN–ST)

Condition	Description[a]
CHP amount (parts)	0.4, 0.8, **1.2**, 1.6
Polymer/monomer feed ratio	30/70, 40/60, **50/50**, 60/40, 70/30
AN/ST feed ratio	35/65, **25/75**, 15/85, 5/95, 0/100
Reaction temperature (°C)	50, 60, **70**, 80
Monomer dropping time (min)	30, 60, **90**, 120

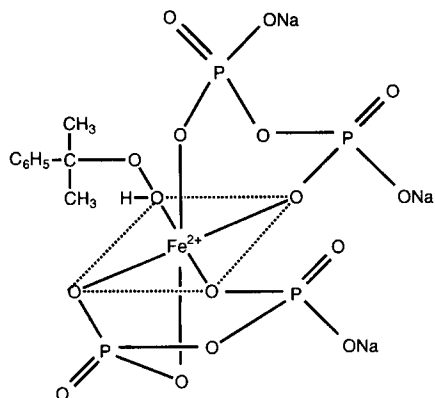[a] Bold numbers indicate standard conditions used in this study.

Figure 1 Fe^{2+}-TSPP-CHP complex.

Conversion

An aluminium dish was weighed (W_1) after being dried at 80°C. About 2 g of latex was put onto this and weighed (W_2), then weighed again (W_3) after drying. Solid content and conversion were calculated from the following equations:

$$Solid\ content\ (\%) = \frac{W_3 - W_1}{W_2 - W_1}$$

$$Conversion\ (\%) = \frac{wt\ of\ synthesized\ polymer}{wt\ of\ fed\ monomer}$$

Infrared Spectroscopy (IR) and Transmission Electron Microscopy (TEM)

The IR spectra were obtained on an Alpha Centauri FT-IR spectrometer (Mattson Instruments, Inc., Wisconsin) at a resolution of 4 cm^{-1}. TEM (Jeol 2000EX2) was used to verify the structure of synthesized polymers.

Particle Size Analysis

A Malvern Autosizer IIc was used to analyze the particle sizes of synthesized polymers.

RESULTS AND DISCUSSION

Initiation Mechanism

A CHP-Fe^{2+} redox system was adapted as the initiator. Figure 1 is a possible model of a CHP-TSPP-Fe^{2+} complex. Water molecules are also able to participate in the complex. Being donated an electron from the Fe^{2+} ion, the oxygen–oxygen bond of CHP in the complex is cleaved to produce
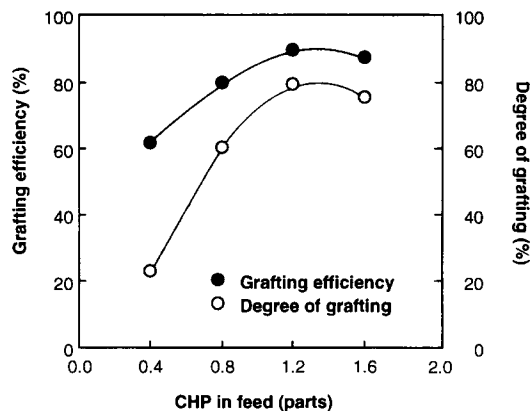

Figure 2   Effect of CHP amount on grafting efficiency and degree of grafting.

C_6H_5—$C(CH_3)_2$—O radical and OH^- ion. Then the radical attacks a monomer or a double bond of polybutadiene. According to Chern and Poehlein,[5] the primary radicals decomposed from initiator mainly attack double bonds of rubber, while polymeric radicals attack allyl hydrogen of rubber. A dextrose molecule comes into the complex in place of the lost CHP and it donates an electron to the oxidized ferrous ion, Fe^{3+}, to make it Fe^{2+} again. Then another CHP molecule participates in the complex in place of the oxidized dextrose. Therefore, the complex may produce radical until all CHP is consumed. The initiator radical is produced mainly in the water phase and is absorbed into the micelle, then it initiates the polymerization. Outside of the micelle, some of the radicals may react with monomers in water to make "ungrafted" homo- or copolymers.

The effect of CHP amount on grafting efficiency and degree of grafting is shown in Figure 2. As the amount of CHP is increased, more radicals are pro-
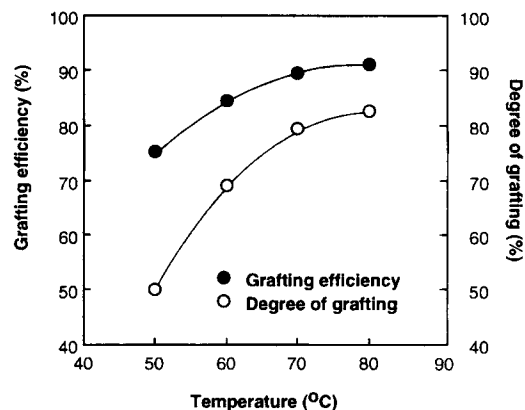

Figure 3   Effect of polymerization temperature on grafting efficiency and degree of grafting.
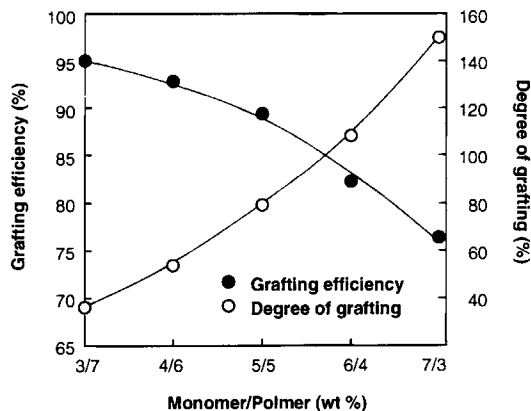
Figure 4 Effect of monomer/polymer ratio on grafting efficiency and degree of grafting.

duced; consequently, this increases the number of grafting sites, which results in higher grafting efficiency and degree of grafting. However, when too many radicals are present the coupling reaction of radicals may occur; this reaction decreases the graft chain length, grafting efficiency, and degree of grafting. In many cases, tert-dodecyl mercaptan is used as a chain transfer agent to control the molecular weight of the grafting chain.[6] But in this study, to make a particle with a thick shell, no chain transfer agent was used. Moreover, DVB was used as a crosslinking agent to increase the molecular weight of the shell. As a result, 1.2 parts per total solid of CHP was the optimum condition and was used throughout the study.

Reaction Temperature

Since the decomposition energy of the CHP–Fe^{2+} redox system is rather low, the graft polymerization
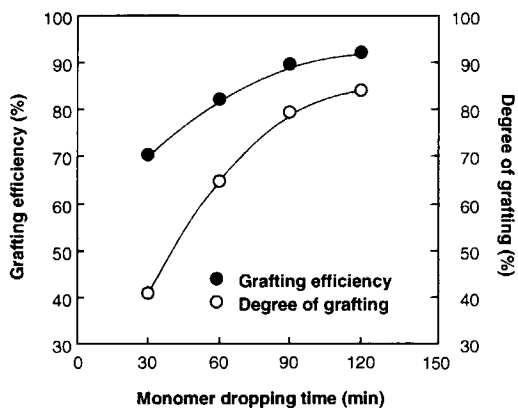

Figure 5 Monomer dropping time vs. grafting efficiency and degree of grafting.
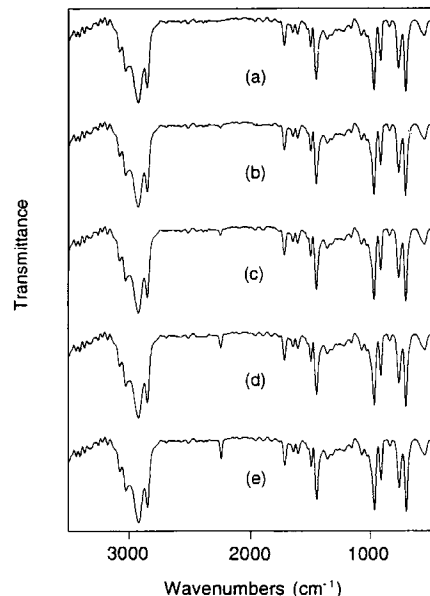

Figure 6 IR spectra of poly(butadiene-g-AN-ST) with different AN contents (wt %): (a) 0%, (b) 5%, (c) 15%, (d) 25%, (e) 35%.

occurred at 50°C. Grafting efficiency and degree of grafting increase as the polymerization temperature increases, as shown in Figure 3. However, it is thought that the thermally induced homopolymerization or copolymerization may take place at a high reaction temperature so 70°C was selected as the standard polymerization condition to achieve a sufficient degree of grafting in this study.

Grafting Monomer/Polybutadiene Ratio

Grafting monomer/polybutadiene ratio (M/P) was changed to 30/70, 40/60, 50/50, 60/40, and 70/30 by

Table II Compositions of Resultant Core–Shell Rubber Particles

Core/Shell[a]	Shell Composition[a] AN	ST	Particle Size[b] (nm)
50/50	0	100	322
50/50	5	95	—
50/50	15	85	—
50/50	25	75	—
50/50	35	65	—
70/30	25	75	304
60/40	25	75	316
40/60	25	75	330
30/70	25	75	336

[a] Weight %.
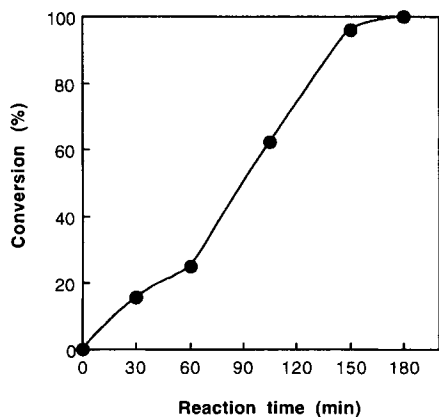[b] Data from Malvern Autosizer IIc.

Figure 7   Polymerization time vs. conversion.

varying the feed ratio in order to make particles with different shell thicknesses. Note that the size of the polybutadiene core is constant. It is reasonable that the degree of grafting and particle size increase with the increase of the M/P value. When more monomers are fed, more grafting reactions are possible, however grafting efficiency decreases as the M/P value increases. It is thought that some of the monomers are more apt to homopolymerize or copolymerize than to graft onto the polybutadiene chain at higher M/P values. The results are illustrated in Figure 4. In this study, it was possible to make particles with different shell thicknesses.

Monomer Dropping Time

In this experiment, the feed ratio of polybutadiene and grafting monomers was kept at 50/50 (wt %) and the feed ratio of AN and ST was fixed at 25/75 (AN/ST, wt %).

As shown in Figure 5, grafting efficiency and degree of grafting increase as the dropping time increases. It is possible that some of the grafting monomers may take part in homopolymerization or copolymerization at short monomer dropping times. It is thought that this results in a decrease of grafting efficiency and degree of grafting. Therefore, it is proposed that sufficient dropping time should be required to obtain stable graft polymerization on a polybutadiene core. In this study, 90 min was thought to be sufficient and was chosen as standard condition.

Synthesis of Particles with Different AN Contents in Shell

For use in epoxy toughening, particles with different AN contents in shell are prepared. The IR spectra

of synthesized poly(butadiene-g-AN–ST) shown in Figure 6 exhibit the characteristic nitrile stretching absorption band at 2225 cm^{-1}. As AN content in shell increases, the size of this absorption band increases. The aliphatic C — H and aromatic C — H stretching absorption bands appear at 2950 cm^{-1} and 3050 cm^{-1}, respectively. The particles with different AN contents in shell were successfully synthesized. When core-shell rubber particles are used in epoxy toughening, the particle dispersion characteristics are affected mainly by epoxy matrix–shell interaction. The solubility parameter of the core–shell rubber particles depends on AN content in shell. The resultant polymers synthesized in this study are summarized in Table II.

Conversion

Figure 7 is the conversion curve of the graft copolymerization reaction. As the conversion is increased, shell becomes thicker, the particle size increases, and further grafting becomes troubled by increased viscosity and by low monomer concentration around the core surface. Figure 8 is the TEM photograph of synthesized particles. Core–shell morphology, which has AN–ST inclusions in its core, is observed.
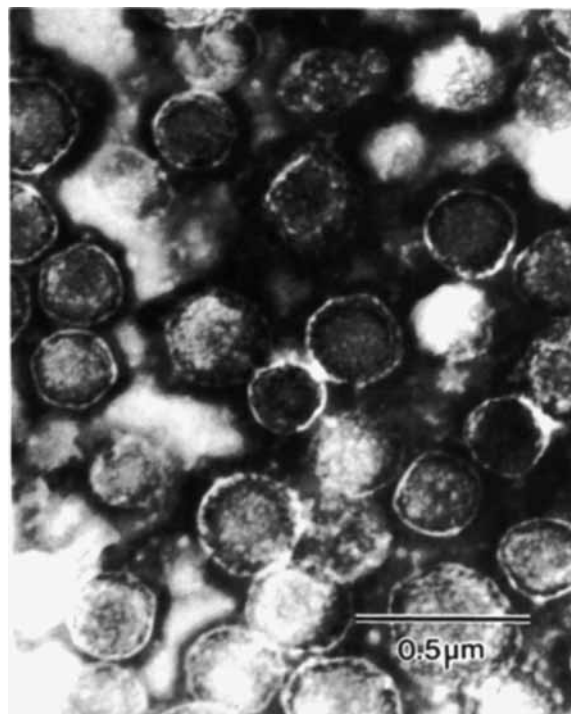

Figure 8   Transmission electron micrograph of poly-(butadiene-g-AN–ST) latex.

CONCLUSION

Graft copolymerization of AN and ST onto polybutadiene was performed via emulsion polymerization. The main process parameters were investigated and with settled reaction conditions, particles with different shell thicknesses and particles with different AN contents in shell were successfully prepared. Core-shell morphology of synthesized particles was confirmed by TEM photographs.

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