

Gel Formation in Diimide-Hydrogenated Polymers

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Received 8 June 2004; accepted 22 October 2004

DOI 10.1002/app.21554

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The hydrogenation of diene-based polymers via diimide is a very attractive alternative to the conventional catalytic hydrogenation route based on gaseous molecular hydrogen. However, serious crosslinking always accompanies it and limits the end-use properties of the polymers. Gel formation in polymers that are hydrogenated via diimide has been investigated in detail through an inspection of all the chemical reactions involved in the process. The results indicate that hydrogen peroxide decomposition, some reactions related to oxygen, and the redox reaction between hydrogen peroxide and hydrazine are capable of

generating radicals. However, radicals generated in the aqueous phase do not appear to initiate the crosslinking of diene-based polymers in the latex form. It is proposed that the primary radicals giving rise to crosslinking are generated in the polymer phase *in situ*, and the step responsible for generating these organic radicals is possibly the diimide disproportionation reaction. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1122–1125, 2005

Key words: crosslinking; gels; rubber; diimide

INTRODUCTION

Hydrogenated elastomers possess improved thermal and oxidative stability in comparison with their parent polymers. The hydrogenation of acrylonitrile–butadiene rubber (NBR) has received considerable attention in industry because hydrogenated NBR provides unique resistance to heat, oil, and aggressive chemicals. Diimide, an active hydrogen source, can conveniently be used to hydrogenate unsaturated polymers, such as polybutadiene rubber (PBR), poly(styrene-*co*-butadiene) rubber, and NBR.^{1–6} Diimide hydrogenation appears to provide a simple and economically beneficial alternative to conventional hydrogenation. Diimide from the thermal decomposition of *p*-toluene sulfonic hydrazide has been used to hydrogenate unsaturated polymers dissolved in organic solvents.^{7,8} Diimide from the reaction between hydrazine and hydrogen peroxide has been used to hydrogenate unsaturated polymers in a latex form.^{1–6} However, hydrogenated rubbers obtained by diimide hydrogenation are fully crosslinked and have very poor mechanical properties. The problem of gel formation during hydrogenation must be solved before the diimide hydrogenation route can be commercialized.

There is very little discussion in the literature regarding the gel-formation mechanism. Xie et al.² suggested the use of inhibitors both in the rubber phase (e.g., *p*-*tert*-butylpyrocatechol) and in the aqueous phase (e.g., sodium *N,N*-dimethyldithiocarbonate) to reduce gel formation. A similar idea was presented by Sarkar.⁵ Belt and coworkers^{3,4} reported that the use of amines, hydroxylamine, imines, azines, hydrazone, or oximes before, during, or after hydrogenation might help to reduce the gel content in hydrogenated rubber. These practices suggest that a radical crosslinking mechanism was assumed by the researchers.

The purpose of this study was to investigate the nature of gel formation in diimide hydrogenated polymers. Specially designed reactions have been carried out to determine the effects of all the possible reactions involved in gel formation.

EXPERIMENTAL

The diimide hydrogenation process involves a redox reaction in the aqueous phase, hydrogenation in the organic phase, side reactions, and the mass-transfer of diimide within the organic phase; the reactant hydrogen peroxide is not stable, and the intermediate diimide is highly reactive. All these factors make the study of gel formation difficult. In this study, an attempt was made to isolate the reactions involved in the diimide hydrogenation process. Systematic experiments were designed to mimic each radical generation situation in the diimide hydrogenation process.

The experiments were conducted in a 500-mL, three-necked, round-bottom flask equipped with an

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Contract grant sponsor: Natural Sciences and Engineering Research Council of Canada.

Contract grant sponsor: Bayer, Inc.

TABLE I
Effects of Individual Chemicals on Gel Information During NBR Hydrogenation

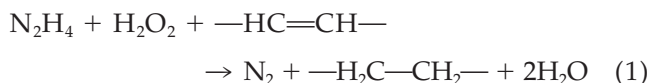
No.	Experimental system	Operation conditions	Observed phenomena
1	100.0 g of NBR latex + 4.0 g of H ₂ O ₂	8.0 h at 40°C	No gel
2	100.0 g of NBR latex + 4.0 g of N ₂ H ₄	8.0 h at 40°C	No gel
3	100.0 g of NBR latex + 1.3 g of H ₃ BO ₃	8.0 h at 40°C	No gel
4	100.0 g of NBR latex	>40 h, 40°C	No gel
5	100.0 g of NBR latex	>40 h, 80°C	No gel

overhead agitator, a temperature-controlled water bath, and a nitrogen inlet tube. Hydrazine hydrate (~99%) and hydrogen peroxide (29.0–32.0%) were purchased from VWR Scientific Products (West Chester, PA). Boric acid was provided by J. K. Baker Co. (Phillipsburg, NJ); sodium dodecyl sulfate (~99%) and styrene (St; ~99%) inhibited by 10–15 ppm 4-*tert*-butylcatechol were purchased from Aldrich Chemical Company Inc. (Milwaukee, WI). Ferrous sulfate (~99.0%) was provided by BDH, Inc. (Toronto, Canada), and formaldehyde sulfoxylate sodium (CH₃NaO₃S; ~97%) was purchased from Fluka Chemical (Buchs, Switzerland). Deionized water was used whenever water was required in the experiments. NBR latex was provided by Lanxess Inc. (Sarnia, Canada).

For emulsion polymerization experiments with St, 100.0 g of deionized water and 0.100 g of SDS were charged into a flask and were followed by the addition of 10.0 g of St and different initiators. The initiation systems included hydrogen peroxide decomposition, the redox reaction between hydrazine and hydrogen peroxide, the redox reaction catalyzed by boric acid, and thermal initiation. The contents were kept at 40.0 ± 0.1°C for 8 h under nitrogen protection if not stated otherwise. The conversion of St into polystyrene was determined from the weight of the solid content after polymerization. For the crosslinking experiments with the NBR latex, 100.0 g of NBR latex was used.

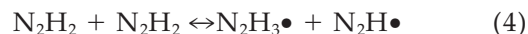
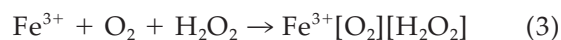
RESULTS AND DISCUSSION

The overall hydrogenation reaction of the unsaturated polymer latex with diimide can be expressed as follows:



The reactants involved in this reaction system include hydrazine, hydrogen peroxide, and an unsaturated polymer. Boric acid is some times used as a promoter.⁵ As the unsaturated polymer is in a latex form, provided from an emulsion polymerization process, some surfactants exist in the system. Furthermore, some impurities may also be present. All these chemicals possibly play some role in gel formation.

Aside from the aforementioned individual chemicals, the roles that the following possible reactions and sources play in gel formation need to be investigated: (1) the electron transfer of the redox reaction between hydrazine and hydrogen peroxide may generate radicals; (2) hydrogen peroxide may generate radicals via Fenton's reaction⁹ [eq. (2)]; (3) oxygen from hydrogen peroxide decomposition, together with the residual hydrogen peroxide, may provide a strong oxidation ability [eq. (3)];¹⁰ and (4) the side reaction of hydrogenation, in which diimide disproportionates,^{2,11} may generate radicals [eq. (4)]:



To investigate the effects of these chemicals on gel formation and the roles that the relevant reactions play in gel formation, we designed and carried out special experiments, and the results are detailed next.

Effects of the individual chemicals on gel formation

Experiments were conducted to investigate the individual effects of hydrazine, boric acid, and hydrogen peroxide through the heating of NBR latex with the individual chemicals for 8.0 h at 40°C. The results, summarized in Table I, indicate that hydrazine, boric acid, or hydrogen peroxide alone does not induce crosslinking in the unsaturated rubber. Retaining the latex at 40–80°C for more than 40 h did not increase the gel content in the rubber.

Analysis of the possibility of crosslinking from aqueous radicals

Radicals may be generated from the redox reaction between hydrazine and hydrogen peroxide and from hydrogen peroxide decomposition. These radicals may be generated in the aqueous phase. Conventional emulsion polymerizations were conducted to deter-

TABLE II
Initiation of St Polymerization by Substances in Diimide Hydrogenation (Reacting for 8.0 h at 40.0°C)

No.	Initiation system	Conversion	Polymer
6	15.0 g of N ₂ H ₄ + 2.0 g H ₂ O ₂	≈10%	Quite soluble, low <i>M_w</i>
7	15.0 g of N ₂ H ₄ + 2.0 g of H ₂ O ₂ + 0.65 g of H ₃ BO ₃	≈30%	Soluble in toluene
8	2.0 g of H ₂ O ₂ + 0.65 g of H ₃ BO ₃	≈3%	Quite soluble, low <i>M_w</i>
9	Thermal	0	

M_w = weight-average molecular weight.

mine whether aqueous radicals could cause crosslinking in the unsaturated polymer.

The thermal initiation of St polymerization is quite slow at 40°C (entry 9 in Table II). The conversion under thermal initiation is negligible. The experiments shown in Table I indicate that both hydrogen peroxide decomposition and the reaction between hydrazine and hydrogen peroxide are capable of radical initiation. The resultant polystyrenes are all quite soluble with no physical strength, and this suggests a low molecular weight. These experiments demonstrate that the substances used in the diimide hydrogenation process are capable of generating radicals in the aqueous phase.

Table I shows that H₂O₂ alone cannot crosslink the NBR latex. NBR is still soluble in acetone even after the NBR latex is heated with different amounts of H₂O₂ at 40°C for 24 h. The radical from H₂O₂ is not capable of crosslinking NBR in the latex form, although the radical is capable of initiating polymerization. It has been deduced that the radicals from the reaction between N₂H₄ and H₂O₂ in the aqueous phase behave in the same way as those from H₂O₂ decomposition. On the other hand, when 2 mL of St was added to a mixture of NBR latex and H₂O₂ under 40°C, a gel formed in just 2 h, and this rendered NBR insoluble in acetone. When we compare the results from these experiments, it becomes obvious that aqueous radicals are hydrophilic and may initiate polymerization in the aqueous phase, but they have little chance to attack NBR chains that are hydrophobic and are separated from the aqueous phase by a bilayer of surfactant molecules. During emulsion polymeriza-

tion, the hydrophilic primary radicals are transformed into hydrophobic polymer radicals by chain propagation. The resultant hydrophobic radicals are then capable of causing crosslinking in the particles. This understanding leads to the conclusion that the radicals generated in the aqueous phase are not the cause of NBR crosslinking during hydrogenation in the absence of a chain propagation mechanism.

Analysis of the possibility of crosslinking from oxygen

The crosslinking of saturated polymers in emulsion polymerizations by oxygen is extensively observed in practice.¹² The gel formation is believed to be related to oxygen residues in the emulsion system. Moreover, H₂O₂ and molecular oxygen together have superior oxidation strength.¹⁰ Hydrogen peroxide may decompose to generate its own oxygen atmosphere in the diimide hydrogenation system.

Table III shows that oxygen alone or oxygen together with hydrogen peroxide (entry 14 and 15) is not capable of crosslinking NBR polymer in the latex particles. On the other hand, with the help of the monomer St, oxygen is capable of crosslinking the saturated polymer polystyrene (entry 10) and unsaturated NBR (entry 16) via diffusion into the organic phase. The difference between these two cases is whether or not the radical can be transferred into the organic phase. The addition of the monomer St helps to transfer the aqueous radicals into the hydrophobic polymer phase. Therefore, the superoxidative radical from H₂O₂ and molecular oxygen is not the source for crosslinking

TABLE III
Experiments with Oxygen Crosslinking (Reacting for 8.0 h at 40.0°C)

No.	Experimental details	Polymer
10	St emulsion polymerization; Initiator: 15.0 g of N ₂ H ₄ + 2.0 g of H ₂ O ₂ without degassing	Completely Crosslinked
11	St emulsion polymerization; Initiator: 15.0 g of N ₂ H ₄ + 2.0 g of H ₂ O ₂ , degassing	Soluble
12	2.0 g of H ₂ O ₂ + 100.0 g of NBR latex, without degassing	Soluble
13	2.0 g of H ₂ O ₂ + 100.0 g of NBR latex, degassing	Soluble
14	2.0 g of H ₂ O ₂ + 100.0 g of NBR latex, without degassing	Soluble
15	2.0 g of H ₂ O ₂ + 100.0 g of NBR latex, + little Fe ²⁺ + CH ₃ NaO ₃ S, without degassing, 40°C for 40 h	Soluble
16	2.0 g of H ₂ O ₂ + 2.0 g of styrene + 100.0 g of NBR latex, degassing	Insoluble

observed in the diimide hydrogenation process because of the absence of a radical-transfer mechanism in the normal hydrogenation system.

Analysis of the possibility of crosslinking from the side reactions of diimide hydrogenation

According to this analysis, the primary radical for gel formation in the diimide hydrogenation process must be generated inside the unsaturated polymer phase *in situ*. Gel formation has been observed for both the diimide hydrogenation of unsaturated polymer latex²⁻⁵ and homogeneous diimide hydrogenation in organic solvents,^{7,8} and this suggests that crosslinking should be directly related to diimide. Diimide has been identified as the intermediate of this hydrogenation route.^{13,14} The hydrogenation reaction involves the simultaneous transfer of two hydrogen atoms from diimide to the unsaturated bonds. Diimide is highly selective for symmetrical double or triple bonds. Until now, there has been no discussion in the literature regarding possible side reactions occurring during diimide hydrogenation.

The diimide disproportionation reaction, as shown in eq. (4), though not directly observed, has been shown to be an energy-favorable pathway for diimide consumption.¹¹ So far, there is no feasible method for checking the existence of radicals *in situ* in the rubber phase. The correspondent crosslinking bonds cannot be identified by spectroscopic methods because of the very low concentration of such bonds. Nevertheless, the gel phenomena observed during the hydrogenation experiments support the radical generation process shown in eq. (4).

Gel formation is not observed at a low degree of hydrogenation (defined as the conversion of C=Cs; <60%). Meanwhile, diimide is 100% efficient in supplying hydrogen for hydrogenation (the efficiency of diimide at performing hydrogenation is defined as the hydrogenation efficiency). As the degree of hydrogenation increases, the hydrogenation efficiency decreases, and the gel content of the resultant polymer increases sharply. Slowing down the addition rate of hydrogen peroxide results in a higher efficiency of diimide and has a beneficial effect on gel reduction. The phenomenon corresponds to the assumed radical process. As the degree of hydrogenation goes up, the hydrogenation reaction slows down, and the concen-

tration of diimide increases accordingly. The increase in the diimide concentration gives way to diimide consumption by way of eq. (4). Consequently, radicals form, and crosslinking results.

CONCLUSIONS

The gel formation occurring during diimide hydrogenation is a radical process. The radicals responsible for crosslinking are generated within the polymer phase. Although the radicals generated within the aqueous phase are capable of initiation, they are not the source of the radicals that cause the crosslinking within the latex particles under normal hydrogenation conditions. The use of radical scavengers in the aqueous phase of the latex does not help to reduce the gel content of the resultant polymer. It has been postulated that the diimide disproportionation reaction within the latex particles generates the primary radicals that cause crosslinking inside the polymer. When the concentration of the unsaturated bonds becomes lower as the hydrogenation proceeds, radicals are generated at an increasing rate. The addition of antioxidants to the polymer phase does show some beneficial effects for gel inhibition. However, the effect is marginal because the large number of generated radicals cannot be scavenged efficiently.

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