# Hydrogenation of NBR Latex by Diimide Reduction Using Selenium Catalysts

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**ABSTRACT:** Acrylonitrile–butadiene rubber (NBR) latex was hydrogenated using diimide in the presence of selenium catalysts under an oxygen atmosphere. The process has been optimized and is extremely effective in the hydrogenation of NBR latex, with more than 3350 carbon–carbon double bonds reduced per atom of selenium in 5 h at 60°C. The amount of gel formed was controlled with gel inhibitors such as Irganox. This process constitutes a new route for obtaining totally hydrogenated acrylonitrile–butadiene polymer with low amounts of gel and very low amounts of selenium contaminants. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 1390–1394, 2010

**Key words:** hydrogenation; NBR latex; catalysis; diimide; selenium

## INTRODUCTION

Hydrogenation gives nitrile–butadiene rubber (NBR) improved chemical and thermal properties.[1,2] The hydrogenated product (HNBR) has greater resistance to oils and solvents, oxygen and ozone, ultraviolet radiation, and other chemical attacks than nitrile rubber.[3]

The conventional catalytic hydrogenation of NBR is performed in organic solvents under hydrogen pressure, using late-transition-metal catalysts, such as rhodium,[4] ruthenium,[5–9] or palladium.[6–10] An alternative is the noncatalytic hydrogenation of NBR, which has been performed in solution using a combination of hydrazine and an appropriate oxidant, such as potassium azocarboxylate, arylsulfonylhydrazine, or *p*-toluene sulfonylhidrazide.[11]

The direct hydrogenation of NBR latex, which overcomes the drawbacks of high costs and environmental impacts associated with organic solvents, has been described using rhodium catalysts.[12] The experience with the hydrogenation of NBR using gaseous hydrogen and transition-metal catalysts showed that this process is relatively expensive and has severe drawbacks, such as the amount of metal retained in the polymer and the formation of gel.

The use of hydrazine, in the presence of hydrogen peroxide and boric acid or cupric ion,[13–18] opened a new avenue because the equipment needed for an atmospheric pressure reaction is simple. The observed crosslinking problems have been partially overcome using additives and optimized reaction conditions.[17]

Herein, we show that NBR latex can be hydrogenated using an original system, based on selenium catalysts under an oxygen atmosphere. We show that the process occurs by diimide forming from hydrazine, through the action of oxygen and diimide and with selenium as the activator.[19,20]

## EXPERIMENTAL

### Materials

The NBR latex 3350 was supplied by Petroflex, containing 33% mol % acrylonitrile units, 11 mol % vinylic carbon–carbon double bond units, and 56% mol % 1,4-carbon–carbon double bonds units.

The reagents utilized were hydrazine 64% from Acros Organics, selenium (as 100 mesh powder) from Aldrich, and oxygen gas 99.99% from Air Liquids.

### Hydrogenation of the NBR latex

The experiments were performed in a 0.5-L glass reactor with a mechanical stirrer, condenser, and addition funnel.

NBR latex solution, selenium, and hydrazine were added to the reactor at each 2-h timepoint. The

temperature was maintained at 60°C, and oxygen gas was flowed at 0.5 L/min or 1 L/min for 8 h.

After the reaction, the latex was coagulated by adding a methanol solution of antioxidant (1 wt %) and an aqueous solution of NaCl (20 wt %). While stirring at 60°C, sulfuric acid (3.5 wt %) was added until the pH reached 4, to eliminate soap and organic acids. The product was filtered and dried at 60°C.

## Characterization

The $^1$H NMR spectra were obtained on a Varian VXR 200 operating at 200 MHz. The chemicals shifts were expressed in ppm and calculated in relation to TMS, an internal standard. IR spectra were obtained on a Bomen FTLA 2000-100 spectrometer operating in the 4000–400 cm$^{-1}$ range. The NBR film was prepared by evaporation of the latex on ZnSe rectangular cell windows. The spectra are available as Supporting Information. The residual catalyst in the polymer was determined using optical emission spectroscopy on Perkin Elmer Optima 2000 DV equipment.

## Determination of the degree of hydrogenation

The conversion of NBR was calculated by IR spectroscopy using the areas under the peaks representing olefinic units at 969 cm$^{-1}$ (=C—H bending of 1–4 units) and 916 cm$^{-1}$ (=C—H bending of vinylic units). The peak for nitrilic groups at 2235 cm$^{-1}$ (—C≡N stretching) was assumed to remain constant.

## Determination of gel content

The hydrogenated product was dried, and 0.5 g was put into 50 mL of methylethylketone for 24 h. After the solution was filtered using a G2 filter, the funnel was dried at 60°C, cooled, and weighed.

## RESULTS AND DISCUSSION

The hydrogenation of NBR latex was systematically studied using selenium catalysts and varying reaction parameters, such as temperature, reaction time, use of antioxidant, and amounts of catalyst, oxygen, and hydrazine.

The conditions used for reference were as follows: 11.04 g of NBR latex (0.124 mol of carbon–carbon double bonds), 10.03 g of hydrazine (0.2 mol), 0.011 g (0.14 mmol) of selenium, 0.5 L/min of oxygen, and 8 h of reaction. The conversion of carbon–carbon double bond was determined by IR spectroscopy and $^1$H NMR, as previously described.[6]

The use of selenium as an activator enhances the reaction rate for the formation of the diimide intermediate,[20] facilitating the oxidation of hydrazine in an oxidizing atmosphere. Table I (entries 3, 5, and 6) shows that increasing the amount of selenium has a strong effect on the efficiency. The hydrogenation grows from 46% with 0.07 mmol of Se (entry 5) to 100% with 0.25 mmol of Se (entry 6) in a system that uses a 0.5 L/min of oxygen flow.

Selenium as used in these runs is a solid; therefore, its granulometry can affect the process, as shown in Figure 1, in which reaction runs performed with 100 and 200 mesh selenium powders are

**TABLE I**
**NBR Latex Hydrogenation by Diimide Method in the Presence of Selenium**

| Entry | Temp. (°C) | Reaction parameters | | | | | Conversion | |
|---|---|---|---|---|---|---|---|---|
| | | C=C (mmol) | Catalyst (mmol) | Time (h) | Oxygen (L/min) | Hydrazine (mmol) | 1,4 (%) | 1,2 (%) |
| 1[a] | 25 | 124 | 0.14 | 8 | 0.5 | 200 | 2 | 10 |
| 2[a] | 40 | 124 | 0.14 | 8 | 0.5 | 200 | 9 | 43 |
| 3[a] | 60 | 124 | 0.14 | 8 | 0.5 | 200 | 75 | 100 |
| 4[a] | 70 | 124 | 0.14 | 8 | 0.5 | 200 | 75 | 100 |
| 5[a] | 60 | 124 | 0.07 | 8 | 0.5 | 200 | 46 | 64 |
| 3[a] | 60 | 124 | 0.14 | 8 | 0.5 | 200 | 75 | 100 |
| 6[a] | 60 | 124 | 0.25 | 8 | 0.5 | 200 | 100 | 100 |
| 7[b] | 60 | 67 | 0.07 | 1 | 1 | 100 | 14 | 43 |
| 8[b] | 60 | 67 | 0.07 | 3 | 1 | 100 | 89 | 100 |
| 9[b] | 60 | 67 | 0.07 | 5 | 1 | 100 | 100 | 100 |
| 10[b] | 60 | 67 | 0.03 | 5 | 1 | 100 | 83 | 100 |
| 11[b] | 60 | 67 | 0.02 | 5 | 1 | 100 | 77 | 100 |
| 12[c] | 60 | 67 | 0.07 | 8 | 1 | 64 | 89 | 100 |
| 13[c] | 60 | 67 | 0.07 | 8 | 1 | 100 | 100 | 100 |
| 14[c] | 60 | 67 | 0.07 | 8 | 1 | 128 | 100 | 100 |

[a] Reaction conditions: 11.04 g of NBR latex and 10.03 g of N$_2$H$_4$.
[b] Reaction performed with 5.52 g of NBR latex and 5.15 g of N$_2$H$_4$.
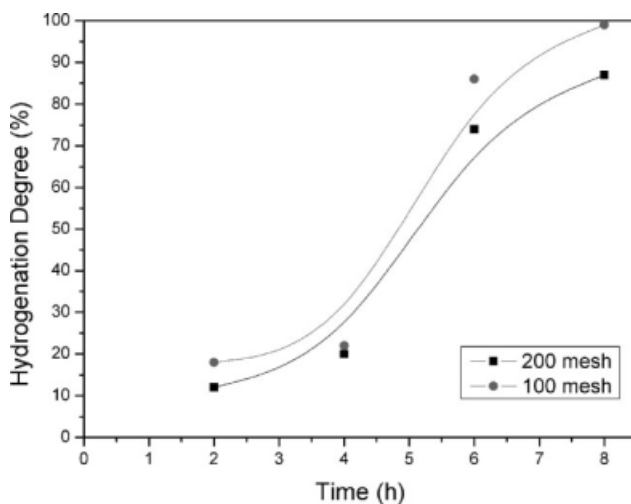[c] Reaction performed with 5.52 g of NBR latex and N$_2$H$_4$ in different amounts.

**Figure 1** Homogeneous hydrogenation of the NBR by the diimide method using selenium catalysts with different granulometry.

compared. It is clear that, with a more finely divided powder, the system becomes more efficient, as the process effectively occurs at the surface of the selenium, which grows as the surface area decreases.

As shown in Table I, the hydrogenation of NBR is sensitive to several reaction parameters, such as temperature, amount of catalyst, time, oxygen flow and amount of hydrazine.

Increasing the reaction temperature from 25 to 60°C enhanced the conversion from 2 to 75% (entries 1–3), but a further increase had no further effect (entry 4). This is not surprising, because it is well known that hydrazine is not stable at higher temperatures, and that its degradation compromises the capacity of the system in the hydrogenation process.[1,2]

The reactor was fed with 5.52 g of NBR latex (67 mmol of C=C), 5.15 g of $N_2H_4$ (100 mmol of hydrazine), and 5.5 mg of selenium (0.7 mmol), with

oxygen flow of 1 L/min under stirring, and the study was performed for different reaction times (entries 7–9). Entry 9 in Table I shows that, after 5 h, there was 100% hydrogenation of 67 mmol of double bonds. It is worth noting that the hydrazine to carbon–carbon double bond ratio $[N_2H_4]/[C=C]$ is 1.4, a value considered low in the current literature.

When lower amounts of catalyst (entries 9–11) were used, the conversion yield decreased, but efficiency in terms of carbon–carbon double bond per selenium atom increased from 957 to 3350.

Upon increasing the amount of hydrazine added to the system from 64 (entry 12) to 100 mmol (entry 13), the conversion grew from 89 to 100%.

These results show that selenium catalysts are an excellent alternative for hydrogenation of NBR latex, because (i) the system is highly active with low amounts of catalyst, and (ii) the hydrazine to carbon–carbon double bond ratio $[N_2H_4]/[C=C]$ is as low as 1.4, which is far lower than current literature values ranging from 2 to 4.[17]

The best results for NBR latex hydrogenation with selenium catalysts indicate that 5.52 g of NBR latex (67 mmol of C=C) can be hydrogenated with 5.15 g of hydrazine (100 mmol) and 5.5 mg of selenium (0.07 mmol) under an oxygen flow of 1 L/min over 8 h of reaction with 100% reduction of carbon–carbon double bonds (entry 13).

## Mechanism for the hydrogenation with selenium

The hydrogenation of carbon–carbon double bonds in the presence of hydrazine, oxygen, and selenium is attributed to the action of diimide, formed in the first step of the reaction in a process catalyzed by selenium, as shown in Scheme 1.

This mechanism has been proposed based on the well-known reactivity of selenium in the decomposition of hydrazine-generating diimide.[20] In fact,
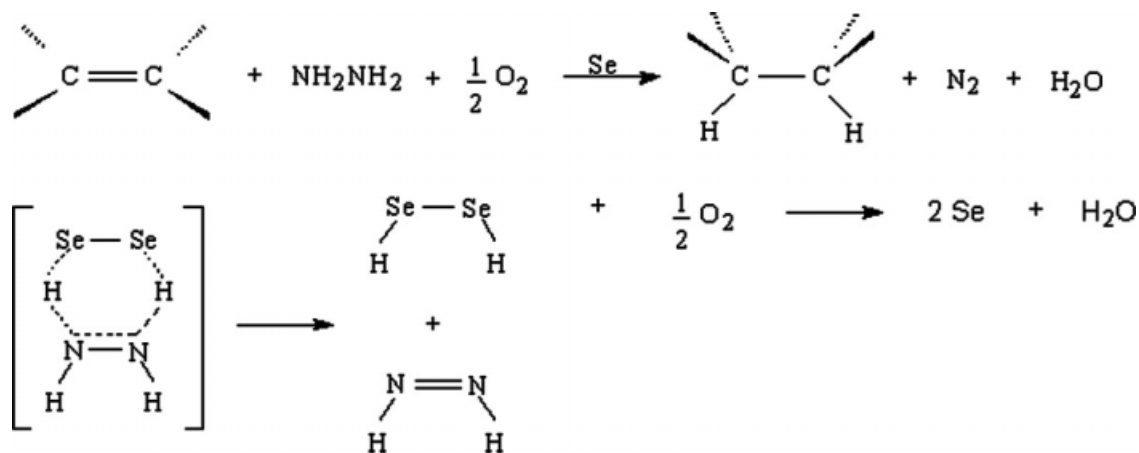


**Scheme 1** Mechanism of hydrogenation of olefins in the presence of hydrazine, oxygen, and selenium.[20]

**TABLE II**
**Effects of the Protocol of Addition of Hydrazine and Addition of Gel inhibitors on the Process of Hydrogenation[a] of NBR Latex**

| Entry | Addition of hydrazine | Addition of gel inhibitor | Conversion (%) | Amount of gel (%) |
|---|---|---|---|---|
| 15 | 1 fraction of 8 mL | – | 96 | 71 |
| 16 | 4 fractions of 2 mL | – | 98 | 46 |
| 17 | 8 fractions of 1 mL | – | 99 | 51 |
| 18 | 4 fractions of 2 mL | Hydroquinone, 4 wt % at starting | 64 | 9 |
| 19 | 4 fractions of 2 mL | Hydroquinone, 4 wt % at the end of the reaction | 87 | 9 |
| 20 | 4 fractions of 2 mL | Irganox, 4 wt % at starting | 97 | 2 |
| 21 | 4 fractions of 2 mL | Irganox, 4 wt % at the end of the reaction | 100 | 11 |

[a] Reaction conditions: 5.52 g of NBR latex (67 mmol of C=C double bonds), 5.15 g of de $N_2H_4$ (8 mL, 100 mmol), 5.5 mg of selenium (0.07 mmol), oxygen flow of 1 L/min, 60°C, and 8 h of reaction.

selenium has been shown to be very active in the formation of the diimide, oxidizing hydrazine, and forming the active species, $N_2H_2$ and $Se_2H_2$. There is no formation of gaseous hydrogen, as shown by gas chromatography and mass spectrometry.

The diimide formed in the first step reacts rapidly with the carbon–carbon double bonds in the formation of the new C—H bonds, without the intervention of selenium.

### Gel formation during NBR hydrogenation

The formation of gel during the hydrogenation of NBR is a problem usually faced in practical uses of HNBR. The crosslinked material seriously hinders the processing of HNBR to obtain pieces. Gel formation occurs in general, especially when very high conversions are required. The hydrogenation process is fundamentally associated with the formation of amines originating from the hydrogenation of CN triple bonds.

Several factors influence the gel formation. Table II shows the effect of the addition protocol for hydrazine (entries 15–17) and the effect of adding gel inhibitors (entries 18–21). Gel inhibitors were added either at the start of the reaction or at the end, to evaluate their effects on the species responsible for crosslinking when it is initially formed in the reaction or during the process of precipitation and drying.

Table II shows that the addition of hydrazine in several fractions causes less gel formation than when the same total amount is added in one fraction (entries 15–17), but gel formation is still high in the absence of inhibitors.

The use of gel inhibitors such as hydroquinone decreases not only the occurrence of crosslinking but also the conversion of double bonds. This effect is pronounced when hydroquinone is added at the start of the reaction (entry 18), showing the Poisson effect of this species on the system, and the effect is lower when it is added at the end (entry 19).

Another gel inhibitor, Irganox B215, which is a synergistic blend of 67% Irgafos 168 (tris(2,4-isopropyl-phenyl)phosphite) and 33% Irganox 1010 (ethyl β-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propianate), has been shown to be more effective in suppressing gel formation than hydroquinone. It is a convenient blend that addresses a range of stabilization needs. As shown in entries 20 and 21, the addition of 4 wt % gel inhibitor decreases the gel formation substantially, particularly when the Irganox is added at the beginning of the reaction.

### Selenium retention in the HNBR

A last concern in using selenium as a catalyst for hydrogenating NBR with hydrazine is the retention of selenium in the final product. The HNBR produced by hydrogenation is coagulated, precipitated, washed, and dried. The ICP-OES analysis showed 98 μg of residual selenium per gram of polymer (analysis of reaction corresponding to entry 20, Table II). This corresponds to retention of 0.1 wt % of the original selenium introduced in the reactor and constitutes a very low level.

### CONCLUSIONS

We have demonstrated that the hydrogenation of NBR by the diimide method using selenium,

hydrazine, and oxygen is an attractive alternative to similar methods described in the literature. The system attains very high conversions in short reaction times, produces low amounts of gel using an appropriate gel inhibitor, and gives a product with very low selenium content (1 mg/g). This system has the advantage of using a very low hydrazine to carbon–carbon double bond ratio; the value of 1.4 is significantly lower than values reported in the current literature to attain similar conversions.[17]

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