

Hydrogenation of Styrene–Butadiene Rubber (SBR) Latexes

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ABSTRACT: The mechanism and the optimum conditions for the reduction of residual double bonds in styrene–butadiene rubber (SBR) latex by hydrogenating the polybutadiene in the latex form were studied. The hydrogenation involves a copper ion (II)-catalyzed procedure in which diimide hydrogenation agent is generated *in situ* at the surfaces of latex particles by a hydrazine/hydrogen peroxide redox system. The surface density of the copper ion in particle surfaces was found to be a crucially important parameter in controlling the degree of hydrogenation. The distribution of the double bonds in the latex particles after the hydrogenation was found to be dependent on the particle size and the extent of crosslinking in the particles. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 2047–2056, 1997

Key words: SBR latex; hydrogenation; copper ion catalyst

INTRODUCTION

Polydiene-based polymers are widely used as rubbers, binders, and adhesives because of their high strength and good elastic properties. However, a disadvantage of these materials is their aging behavior which is caused by the oxidation of the residual double bonds in the polydienes which could deteriorate the properties of the polymers.

Conventional processes to hydrogenate the residual double bonds present in polydiene-based polymers, such as butadiene rubber (BR), styrene–butadiene rubber (SBR), and acrylonitrile–butadiene rubber (NBR), are carried out in polymer solutions, either by transition catalytic hydrogenation using pressurized hydrogen^{1–5} or through a noncatalytic diimide reduction process.^{6,7} There are some obvious problems for these kinds of hydrogenation processes. Besides the high cost of hydrogenation equipment and the catalyst and low efficiencies resulting from the limited solubility and solvent-induced environmental concerns, this method can be used only for linear

polydiene polymers because of the requirement for a polymer solution. Moreover, these methods are not feasible when a hydrogenated polydiene is needed in the latex form.

A breakthrough process was developed by Wideman⁸ in 1984 to directly convert BR, SBR, and NBR latexes into their saturated forms. He described a procedure which involved a system containing hydrazine hydrate, an oxidant, and a metal–ion catalyst. A hydrazine/hydrogen peroxide redox system was typically used with the copper ion as the catalyst, and an 80% degree of hydrogenation for NBR latex was attained. Recently, a series of studies on the mechanism for the hydrogenation process in latex polymers was reported by Parker and Roberts.⁹ Based on early studies^{10–14} on the reductions of the multiple bonds in olefins with metal-catalyzed hydrazine/oxidant systems, Parker and Roberts proposed a diimide reduction mechanism for the latex in which the diimide hydrogenating agent was generated at the surfaces of particles from a hydrazine/hydrogen peroxide redox system. Carboxylated surfactants adsorbed at the latex particle surfaces play an important role in this procedure by forming hydrozinium carboxylates with hydrazine and a dimeric cupric complex with copper

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ions. An enzyme-like catalysis mechanism for the dimeric cupric species was proposed.¹⁵ Diimide intermediates which are primarily generated at the adsorbed surfactant layer at the latex particle surfaces are stabilized by the dimeric cupric species and effectively reduce the residual carbon-carbon double bonds within the limited lifetime of the diimide intermediate. Hydrogenated polydiene-based polymers did not only exhibit excellent ozone, oxidation, and UV resistance as expected,^{9,16} but also showed improved mechanical properties in some circumstances.¹⁷⁻¹⁹

The present work was focused on determining the optimal conditions for the hydrogenation process of latex polymer in terms of factors such as the loci and concentration of the copper ion catalyst, latex particle size, and the gel fraction of SBR latexes. The structure of the hydrogenated SBR latex particles with regard to the distribution of the double bonds in the latex particles during the hydrogenation process was investigated through the analysis of the degree of hydrogenation for the different types of double bonds, i.e., *trans*, *cis*, or vinyl. Morphological observations of the hydrogenated latex particles by transmission electron microscopy (TEM) were also carried out to confirm the structures.

EXPERIMENTAL

Materials

The monomers used, butadiene (Bd, Matheson Gas Products, Inc.) and styrene (S, Fisher Scientific) were treated by passing them through inhibitor-removal columns. Purified stearic acid, lithium hydroxide (Fisher Scientific), and cupric sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; J. T. Baker Chemical Co.) were used as received. Hydrazine hydrate ($\text{H}_2\text{NNH}_2 \cdot \text{H}_2\text{O}$) and hydrogen peroxide (H_2O_2 , 50%), reagent grade (Fluka), Dowfax 2A1 (a sodium dodecyl diphenylether disulfate surfactant, Dow Chemical), and Dow Corning Antifoam 1430 were used as received. SBR-1502 latex (Goodyear Rubber & Tire Co.) was also used as received.

Preparation of SBR Latexes

SBR latexes with various particle sizes and gel fractions were prepared by emulsion polymerization techniques in 250 mL pressure bottles at 65 and 70°C by end-over-end rotation in a thermostated bottle polymerization unit at 40 rpm ac-

ording to the recipes shown in Table I. To obtain the latex particles with desired particle sizes and gel fractions, the surfactant concentrations, polymerization time, and temperature were varied. For latexes obtained at conversions lower than 100%, the remaining monomers in the latexes were removed immediately after the termination of the polymerization by flash evaporation, which was repeated at least three times. Distilled-deionized (DDI) water was added to the latexes in between the evaporation processes. The particle sizes of the latexes were determined by using dynamic light scattering (Nicomp Model 370 submicron particle sizer) and transmission electron microscopy (TEM), while the gel fractions were determined by a solvent (toluene) extraction technique which was described in a companion article.²⁰

Hydrogenation of SBR Latexes

The recipes used in the hydrogenation study are shown in Table II. An aqueous solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and Dowfax 2A1 was added to SBR latex in a 250 mL flask. The $\text{H}_2\text{NNH}_2 \cdot \text{H}_2\text{O}$ was then charged into the flask. The mixture was warmed to 50°C with stirring. H_2O_2 (50%) was then added dropwise over a 7 h period. Small amounts of antifoam agent (Dow Corning Antifoam 1430) were periodically added during the reaction as required.

IR Analysis for Determination of the Degree of Hydrogenation

The final conversion of the double bonds to single bonds in the hydrogenated SBR [H-SBR] latex was determined by infrared spectroscopy (FTIR). The latex film formed from diluted latex was cast onto a Zn—Sn plate at atmospheric pressure and then dried in a desiccator at room temperature and used for the IR measurement. The thickness of the latex films for the IR measurements was controlled such that the IR absorbances were in the range of 0.3–0.7 cm^{-1} .

RESULTS AND DISCUSSION

IR Analysis

Figure 1 shows the IR spectra of both nonhydrogenated SBR and partially hydrogenated SBR latex. The SBR spectrum shows distinct peaks for *trans*,

Table I Recipes Used for the Preparation of SBR Latexes

Component (g)	SBR-S-LG	SBR-S-HG	SBR-L-LG	SBR-L-HG
Butadiene	45.00	45.00	45.00	45.00
Styrene	5.00	4.50	5.00	4.50
Divinylbenzene	—	1.00	—	1.00
<i>n</i> -Dodecyl mercaptan	0.10	—	0.10	—
Potassium persulfate	0.25	0.25	0.25	0.25
Stearic acid	0.50	1.80	0.50	0.70
Lithium hydroxide	—	—	0.040	0.056
Sodium hydroxide	0.067	0.24	—	—
Distilled-deionized (DDI) water	90.00	90.00	90.00	90.00
Conversion (%)	64	100	57	100
Particle size (nm)	80	60	230	240
Gel fraction (%)	41	100	34	100
Polymerization temp (°C)	70	70	65	65

cis, and vinyl double bonds at 966, 722, and 910 cm^{-1} wavenumbers, respectively; the percentages of these three types of double bonds as determined from their absorbance intensities are 62, 18, and 20%, respectively. The peak at wavenumber 700 cm^{-1} representing the phenyl ring in the styrene unit was used as an internal standard to determine the relative concentrations of *trans* and vinyl double bonds. It can be noted that the absorbance peak for the *cis* double bond at wavenumber 722 cm^{-1} slightly increased after the hydrogenation, instead of decreasing as was expected. This increase is caused by the overlap from the absorbance of polyethylene formed after the hydrogenation. After the hydrogenation, the 1,4-polybutadiene segments were converted to polyethylene, which has two absorbance peaks around 720 and 730 cm^{-1} wavenumbers for amorphous- and crystalline-state polymer chains, re-

spectively. The 720 cm^{-1} peak would overlap with the 722 cm^{-1} peak for the *cis* double bond and cause the increase for this peak in this range. It had been reported^{21,22} that the reactivity for *cis* double bonds is about the same as that for the *trans* double bonds for the hydrazine/oxidant-induced diimide hydrogenation reaction. Since the concentration of *cis* double bonds was lower than that of the *trans* double bonds in the latex particles, a lower percentage of hydrogenation for the *cis* double bonds is expected. In this study, the degree of hydrogenation for the *cis* double bonds is assumed to be 10% less than that for the *trans* double bonds which could be determined directly from the phenyl ring internal standard. It can also be noted that a new peak appears at 735 cm^{-1} after the hydrogenation. This peak could represent the crystalline polyethylene segments formed after the hydrogenation of 1,4-polybutadiene segments.

Table II Recipe Used for the Hydrogenation of SBR Latexes with Different Copper Ion Concentrations

Component	Weight (g)
SBR latex (20% solids)	100 (0.378 mol double bond)
Hydrazine hydrate ($\text{H}_2\text{NNH}_2 \cdot \text{H}_2\text{O}$)	18.9 (0.378 mol)
Hydrogen peroxide (H_2O_2 , 50 wt %)	25.5 (0.378 mol)
Cupric sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)	Varying amount (g) (1×10^{-3} to 4×10^{-2} for SP Latex ^a ; 4×10^{-5} to 1×10^{-3} for LP ^b latex)
Dowfax 2A-1	Varying amount (g) (0.02–0.08)

^a SP: Small particle latex, 50 nm in diameter.

^b LP: Large particle latex, 230 nm in diameter.

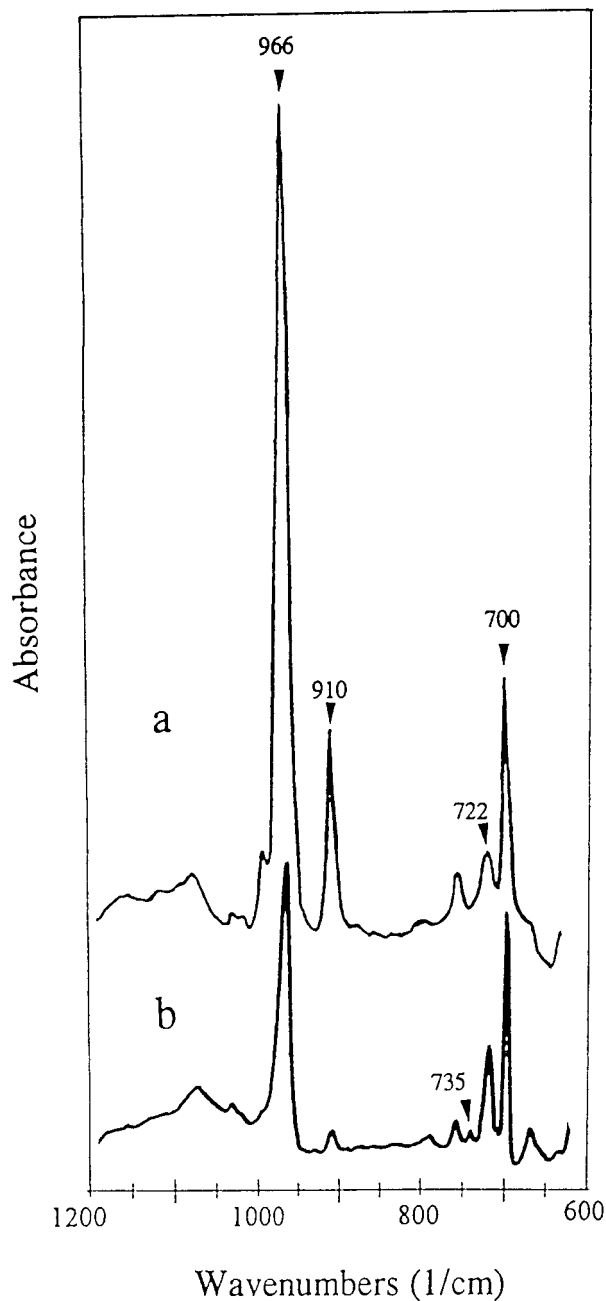
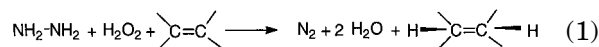


Figure 1 IR spectra of (a) nonhydrogenated SBR and (b) partially hydrogenated SBR latexes.

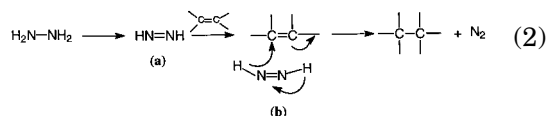
Location and Concentration of Copper Ion

The overall hydrogenation reaction using hydrazine/oxidant is shown below:

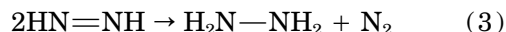


The reduction mechanism of this $\text{H}_2\text{N-NH}_2/\text{H}_2\text{O}_2$ redox system has been extensively studied

in homogeneous reaction systems for small molecules.^{10-13,23,24} These studies indicated that this reduction procedure involved an intermediate diimide structure (a) according to the following scheme:



In this procedure, the diimide formed in the first step is a mixture of *cis* and *trans* isomers. The reduction of carbon-carbon double bonds with diimide can only be carried out by the *cis*-diimide involving a stereospecific *cis* addition of hydrogen with a cyclic diimide transition state (b). At the same time, diimide is very unstable and is capable of reacting with itself to form the disproportionation products, hydrazine and nitrogen:



The copper ion is able to greatly accelerate the formation of diimide from the $\text{H}_2\text{N-NH}_2/\text{H}_2\text{O}_2$ redox system. A simple experiment was done by slowly adding a few drops of H_2O_2 (50%) to a 20% $\text{H}_2\text{N-NH}_2$ aqueous solution in a beaker with and without the presence of the copper ion. Great caution must be taken when carrying out this reaction due to the possible explosive redox reaction. Properly diluted, instead of neat, reactants must be used. It was found that the system with copper ions reacted remarkably fast, while the system without the copper ions present reacted much more slowly. This indicates that for the heterogeneous latex system used in this study the location and concentration of the copper ions are extremely important.

Location of Copper Ions

Copper ions can be present at three locations in a polymer latex: in the water medium, at the polymer particle surfaces, and inside of the particles. Obviously, localizing copper ions in the water phase will lead only to reaction (3) because there are no carbon-carbon double bonds to be reduced. This has been proven in Parker and Roberts' work⁹ by complexing copper ions in water with aqueous ethylenediamine tetraacetic acid tetrasodium salt (Na_4EDTA). Their results showed that no double bonds could be reduced in this case. To localize the copper ions inside of the latex parti-

cles, a small amount of oil-soluble 2-(acetoacetoxy)ethyl methacrylate (AAEM) was used. The results, however, were negative, i.e., a much lower degree of hydrogenation (DH) was attained compared to the system without AAEM. This was due to the low diffusivity of the highly water-soluble species, $\text{H}_2\text{N}-\text{NH}_2$ and H_2O_2 , into the polymer particles. To reach a higher degree of hydrogenation, the copper ions should reside only at the surfaces of the latex particles, which can be accomplished by ionically associating them with acidic groups present in the surfactants (e.g., carboxylated surfactants such as sodium stearate) adsorbed at the latex particle surfaces. In practice, coagulum would form instantly in a latex stabilized with a carboxylated surfactant when a copper ion solution is added because Cu^{2+} would bridge the carboxylate groups present in the surfactants. A small amount of surfactant that is stable to copper ions has to be added together with the copper ions to stabilize the system. Dowfax 2A-1 was used for this purpose. Another important function of a carboxylated surfactant is to form hydrozinium carboxylate⁹ by which the hydrozinium ion could also be present on the particle surface.

Concentration of Copper Ions at the Particle Surface

Considering the competitive reactions shown in reactions (2) and (3), a high concentration of carbon-carbon double bonds and low concentration of copper ion favors the reduction reaction (2) over the disproportionation reaction (3). At the particle surface, the concentration of double bonds is fixed by the composition of the polymer latex. The concentration of diimide formed should be controlled at a level where it is high enough for the reduction of double bonds to occur and yet low enough to minimize the extent of the disproportionation reaction of the diimide. Thus, the concentration of copper ions at the particle surfaces is the key factor which needs to be controlled. Table II shows the recipe used for the hydrogenation of SBR latex. One of the SBR latexes used in this recipe was the carboxyl surfactant-stabilized SBR-1502 latex. The particle size is 50 nm as measured by dynamic light scattering (Nicomp) and is labeled SP (i.e., "small particle"). Another SBR latex used was the SBR-L-LG latex described in Table I which is labeled LP (i.e., 230 nm, "large particle"). Various amounts of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were added to the latex to investigate the influence of the copper ion concentration on the degree of hy-

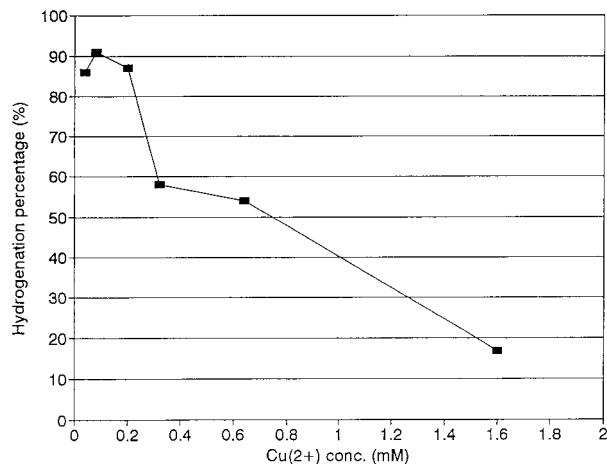


Figure 2 Hydrogenation percentage with different molar concentrations of copper ion in the SP latex system (50 nm).

drogenation. The influence of the particle size of the SBR latexes will be discussed by comparing the SP and LP latex systems. It should be mentioned that the purpose of this experiment was to investigate the optimum copper ion concentration needed for the hydrogenation reaction to occur and not to determine the overall conditions necessary to achieve the highest degree of hydrogenation. Actually, there will be some hydrazine remaining in the system after completion of the hydrogenation reaction. The degree of hydrogenation can be increased by adding additional hydrogen peroxide.

Figure 2 shows the degree of hydrogenation (DH) with different copper ion concentrations in the SP latex system. It is clearly shown that DH is very sensitive to the overall copper ion concentration. A maximum DH could be reached at very low copper ion concentrations ranging between 0.05 and 0.2 mM (based on total latex system). A higher copper ion concentration decreases the DH. For the LP system, as shown in Figure 3, a similar tendency is shown, except that the concentration of copper ions for the peak DH appears over a range of about 0.005–0.015 mM (based on total latex system) which is about one-tenth of that found in the SP system. By converting the copper ion concentration to the number of copper ions per 1000 nm² of particle surface, with the known particle sizes for both the SP and LP systems, it is interesting to note that, as shown in Figure 4, the maximum DH occurs over the same range (about two copper ions or one dimeric complex per 1000 nm² of particle surface) for both the

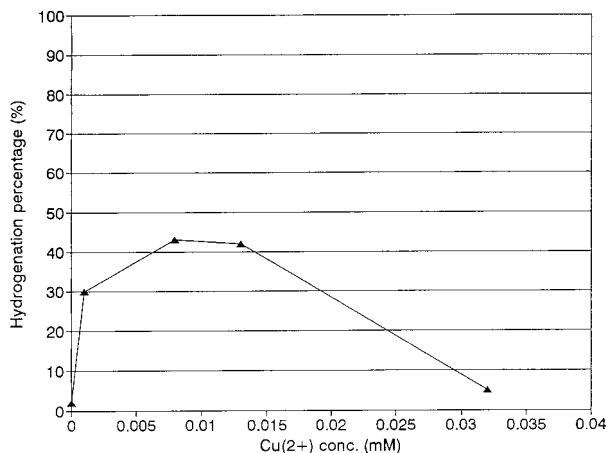


Figure 3 Hydrogenation percentage with different molar concentrations of copper ion in the LP latex system (230 nm).

SP and LP systems. This result indicated that under these conditions the concentrations of copper ions at the particle surfaces are appropriate to enhance the extent of the diimide/double-bond reduction and to minimize the diimide disproportionation reaction. However, at higher copper ion concentrations, the rate of diimide formation would be faster; this would enhance the diimide disproportionation reaction compared to the reduction reaction. At even higher copper ion concentrations, some free copper ions may also be present in the water medium; this would make the $\text{H}_2\text{N}-\text{NH}_2/\text{H}_2\text{O}_2$ reaction to occur mostly in water. As a result, the double-bond reduction will be decreased to a very low level.

Figure 4 also shows that the overall DH for the LP system is about two-fold lower than that obtained for the SP system around the peak region. As mentioned above, the reactions between $\text{H}_2\text{N}-\text{NH}_2$ and H_2O_2 could occur in either the water phase or at the particle surface, regardless of the presence of copper ions. With appropriate amounts of copper ions localized only at the particle surface, the rate of formation of diimide at the particle surfaces would be much higher than in the water medium. However, this competition reaction always exists during the entire hydrogenation process. As shown in Figure 4, the condition needed for reaching the maximum DH is determined by the surface area density of copper ions at the particle surface for either the SP or LP system. Thus, the total number of copper ions at the particle surface is limited by the surface area of the total latex particles. In other words, the total catalyzed reaction sites for the formation of

diimide are limited by the total surface area. This limit would certainly be reflected by the overall rate of double-bond reduction competing with the reaction in water. At the optimum surface area density of copper ions, which is about the same for either the SP or LP system, i.e., $2 \text{ Cu}^{2+}/1000 \text{ nm}^2$ surface, the total number of copper ions in the LP latex system is much less than that for the SP latex system because of the much smaller total surface area for the latexes with the same solids content (20%). This could be one of the reasons that led to the decreased overall DH for the LP system. Another possible factor that could influence the DH for the LP system is the increased distance for the diffusion of the diimide molecules from the surface to react with double bonds residing in the inner side of the particles due to the larger particle size. The longer the diffusion distance, the longer the lifetime needed for the diimide before reaching a double bond and the greater the probability for the disproportionation reaction of diimide itself to occur during the diffusion process. Obviously, the relative extents of these two competitive reactions are decided by the local concentrations of double bonds and diimide molecules, which are dependent on the rates of diffusion of both polymer chains and diimide molecules. To further investigate the mechanism of this hydrogenation process, a series of SBR latexes with different gel fractions and particle sizes was used in subsequent hydrogenation reactions.

Distribution of Double Bonds in the Latex Particles After Hydrogenation

First of all, parallel hydrogenation reactions were carried out on two latex systems with high and

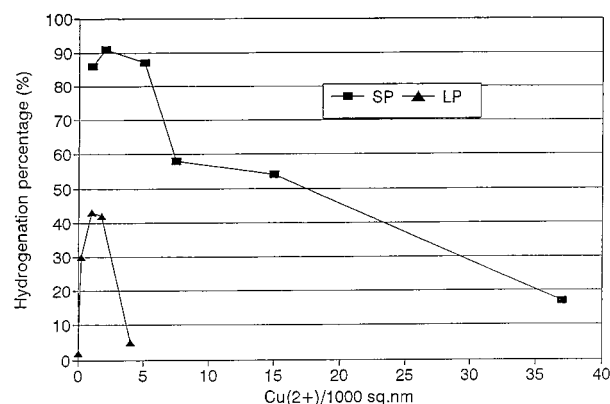


Figure 4 The relationship between the hydrogenation percentage and the surface area density of copper ions at the particle surface ($\text{Cu}^{2+}/1000 \text{ nm}^2$) for the SP and LP latex systems.

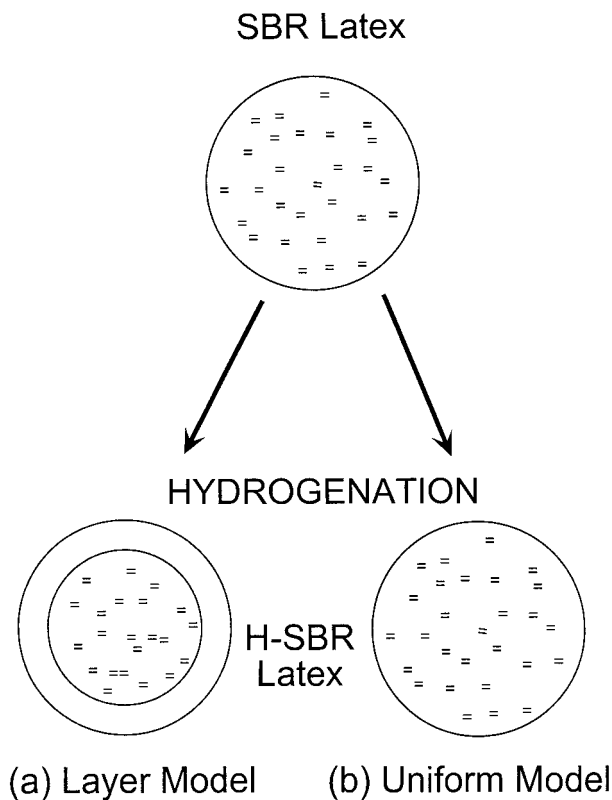


Figure 5 Two models for the distribution of double bonds in hydrogenated SBR latex particles: (a) layer model; (b) uniform model.

low gel fractions (HG, 95% and LG, 23%); the average particle sizes for both latexes were 60 and 50 nm, respectively. High degrees of hydrogenation were attained in both systems, i.e., 91 and 93% for the HG and LG system, respectively. Although the mobilities of polymer chains in the latex particles for these two systems are expected to be quite different, it seems that the high gel fraction does not exert much influence on the diffusion of the small diimide molecules generated at the particle surfaces. In other words, the particle size is small enough for the diimide molecules to diffuse from the surface to the center of the particle.

For latexes with larger particle sizes, as shown in Figure 3, a low degree of hydrogenation of only 42% was reached at the optimum hydrogenation condition after a 1/1 molar ratio of the $\text{H}_2\text{NNH}_2/\text{H}_2\text{O}_2$ redox system to residual double bonds during hydrogenation was employed. In this type of partially hydrogenated SBR latex, two possible structures could be present. Since the hydrogenation reactions take place during the process in which the diimide hydrogenation agent which is

formed at the particle surfaces diffuses into the interior of the particles, a relatively highly hydrogenated layer could form close to the particle surface. However, diffusion of the soft SBR chains inside of the particles occurs at all times, especially at the hydrogenation temperature of 50°C. This diffusion of polymer chains would tend to diminish the formation of the hydrogenated layers and would instead lead to a structure in which the double bonds are uniformly distributed. We can define these two kinds of model structures, as shown in Figure 5, as either a layer model (a) or a uniform model (b). To verify these two possible models, repeat hydrogenation reactions were carried out in another series of SBR latexes with high and low gel fractions using SBR-L-LG and SBR-L-HG latexes as described in Table I.

Figure 6 shows the degree of hydrogenation after each hydrogenation process. The numbers 1, 2, and 3 on the X-axis represent the molar ratio of the hydrogenation redox components ($\text{H}_2\text{NNH}_2/\text{H}_2\text{O}_2$) to the residual double bonds in the SBR latex corresponding to three repeat hydrogenation reactions. A time interval of 8 h was allowed between hydrogenation reactions. Figure 6 shows that the degree of hydrogenation increased gradually for the LG system after each hydrogenation. The differences in the hydrogenation levels between runs were 37, 22, and 12%. These numbers support the uniform model, i.e., double bonds in the latex particles are uniformly distributed at all times due to the diffusion of polymer chains. If 37% of the double bonds in the particles would be hydrogenated after each hydrogenation process, it can be easily calculated that the increased percentages of the hydrogenation between the first

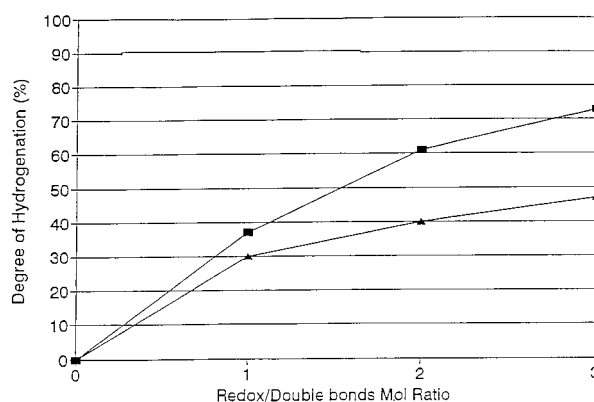


Figure 6 Degree of hydrogenation after each run for three successive 1/1 molar ratio hydrogenations of the (■) high gel (HG) and (▲) low gel (LG) SBR latex systems (particle sizes: HG = 240 nm; LG = 230 nm).

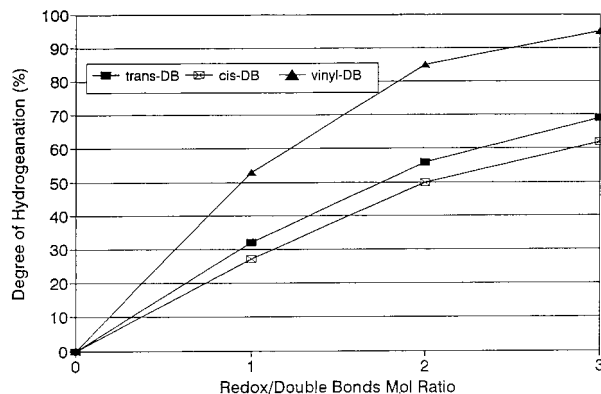


Figure 7 Degree of hydrogenation for each type of double bond in the LG SBR latex system; particle size = 230 nm.

and the second, and the second and the third, hydrogenation should be 23 and 11.5%, respectively. The experimental results obtained, i.e., 22 and 12% (differences between the first and the second, and the second and the third hydrogenations), are very close to these values. The extent of the hydrogenation zone (i.e., thickness) inward from the surface of the particles, which should be about 37% of the total volume of the particle, is estimated to be about 20 nm. However, this model obviously does not fit the HG latex system. The increase in hydrogenation after each run for the HG system is much lower than that of the LG system, especially after the first run. The increase in the degree of hydrogenation after each run was shown to be 30, 10, and 7%, respectively. This result suggests that a layer close to the surface of the particles which has a relatively higher degree of hydrogenation due to the low mobility of those highly crosslinked polymer chains may exist. The concentration of double bonds in this layer is lower than the inner portion of the particle after the first run. As a result, the disproportionation reaction among diimide molecules becomes more competitive in this layer and, consequently, results in a low degree of hydrogenation after the second and third runs. An alternative explanation for this observation may be that the diimide remained copper bound.

This explanation can be further confirmed by investigating the degree of hydrogenation for different types of double bonds in the SBR latex systems. The percentages of the three types of double bonds, i.e., *trans*, *cis*, and vinyl, in the SBR latex system are 62, 18, and 20%, respectively. Kinetic studies²¹ on the rate of the reaction of diimide with olefins showed that the hydrogenation rate

for vinyl double bonds is almost 10 times faster than those for *trans* and *cis* double bonds. Figure 7 shows the degree of hydrogenation for each type of double bond in the LG latex system. After the first run, more than 50% of the vinyl double bonds were hydrogenated, while the degrees of hydrogenation for the *trans* and *cis* double bonds were about 30%. More significantly, almost all of the vinyl double bonds were hydrogenated after the third run, while there were still 30% of the *trans* and *cis* double bonds remaining in the system. For the uniform model, all the double bonds are highly mobile, and the possibility that any type of double bond is present in the hydrogenation zone depends only on the concentrations of the bonds instead of their initial loci. Thus, vinyl double bonds, which have a much higher reaction rate with diimide, should certainly be consumed faster. This is not the case for the HG latex system. Figure 8 shows the analysis for the HG latex under the same conditions as that shown in Figure 7. The differences between the percentage of hydrogenation for each type of double bond are very small compared with the LG latex system. After the third run, the vinyl double bond does not exhibit a significantly higher percentage of hydrogenation. As mentioned above, the mobility of polymer chains in these HG latex particles is greatly restricted and all of the double bonds are fixed at a specific location after the latex particle is formed. Consequently, only those double bonds that are initially located in the hydrogenation zone could be hydrogenated. In this way, the percentage of hydrogenation for each type of double bond should be about the same.

Figure 9 shows TEM micrographs of the LG (C) and HG (D) latex particles after the third

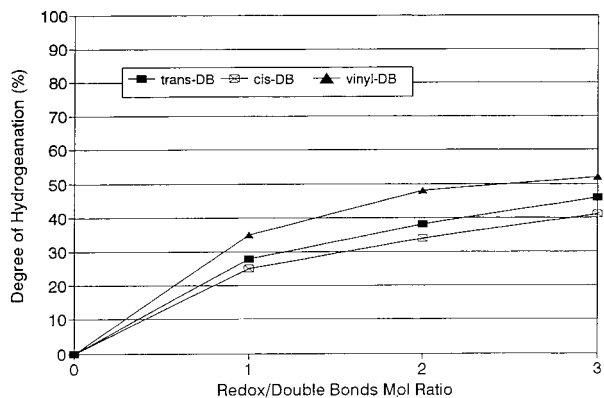


Figure 8 Degree of hydrogenation for each type of double bond in the HG SBR latex system; particle size = 240 nm.

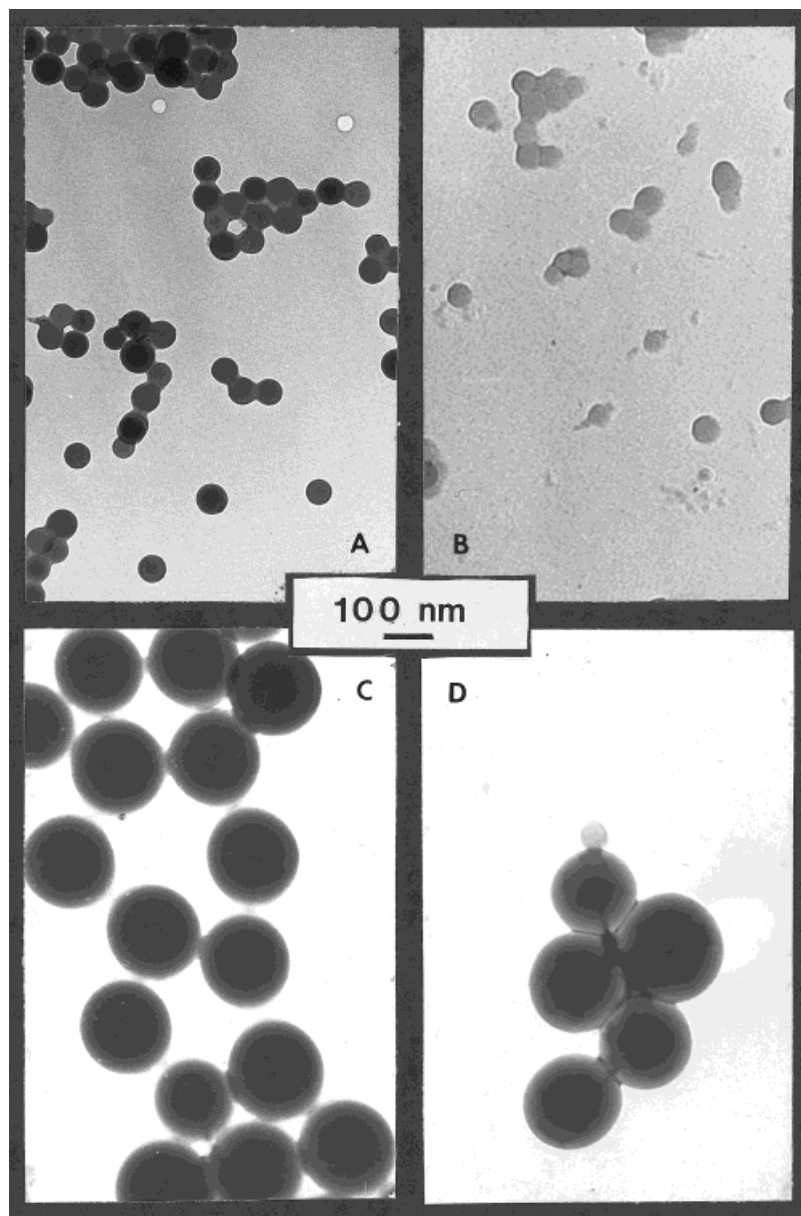


Figure 9 TEM micrographs of (A) nonhydrogenated SBR latex, 80 nm in diameter; (B) completely hydrogenated SBR latexes, 80 nm in diameter; (C, D) partially hydrogenated SBR latex, 230 and 240 nm, respectively, for (C) LG and (D) HG latexes.

hydrogenation step. Since the OsO_4 staining agent can only stain double bonds, lightly colored domains should indicate lower double-bond concentrations. For comparison, a control SBR latex (with no hydrogenation; particle size = 80 nm) (A) and the SBR latex with a degree of hydrogenation of 90% (B) are also shown. The nonhydrogenated SBR (A) shows relatively sharp particle edges because the concentration of the OsO_4 inside the particle is high. On the other hand, the 95% hydrogenated latex (B) exhibits a much

lighter color due to the small amount of the double bonds available for OsO_4 staining. For the partially hydrogenated cases (C) (particle size = 230 nm) and (D) (particle size = 240 nm), the contrast between the center and the surface of the hydrogenated LG particles (C) is quite vague compared with that of HG particles (D), where a sharp contrast can be observed. The contrast shown in Figure 9(C) could simply be the contrast due to thickness differences. The sharp contrast shown in Figure 9(D), on the other hand, could represent

contrast due to a concentration difference in addition to thickness. It is interesting to note that there is a lightly colored small particle appearing in Figure 9(D). The light color indicates that this particle is highly hydrogenated throughout the particle because of its small particle size, even though it has a high gel fraction.

Finally, it should be mentioned that the gel fractions of SBR latexes were found to increase after the hydrogenation. The gel fractions for SBR-S-LG and SBR-L-LG latexes used in this study increased from 41 and 34% to 52 and 38%, respectively, after the equimolar hydrogenation process (i.e., molar ratio of the $\text{H}_2\text{NNH}_2/\text{H}_2\text{O}_2$ redox system to residual double bond = 1/1). The redox system used for the hydrogenation could have generated radicals which induced the formation of crosslinks among residual double bonds in the SBR latex particles. The increase of gel fractions after hydrogenation might also be caused by the formation of crystalline hydrogenated SBR, which does not dissolve in toluene at the temperature (23°C) used for the gel fraction measurements.

SUMMARY

From the results shown above, it can be concluded that in addition to other parameters, such as temperature, pH, and the addition rate of the hydrogen peroxide, the surface area density of copper ions at the latex particle surface is a key factor which influences the optimum conditions for hydrogenation. The optimum surface area density is estimated as $2 \text{ Cu}^{2+}/1000 \text{ nm}^2$. The hydrogenation reaction does occur radially from the particle surface inward. The gel fraction in the latex particles does not influence the diffusion of diimide molecules very much, but greatly influences the mobility of polymer chains within the particles. Therefore, the LG latex system fits the uniform model describing the hydrogenation reaction, while the HG latex is closer to the layer model. The hydrogenation zone (thickness) from the particle surface inward where diimide molecules can diffuse before disproportionation reactions occur among themselves is about 20 nm.

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