Hydrogenation of Acrylonitrile–Butadiene Rubber Latexes

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ABSTRACT: The hydrogenation of acrylonitrile–butadiene rubber (NBR) latex was carried out by a system consisting of hydrazine hydrate and hydrogen peroxide, with boric acid as catalyst. Highly saturated hydrogenated NBR (HNBR) latex was obtained through the optimization of the reaction conditions. The dried HNBR was found to be heavily gelled. The cause for the crosslink of dried hydrogenated NBR products was investigated. With the improvement of the hydrogenation system, that is, by adding gel inhibitor to the system, the crosslinking was controlled to a large extent, and dried HNBR with gel content of about 3% was prepared by the improved system. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 2072–2078, 2004

Key words: hydrogenation; acrylonitrile–butadiene rubber; latex

INTRODUCTION

Acrylonitrile rubber is widely used in the automotive, aerospace, and oil-well industries because of its high oil resistance properties.[1] However, a disadvantage of this material is its aging behavior, which is caused by the oxidation of the residual double bonds in the butadiene segments, which could deteriorate the properties of the polymer.

Further saturation of the residual double bonds through the hydrogenation process is the commonly used method to overcome this deficiency. Conventional hydrogenation processes of acrylonitrile–butadiene rubber (NBR) are carried out in polymer solution, using pressured hydrogen, rhodium, and palladium complex catalysts.[2–4]

There are some obvious problems with these kinds of hydrogenation processes. Besides the high cost of hydrogenation equipment and the noble metal catalyst systems, complex process, low efficiencies resulted from the limited solubility, and solvent-induced environmental concerns, there is only one state of the product obtained—bulk rubber. It is not feasible when a hydrogenated product is needed in the latex form.

Direct conversion of NBR latex into hydrogenated NBR (HNBR) latex is the common goal of the experts in this field. For this purpose much work has been done by many famous scientists.

Hydrogenation of NBR latex was conducted by Rempel[5] in 1984, and HNBR with the hydrogenation of 98% was obtained by using noble metal rhodium complex as catalyst and high-pressure hydrogen gas as the source of hydrogen in this process.

A breakthrough method for the direct conversion of NBR latex to HNBR latex without the use of high-pressure hydrogen gas, precious metal catalysts, organic solvent, and special facilities was developed by Wideman[6] in 1984. In this process, a hydrazine hydrate/hydrogen peroxide redox system was typically used with the copper ion as catalyst. HNBR product with 75–80% hydrogenation was obtained.

It was later revealed by Parker[7–9] that the conversion of NBR latex to HNBR latex by the Wideman technique is prone to a crosslinking side reaction that occurs concurrently with the desired reduction double bonds. This crosslinking reaction produces gelled or crosslinked saturated hydrogenated NBR latex particles. Processes for breaking up the gel structures through posttreatment with ozone, hydroxylamine, etc., were also introduced.

This method was then used by Bhowmick[10–12] for a series of studies on the hydrogenation of styrene–butadiene rubber (SBR) and carboxylated styrene–butadiene rubber (XSBR) latex. The possibility of crosslinkings during hydrogenation reaction was also mentioned.

A new process similar to Wideman's, but using boric acid instead of copper ion as catalyst, was developed by Belt[13] in 2000. The crosslinking problem during the hydrogenation process as Wideman described was overcome in this system. Soluble HNBR latex was obtained by this procedure. But the dry bale rubber was revealed to be gelled in the subsequent patents.[14,15]

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This work was conducted to optimize the reaction conditions of this new process for making highly saturated HNBR latex. The other important aspect of this work was to minimize the gel content in dried HNBR through our improved technique.

EXPERIMENTAL

Materials

NBR latex, with an acrylonitrile content of 33.3% and solid content of 26.3%, was obtained from Taiwan Nantex Industry Corporation Ltd. (Taiwan, China). Hydrazine hydrate (85%), hydrogen peroxide (30%), and boric acid were received from the standard sources.

Hydrogenation of NBR latex

NBR latex, 25 mL, containing 81.2 mmol C=C double bonds, was added to a 250-mL three-necked flask equipped with a dropping funnel, reflux condenser, and mechanical stirrer. A specific volume of 85% aqueous hydrazine hydrate was charged into the flask. The mixture was warmed to a particular temperature with stirring. A solution of hydrogen peroxide (30%) and boric acid (dissolved in water) was then introduced dropwise over a specific period of time.

Characterization

Infrared (IR) spectroscopy

IR analyses were performed on a Japanese NiCOLET 60SXB FTIR. The copolymers were analyzed as solution casting films from $CHCl_3$ solution of coagulated products on KBr plates.

Determination of the degree of hydrogenation

The unsaturation of the products was analyzed using Bromo-Iodometry method according to GB1676-81 (Chinese National Standards). This method has been proved by our group[16] to coincide with ^{1}H-NMR technique reported by Marshall.[17]

The C=C double bonds in rubber molecules react with excessive iodine bromide (IBr) reagent. The residual (IBr) is consumed by 10% solution of potassium iodide (KI) to form iodine molecules. Then the newly formed iodine molecules can be titrated with a standard solution of sodium thiosulfate. The unsaturation of the nitrile rubber before and after hydrogenation is calculated from formula (1), and the degree of hydrogenation is obtained through formula (2).

$$H_0 \text{ or } H_1 = (V_0 - V_1)C/2W \tag{1}$$

$$H = (H_0 - H_1)/H_1 \times 100\% \tag{2}$$

where V_0,V_1 are the volume of $Na_2S_2O_3$ solution consumed in blank (no polymer) and sample test respectively; C is the equivalent concentration of $Na_2S_2O_3$ solution; W is the weight of the sample in gram; H_0 ,H_1 are the unsaturation of NBR before and after hydrogenation; H is the degree of hydrogenation.

Determination of gel content in dried hydrogenated NBR

Dried HNBR 0.5 g (w_1) was put into 50 mL $CHCl_3$ and kept for 24 h. Vacuum filtration of the solution was conducted by using a G_2 abrasive funnel (w_2), and the gel containing funnel was dried at 60°C (w_3). Gel content can be calculated from the following formula:

$$\text{gel content} = (w_3 - w_2)/w_1 \times 100\%. \tag{3}$$

RESULTS AND DISCUSSION

IR analysis

Figures 1 and 2 show the IR spectra of NBR and hydrogenated NBR latex with 52, 71, and 96% hydrogenation respectively. It is confirmed from the IR spectra that the nitrile groups in the polymer chain is not reduced after hydrogenation reaction, since there is no peak at around 3500 cm^{-1} for —NH_2 group and the distinct peak at 2237 cm^{-1} for CN group still exists. As the level of hydrogenation increases, peak at 970 cm^{-1} due to 1,4-*trans* unit and the absorbance at 917 cm^{-1} for 1,2-vinylic in butadiene segment gradually decrease. The absorbance at 723 cm^{-1} due to $(\text{—}CH_2\text{—})_{n\geq 4}$ rocking vibration slightly increases with hydrogenation. (Peaks between 2240 and 2800 cm^{-1} are due to carbon dioxide in air).

Effect of process parameters

The effect of different reaction parameters on NBR latex hydrogenation was studied by variation of the addition manner for hydrogen peroxide, the concentration of boric acid and hydrazine hydrate, reaction temperature, and reaction time.

Effect of addition manner for hydrogen peroxide

Three methods, batchwise (adding 1/6 of the total volume each time), dropwise, and dropwise plus stirring at room temperature after finishing addition, were used for the addition of hydrogen peroxide. The hydrogenation reaction was carried out in the presence of 95.1 mmol hydrazine hydrate and 79.3 mmol hydrogen peroxide and 2.64 mmol boric acid catalyst at 60°C for 6 h. The results are shown in Figure 3.

Of the above three manners, dropwise plus stirring at room temperature after finishing addition is the

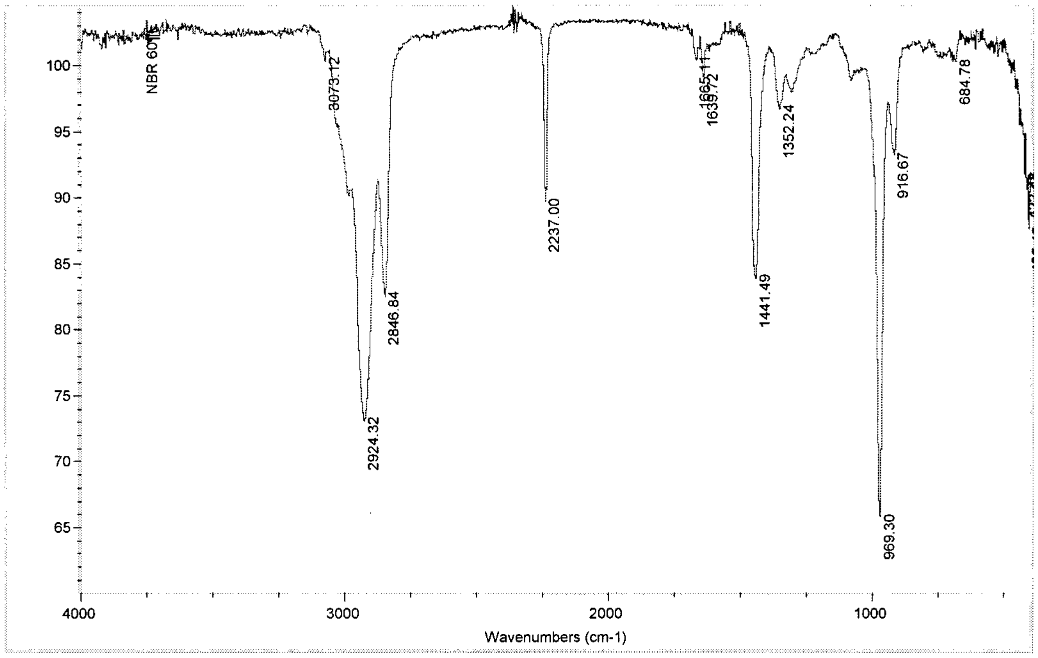

Figure 1 IR spectrum of NBR.

most effective way. The lowest hydrogenation was obtained in the batchwise one.

Comparing the batchwise with the dropwise manner, both have the same reaction time, but in the batchwise manner a large amount of hydrogen peroxide is instantaneously added to the system in one addition. A fraction of it may decompose before taking part in redox reaction, resulting in the decrease of diimide molecules. And also by this manner, lots of diimide molecules are instantaneously formed, so the possibility of diimide disproportionation reaction would increase.

The difference between dropwise and dropwise plus stirring at room temperature after finishing addition is the postreaction. The later is more effective than the former. This result indicates that finishing the addition of hydrogen peroxide does not mean the end of the reaction; the C═C double-bond reduction by the *in situ* resulting diimide is a slow process. It takes time for all of the diimide molecules to reach the

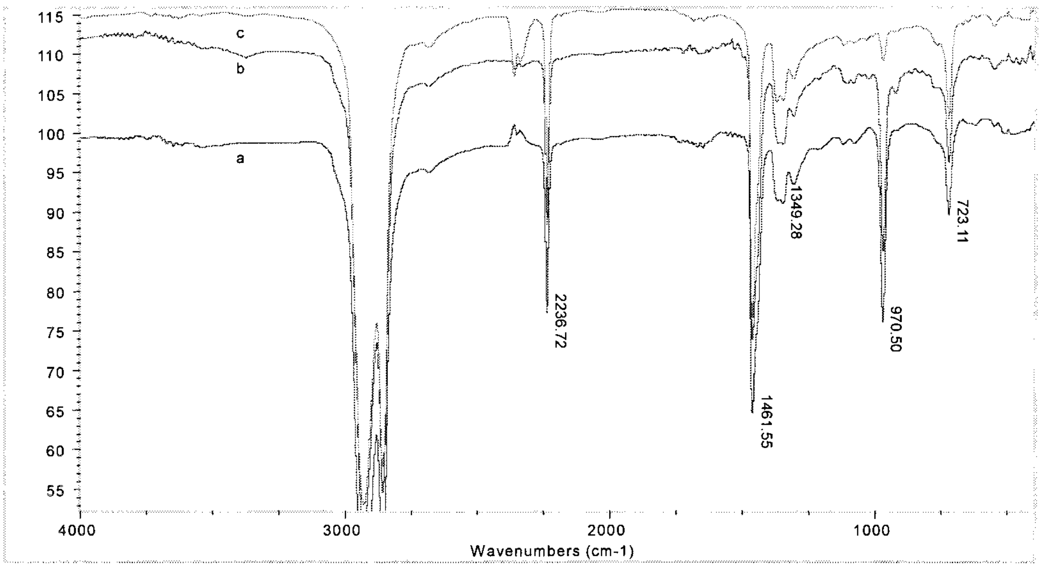

Figure 2 IR spectra of hydrogenated NBR with (a) 52%, (b) 71%, and (c) 96% hydrogenation, respectively.

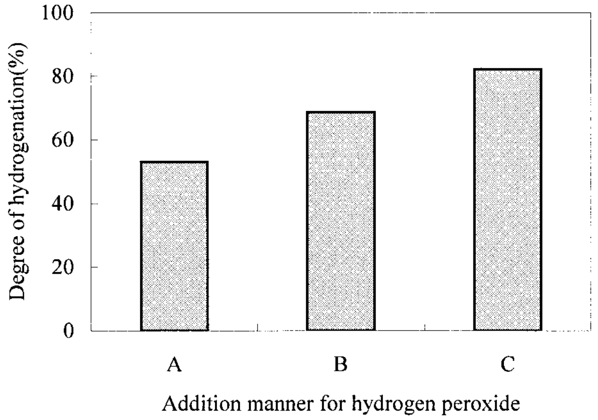

Figure 3 Effect of the addition manner for hydrogen peroxide on degree of hydrogenation (A) batchwise, (B) dropwise, and (C) dropwise plus stirring at room temperature after finishing addition.

double bonds, react with them, and get a high saturation. For simple operation and relative comparison, the dropwise manner was used in the following experiments.

Effect of the concentration of boric acid catalyst

The effect of boric acid concentration on the percent hydrogenation was studied for a period of 6 h at 60°C in the presence of 95.1 mmol hydrazine hydrate and 79.3 mmol hydrogen peroxide. The mol ratio of boric acid to double bonds was varied from 0.025 to 0.133. The hydrogenation increases rapidly with the ratio from 0.025 up to 0.05 and followed by slightly increase with the catalyst concentration (Fig. 4). Increasing the concentration of boric acid makes the rate of the diimide formation faster, and enhances the extent of the diimide/double-bond reduction.

Effect of the concentration of hydrazine hydrate

The hydrogenation reaction was conducted by varying the mol ratio of hydrazine hydrate to double bonds from 1 to 2 (the mol ratio of hydrazine hydrate to hydrogen peroxide remains unchanged) at 60°C, in the presence of 2.64 mmol boric acid for 6 h of reaction time. The results are plotted in Figure 5. The level of hydrogenation increases with the mol ratio of hydrazine hydrate to double bonds. With the increase of mol ratio of hydrazine hydrate to double bonds, more diimide molecules will be derived from the redox system, the rate of the diimide/double bonds reduction will increase. The hydrogenation of 94.7% was obtained when 2 mol of hydrazine hydrate per mole butadiene was used.

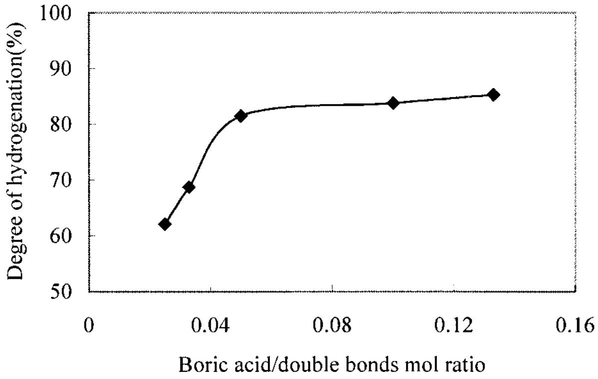

Figure 4 Effect of catalyst (boric acid) concentration on degree of hydrogenation. Hydrazine hydrate 95.1 mmol, hydrogen peroxide 79.3 mmol, temperature 60°C, time 6 h.

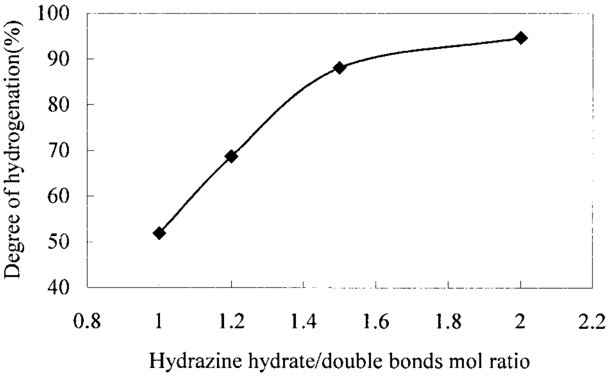

Figure 5 Effect of hydrazine hydrate concentration on degree of hydrogenation. Boric acid 2.64 mmol, temperature 60°C, time 6 h.

Effect of reaction temperature

The hydrogenation reaction was studied from 40 to 80°C in the presence of 95.1 mmol hydrazine hydrate, 79.3 mmol hydrogen peroxide, and 2.64 mmol boric acid for 6 h. The extent of hydrogenation increases with an increase in temperature up to 70°C; maximum hydrogenation of 81.3% is achieved. After 70°C, the degree of hydrogenation decreases because of the decomposition of the reactants at higher temperature (Fig. 6).

Effect of reaction time

The effect of reaction time was studied at 60°C in the presence of 95.1 mmol hydrazine hydrate, 79.3 mmol hydrogen peroxide, and 2.64 mmol boric acid catalyst. The results over a range of time from 1 to 12 h are plotted in Figure 7. With increase in reaction time, the level of hydrogenation increases. Prolonging reaction time means adding hydrogen peroxide in a slower rate, that makes the formation of diimide in a reasonable way, provides time for diimide molecules to diffuse, react with the double bonds, and also minimizes the possibility of hydrogen peroxide decomposition and diimide disproportionation.

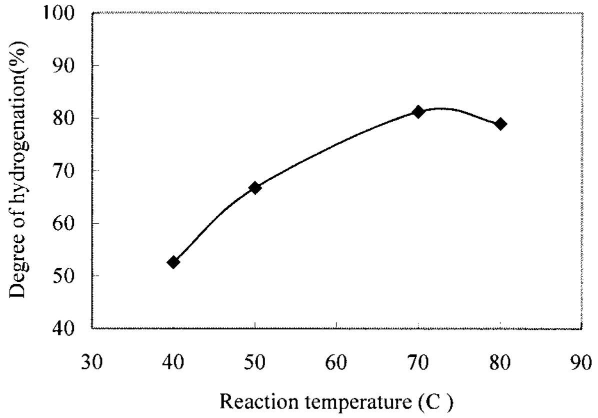

Figure 6 Effect of reaction temperature on degree of hydrogenation. Hydrazine hydrate 95.1 mmol, hydrogen peroxide 79.3 mmol, boric acid 2.64 mmol, time 6 h.

Source substance leading to crosslinking in dried HNBR

Soluble HNBR latex (coagulated HNBR products are completely soluble in $CHCl_3$) with hydrogenation of over 90% was obtained by optimization of the hydrogenation process. Dried HNBR was found to be heavily gelled no matter what kind of drying methods and what solvents were used. Effect of drying methods on gel content and solubility of dried HNBR in different solvents are shown in Figure 8 and Table I.

Hydrogenated NBR in bulk form is the other state except latex required in practical applications. To take control of the crosslinking in dried HNBR, the course of the crosslinking was examined.

Combination experiments were carried out by reacting hydrazine hydrate (129 mmol), hydrogen peroxide (120 mmol), and boric acid (10.5 mmol) with NBR latex respectively first, followed by two of the three components, and finally the whole system at 40°C for 6 h. The results are shown in Table II. Gel was found in all dried products obtained from the reaction process in the presence of hydrogen peroxide, whether hydrogen peroxide acted with NBR latex alone or in combination with other components. And in other experiments involving hydrazine hydrate, boric acid, and their combination without hydrogen peroxide, the level of gel content is similar to that in the control experiment.

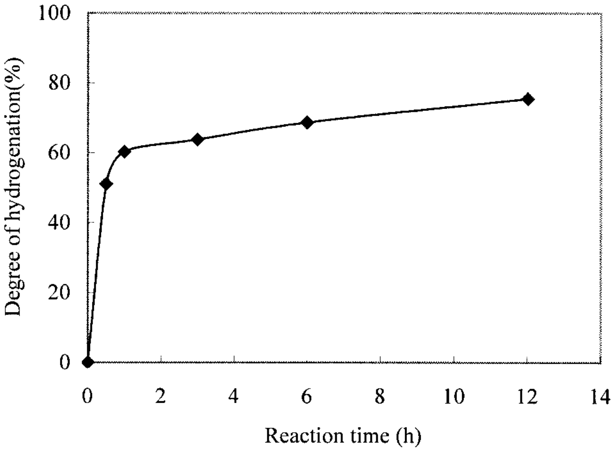

Figure 7 Effect of reaction time on degree of hydrogenation. Hydrazine hydrate 95.1 mmol, hydrogen peroxide 79.3 mmol, boric acid 2.64 mmol, temperature 60°C.

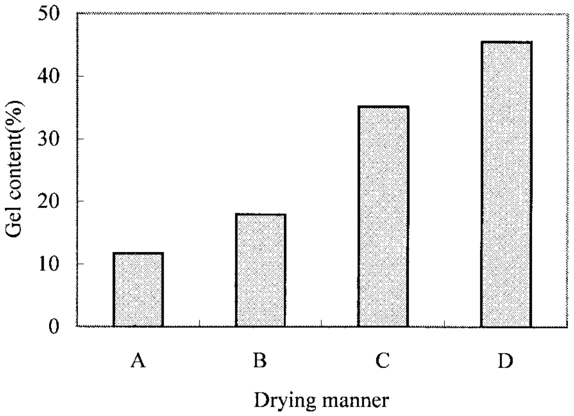

Figure 8 Effect of drying manner on gel content. (A) Drying in air at room temperature, (B) drying in glove box (N_2 atmosphere), (C) drying under vacuum at room temperature, and (D) drying in oven at 60°C, time 1 h.

For further confirmation of this result, hydrogen peroxide with concentrations of 3, 5, 10, and 20% (wt) was used to act with NBR latex in the same procedure as the hydrogenation reaction. All resulting dried polymer products are gelled, too (Table III). These results indicated that hydrogen peroxide is the key substance leading to crosslinking in dried HNBR.

Removal of the residual hydrogen peroxide

The following posttreatment methods were used to remove the residual hydrogen peroxide after hydrogenation:

1. heating the diluted hydrogenated latex to 90°C, stirring for hours for promoting the decomposition of hydrogen peroxide;

TABLE I
Solubility of Dried HNBR in Different Solvents

Solvents	Solubility
Chloroform	swell
Chlorobenzene	swell
Xylene	swell
Methyl ethyl ketone	swell
Methyl dichloride	swell
Acetone	swell

TABLE II
Results of the Components Reacting with NBR Latex

Reactants	Solubility of dried HNBR in $CHCl_3$[a]	Gel content (%)
NBR	+	0.8
30% H_2O_2	−	69.0
Boric acid	+	0.1
85% Hydrazine hydrate	+	1.1
85% Hydrazine hydrate + boric acid	+	1.3
30% H_2O_2 + boric acid	−	61.9
30% H_2O_2 + 85% hydrazine hydrate	−	51.9
30% H_2O_2 + 85% hydrazine hydrate + boric acid	−	67.2

Conditions: hydrazine hydrate 129 mmol, hydrogen peroxide 120 mmol, boric acid 10.5 mmol, temperate 60°C, time 6 h.

[a] "+" soluble, "−" insoluble.

2. treating the hydrogenated latex with 10% potassium iodide solution;
3. coagulating the latex in isopropanol, dissolving the wet polymer in chloroform, repeating this process for three times;
4. coagulating the hydrogenated latex in different media (isopropanol, 2% calcium chloride, 36% magnesium sulfide);
5. coagulating in different ways(dropping the latex into the coagulating agent or doing this in the opposite way).

Dried HNBR samples resulted from these treatments are all insoluble in chloroform. This result suggested that the crosslinking in dried HNBR is not induced by residual hydrogen peroxide after hydrogenation; hydrogen peroxide in the reaction system during hydrogenation is the cause of crosslinking.

Improvement of the redox system

TABLE III
Results of Hydrogen Peroxide Acting with NBR Latex

Concentration of H_2O_2 (%)	Gel content (%)
20	61.9
10	69.0
5	58.3
3	58.6

Conditions: hydrogen peroxide 120 mmol, temperature 60°C, time 6 h.

TABLE IV
Effect of Gel Inhibitors

Gel inhibitor	Degree of hydrogenation (%)	Gel content (%)
—	85	67.2
DTBMP	82	30.0
Hydroquinone	80	3.1

Conditions: gel inhibitor, 4% (weight to polymer); others as in Table II.

According to the properties of hydrogen peroxide, radicals may be generated by hydrogen peroxide; with the effect of hydrogen peroxide, the polymer may become a potential crosslinking group carrier that may function in the drying process after coagulation.

To minimize the gel content in dried HNBR, 2,6-di-tert-butyl-4-methyl phenol (DTBMP) and hydroquinone were used as gel inhibitors. The inhibitors were added into the reaction system before hydrogenation; the results are shown in Table IV.

Gel content in dried HNBR was minimized to a large extent compared with the control experiment. Hydroquinone is more effective than DTBMP on the control of crosslinking. This may be due to the incompatibility of DTBMP with the reaction system, although an emulsion was formed before application. Hydroquinone is a water-soluble chemical, it mixes well with the reaction system, radicals generated in the system will be effectively eliminated, and the formation of the potential crosslinking group on the polymer will be avoided.

Another series of confirmation experiments were performed by adding hydroquinone to the reaction of NBR latex with 3, 5, 10, and 20% hydrogen peroxide respectively. The results are listed in Table V.

In the above mentioned experiments (Table III) without hydroquinone, gel content in dried polymer is around 60% and it is significantly minimized to about 3% in the presence of hydroquinone. Hydroquinone is a powerful gel inhibitor for this system.

CONCLUSIONS

The hydrogenation of NBR latex was carried out by a redox system consisting of hydrazine hydrate and

TABLE V
Results of H_2O_2 Acting with NBR Latex in the Presence of Hydroquinone

Concentration of H_2O_2 (%)	Solubility of dried polymer in $CHCl_3$	Gel content (%)
20	Soluble	3.1
10	Soluble	1.6
5	Soluble	—
3	Soluble	3.6

Conditions as in Table III.

hydrogen peroxide, with boric acid as catalyst. The saturation extent of NBR through hydrogenation was proved by the comparison of IR spectra of NBR and HNBR with different hydrogenation. The optimization of the reaction conditions was investigated. The increase of the mol ratios of hydrazine hydrate, boric acid to C=C double bonds and the prolongation of reaction time are favorable to the extent of hydrogenation. Of the three addition manners for the addition of hydrogen peroxide—batchwise, dropwise, and dropwise plus stirring at room temperature after finishing addition—the third one is the most effective way. The lowest hydrogenation was obtained with the batchwise method. Soluble hydrogenated NBR in latex form with the hydrogenation of over 90% was obtained. Dried HNBR was found to be heavily gelled. The reactant, hydrogen peroxide, was the source leading to the formation of gel in bulk hydrogenated NBR. With the improvement of the hydrogenation system, that is, adding the powerful gel inhibitor hydroquinone to the system before hydrogenation, crosslinking is controlled to a large extent, and bulk HNBR with gel content about 3% was prepared in the presence of hydroquinone.

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