Hydrogenation of Nitrile–Butadiene Rubber Latex to Form Thermoplastic Elastomer with Excellent Thermooxidation Resistance

Hong-Quan Xie, Xiao-Dong Li, Jun-Shi Guo

Department of Chemistry, Huazhong University of Science and Technology, Wuhan, 430074, People's Republic of China

ABSTRACT: Hydrogenation of nitrile–butadiene rubber latex was carried out using hydrazine and hydrogen peroxide, with copper sulfate as catalyst and without pressurized hydrogen and organic solvent. A special inhibitor was used during hydrogenation to reduce gel formation. Various hydrogenation conditions were studied. The gel content of the hydrogenation product can be reduced to ~15%, and hydrogenation degree can reach ~87%. The hydrogenated product was characterized by infrared spectroscopy, proton nuclear magnetic resonance spectroscopy, and differential scanning calorimetry. The hydrogenated product behaved as an oil-resistant thermoplastic elastomer with excellent thermooxidation resistance, due to the absence of most double bonds and the presence of crystalline domains of polyethylene segments formed by hydrogenation of polybutadiene segments and nitrile groups. The higher the hydrogenation degree, the higher were the mechanical properties and thermooxidation resistance of the product. The product with a hydrogenation degree of 87% withstood thermooxidation quite well at 150°C for 65 h, maintaining ~98% of its tensile strength and 96% of its ultimate elongation. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 1026–1031, 2003

Key words: rubber; elastomers; crystallization; latices; polybutadiene

INTRODUCTION

Polybutadiene-based polymers are widely applied as rubbers, adhesives, coatings, plastics modifiers, etc. because of their high strength and good elastic properties. However, a main disadvantage of these materials is their poor aging properties, which are caused by the oxidation of the residual double bonds in vulcanized polybutadienes. A method to improve the aging properties of these polymers is to hydrogenate the residual double bonds. The conventional hydrogenation process is performed in polymer solutions with a noble metal catalyst and using pressurized hydrogen.[1] However, some obvious problems exist in this process; such as, safety of pressurized hydrogen, high cost of hydrogenation equipment and the noble metal catalyst, which is difficult to recover, low efficiency resulting from the limited solubility of polymer, and the solvent-induced environmental problem.

A new direction in this area is to hydrogenate rubber in its latex form. Wideman[2] discovered that an elastomer in latex form can be converted directly into its saturated latex form when treated with hydrazine hydrate, an oxidant, and a metal ion catalyst without using any pressure vessel, organic solvent, or hydrogen gas (so-called diimide reduction technique). Later, Parker et al.[3] hydrogenated a nitrile–butadiene rubber (NBR) latex using the diimide reduction technique, but the hydrogenated product contained a large amount of gel and could only be used as a binder for paper gaskets using a beater addition process.[4] Later, these authors[5] prepared hydrogenated styrene–butadiene rubber (SBR) latex by the diimide reduction technique and indicated that the material is a thermoplastic elastomer with excellent thermooxidation resistance, because most 1,4-polybutadiene segments of SBR are converted into polyethylene segments by hydrogenation. These segments can crystallize even in the unstretched state at ambient temperature to form crystalline domains. Thermoplastic elastomers are a relative new class of rubbers. Their properties are similar to those of vulcanized elastomers, without the need to use any vulcanizing agent or vulcanizing process. They can be processed like thermoplastics because of their physical crosslinking that is formed by glassy domains, crystalline domains, or ionic domains.[6]

Parker and Roberts[3] proposed a diimide reduction mechanism for the hydrogenation of latex in which the diimide hydrogenating agent is generated from a hydrazine/hydrogen peroxide system at the surfaces of latex particles. Carboxylated surfactants adsorbed at the latex particle surfaces play an important role by

Correspondence to: H-Q. Xie (xiehonqi@public.wh.hb.cn).

forming hydrazinium carboxylates with hydrazine and copper ions. The diimide intermediates generated are stabilized by Cu^{2+} and effectively reduce the carbon–carbon double bonds.

He et al.[7] studied the conditions for the hydrogenation of SBR latex containing some gels via the diimide reduction process. They pointed out that the surface density of the copper ions in particle surfaces is an important parameter in controlling the degree of hydrogenation, and the hydrogenation of double bonds depends on the latex particle size and the extent of crosslinking in the particles. They found that the gel fraction of SBR latex increases after the hydrogenation. Sarkar et al.[8] reported the effects of various reaction conditions for hydrogenation of SBR latex (namely, reaction time and temperature, pH of the latex, and concentrations of hydrogen peroxide, hydrazine, and catalyst) on the hydrogenation degree calculated from nuclear magnetic resonance (NMR) spectroscopy and noted an increase of glass transition temperature with increasing hydrogenation degree due to the development of crystalline segments. Sokolov[9] studied the hydrogenation of NBR latex using the diimide system and indicated that oxygen is more effective than air as an oxidant in the hydrogenation reaction and that gel formation increases obviously at reaction temperatures from 10 to 60°C. The hydrogenation degree can reach 58%. To reduce the gel content formed in the hydrogenation of NBR latex, Parker et al. [10,11] pointed out that at the end of hydrogenation, ozone was used to destroy the remaining double bonds. This procedure was followed by treatment with sodium hydroborate or hydroxylamine to form hydroxyl or oxime groups, respectively. Guo and Rempel[12] carried out catalytic hydrogenation of an NBR emulsion, using $RuCl_2(PPh_3)_3$ as catalyst and ketone as solvent under hydrogen pressure of ~8 MPa at 120–150°C, and obtained hydrogenated NBR (HNBR) with a hydrogenation degree of 70–95%. Recently, we have reported the hydrogenation of carboxylated styrene–butadiene rubber latex and its neutralization with metallic ions to form ionomers.[13]

This paper deals with the hydrogenation of NBR latex using the diimide reduction process to optimize the conditions for reducing the gel content of the hydrogenation product and obtaining an oil-resistant, thermoplastic elastomer with excellent thermooxidation resistance.

EXPERIMENTAL

Materials

Nitrile-butadiene latex (NBRL), with a solid content of 44.98%, a nitrile–butadiene weight ratio of 31:69, and produced by a low temperature method, was supplied by a pilot plant of the Lanzhou Company of Chemical Technology. Hydrazine hydrate (60%), hydrogen peroxide (30%), ferrous sulfate, cobalt sulfate, nickel sulfate, copper sulfate, silver nitrate, n-heptanol, n-octanol, sodium hydroxide, sodium chloride, potassium hydroxide, sulfuric acid, benzene, and ethanol were chemically pure. The exact concentration of hydrazine and hydrogen peroxide were determined by titration. Antioxidant 264, styrenated phenol, hydroquinone, p-tert-butyl-pyrocatechol were of industrial grade. Carbon tetrachloride, potassium iodide, sodium thiosulfate, and starch were analytical reagents.

Hydrogenation of NBRL via diimide reduction method

NBRL was diluted with an equal amount of water. An inhibitor, p-tert-butyl-pyrocatechol, was added. After stirring for 1 h, hydrazine hydrate and copper sulfate were added as catalysts, and the mixture was stirred for 1/2 h. Then, the mixture was heated to 40°C. Hydrogen peroxide was dropped in with a velocity so that the temperature of the mixture was not raised up quickly. During addition of hydrogen peroxide, if too many bubbles were formed, one drop of n-octanol was added as an antifoaming agent. After finishing the addition of hydrogen peroxide, the reaction mixture was kept at the reaction temperature for 2 h.

Preparation of hydrogenated NBR (HNBR)

The hydrogenation product of NBRL was added to four times its volume of 2.5% NaCl solution while the solution was stirred. Then, a small amount of dilute sulfuric acid was added to the uniform mixture to coagulate the hydrogenated rubber (HNBR). The hydrogenated rubber was divided into small lumps and washed with distilled water to pH 7. Water was squeezed out from the product, which was then dried under an infrared (IR) lamp and then in a 50°C vacuum drier.

Determination of gel content of NBR and HNBR

A 0.2-g sample was finely cut and accurately weighed. Then, 50 mL of chlorobenzene was added and the mixture was stirred thoroughly for 1 day in the dark. The gel-containing solution was filtered on an accurately weighed, 400-mesh stainless steel filter bag. After washing with chlorobenzene and drying, the residue with the filter bag was weighed and the percent gel content was determined as follows:

$$\text{Gel content, \%} = (G_2 - G_0)100/G_1$$

where G_2, G_0, and G_1 are the weights of dried residue with the filter bag, filter bag, and the sample, respec-

tively. Two of the same samples were used to determine the gel content, and the average value was taken.

Determination of hydrogenation degree of HNBR

The double bond content of NBR or HNBR cannot be accurately determined by IR spectroscopy because the absorption at 740 cm^{-1} for *cis*-1,4 double bonds is overlapped by the absorption at 725 cm^{-1} for the polyethylene segments formed from hydrogenation of 1,4-polybutadiene segments. Thus, we used an improved iodometric method for determining the double bond content or hydrogenation degree. The improved iodometric method was carried out as follows: A 0.1-g sample of NBR or 0.5-g sample of HNBR was accurately weighed and placed in an iodometric flask separately. Then, 50 mL of chlorobenzene was added, and the mixture was heated to 45°C with stirring for 1 h to obtain a clear solution. If there was an insoluble gel, the solution was filtered and washed with chlorobenzene first. Next, 25 mL of 0.lM ICl was accurately measured into the iodometric flask and a small amount of 15% KI solution was used to seal the stopper of the flask. The iodometric flask was stored in the dark for 1.5 h. Then, 25 mL of 15% KI was added to the flask and the flask was shaken for 2 min. Then, 50 mL of distilled water was added and the solution was titrated with 0.1M standard Na$_2$S$_2$O$_5$, using 1% starch solution as indicator. A blank test was carried out under the same conditions. The percent double bond content (DB%) was determined as follows:

$$\text{Double bond content(DB), \%} = 2.705(V_\text{o}-V)M/G$$

where V_o and V are the amounts (mL) of Na$_2$S$_2$O$_5$ used for titration of the blank and the sample, respectively, G is the weight of dried sample or the weight of dried sample minus weight of dried gel, and M is the molar concentration of Na$_2$S$_2$O$_5$.

The hydrogenation degree (expressed as a percentage) was determined as follows:

Hydrogenation degree, %

$$= (1-\text{DB}_\text{HNBR}/\text{DB}_\text{NBR})100$$

Characterization and testing

The IR spectra were taken on an IR-435 spectrophotometer, after the sample was dissolved in chlorobenzene and the polymer solution was coated on a KBr crystal. Proton nuclear magnetic resonance spectroscopy (^{1}H-NMR) spectra were recorded on a Bruker NMR spectroscope using CDCl$_3$ as solvent and tetramethylsilane as internal standard. Differential scanning calorimetry (DSC) curves were performed on a Perkin-Elmer 7 differential scanning calorimeter with

TABLE I
Effect of Different Inhibitors on the Hydrogenation of NBR Latex

Inhibitor[a]	Gel content (%)	Hydrogenation degree (%)
—	94.3	—
Hydroquinone	42.1	50.8
Antioxidant 264	34.8	62.1
Styrenated phenol	48.5	50.0
p-tert-Butyl-pyrocatechol	21.7	74.7

[a] Amount of inhibitor used is 4×10^{-2} g/g dried rubber

a heating rate of 5°C/min in the temperature range 25–70°C. The mechanical properties test was carried out on a XL-2500 tensile tester at 25–30°C, with an extension rate of 300 mm/min. The permanent set was measured as percent elongation 3 min after the specimen was broken and reunited.

RESULTS AND DISCUSSION

Hydrogenation of NBR latex

Hydrogenation of NBRL via the diimide reduction process induces gel formation in the absence of inhibitor, as shown in Table I. This phenomenon was also observed by Parker et al.[4,10,11] and may be attributed to the fact that hydrogen peroxide in the reactants can decompose to form · OH radicals, which can react with double bonds to form a gel. This reason may be why the product from hydrogenation of NBRL with a Ru catalyst, reported by Rempel et al.,[12] did not contain gel.

Thus, various inhibitors were tried as additives to the hydrogenation system to capture the free radicals and reduce the gel content. The results in Table I show that without addition of inhibitor, the gel content reaches ~94%, but in the presence of 2.2 wt % antioxidant 264 based on the rubber, the gel content is lowered to 35% and the hydrogenation degree of the product reaches ~62%. However, if *p-tert*-butyl-pyrocatechol is used as inhibitor, the gel content can diminish to ~20% and the hydrogenation degree reaches ~75%.

The effect of the amount of *p-tert*-butyl-pyrocatechol (wt % of dried rubber) on the gel content and hydrogenation degree of XNBR is illustrated in Figure 1. The gel content decreases abruptly with addition of the inhibitor, but keeps almost constant with further increases of the inhibitor. The hydrogenation degree of the product increases with an increase of the inhibitor, and a maximum hydrogenation degree occurs at 2.3% *p-tert*-butyl-pyrocatechol. The hydrogenation degree then decreases with further increase of the inhibitor amount. Excess inhibitor may interfere with the reaction between hydrogen peroxide and hydrazine in the
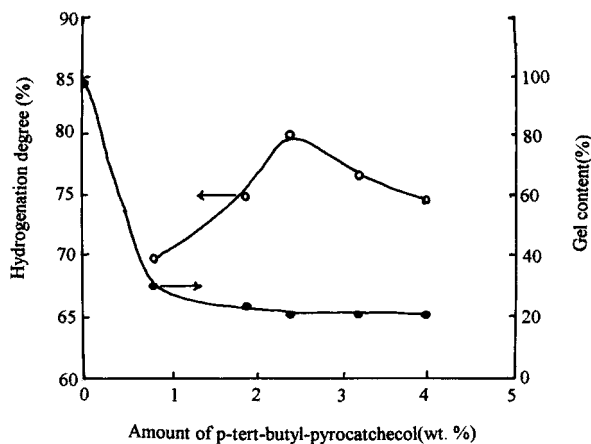
Figure 1 Effect of amount of *p-tert*-butyl-pyrocatchecol on the hydrogenation of NBR latex.

formation of diimide, resulting in a decreasing hydrogenation degree.

The effects of $CuSO_4$ amount on the hydrogenation degree and gel content of HNBR are shown in Figure 2. With increasing amounts of $CuSO_4$, the gel content increases almost linearly, whereas a maximum hydrogenation degree occurs at ~4.2×10^{-4} mmol $CuSO_4$. /g dried rubber. Cu^{2+} can not only act as a catalyst for the diimide formation from hydrogen peroxide and hydrazine, but can also promote the production of free radicals. Excess Cu^{2+} may catalyze the radical formation reaction between hydrogen peroxide and H at the αC of CN, resulting in gel formation that inhibits the reaction between diimide and double bonds of the rubber, thus decreasing the hydrogenation degree.

Amounts of hydrazine hydrate and hydrogen peroxide used are the main parameters in determining the hydrogenation degree. The results in Figure 3 show that with increasing hydrazine amount, the hydrogenation degree increases, whereas the gel content decreases. When the molar ratio of $N_2H_4/C{=}C$ reaches ~2, the gel content of the product decreases to ~15% and the hydrogenation degree reaches ~87%.
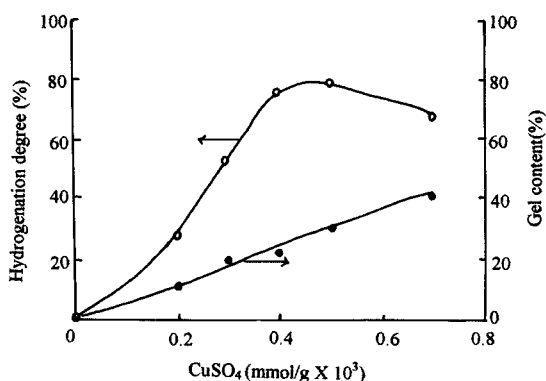

Figure 2 Effect of $CuSO_4$ amount on the hydrogenation of NBR latex.

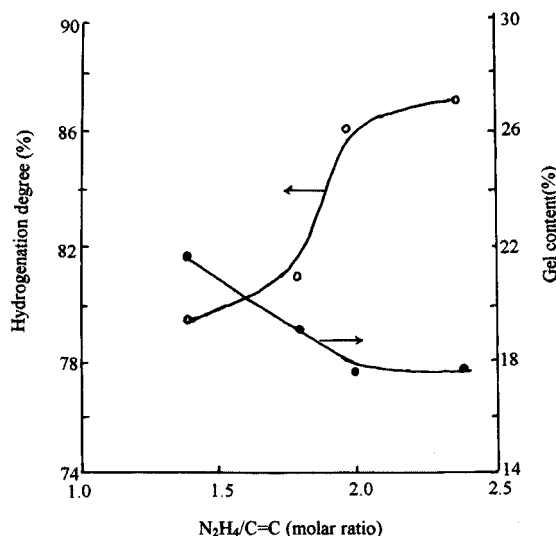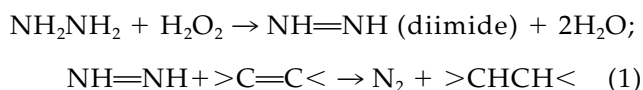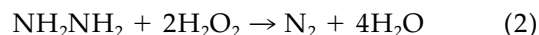**Figure 3** Effect of molar ratio of $N_2H_4/C{=}C$ on hydrogenation of NBR latex.

This result is because there are two possible reactions between hydrazine and hydrogen peroxide:

$$NH_2NH_2 + H_2O_2 \rightarrow NH{=}NH \text{ (diimide)} + 2H_2O;$$

$$NH{=}NH + >C{=}C< \rightarrow N_2 + >CHCH< \quad (1)$$

and

$$NH_2NH_2 + 2H_2O_2 \rightarrow N_2 + 4H_2O \quad (2)$$

In the presence of double bonds of polybutadiene segments and metallic ion as catalyst, the reactions shown in eq. (1) predominate; that is, diimide is produced and reacts with the double bonds, thereby raising the hydrogenation degree. In contrast, when amount of double bonds of polybutadiene segments is less and the amount of hydrogen peroxide is higher, the reaction shown in eq. (2) predominates and forms more nitrogen. The more the hydrazine, the more the diimide is produced, which increases the hydrogenation degree, inhibits the decomposition of H_2O_2 and thus the formation of gel.
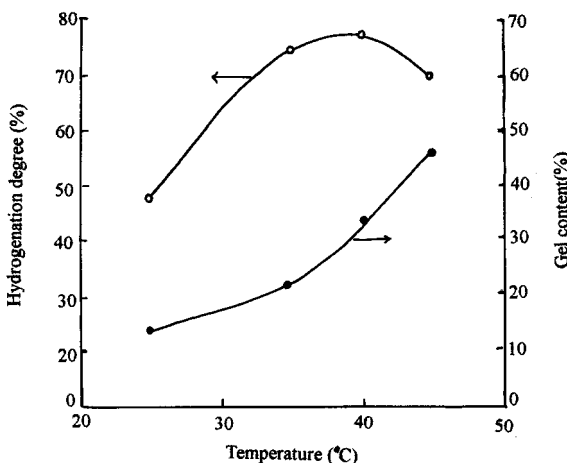
The results shown in Figure 4 indicate that with increasing molar ratio of H_2O_2/N_2H_4, the hydrogenation degree increases to a maximum at 1.25 and then decreases, but the gel content keeps nearly constant at first and then increases above the molar ratio of 1.0. This phenomenon may be ascribed to the two competitive reactions between hydrazine and H_2O_2 [i.e., the reactions shown in eq. (1) and the side reaction shown in eq. (2)]. Excess H_2O_2 may not only promote the side reaction , but may also decompose to form free radicals, which can induce the crosslinking reaction be-
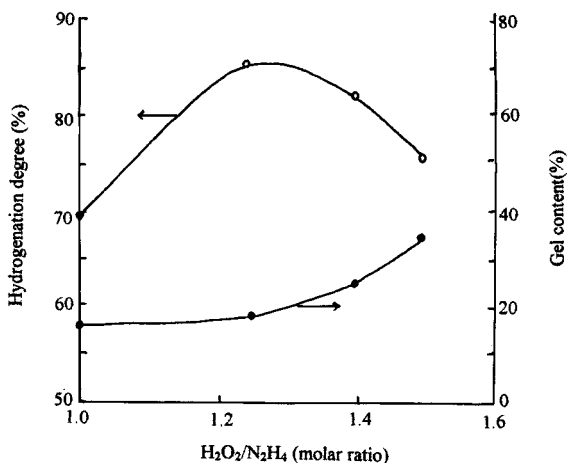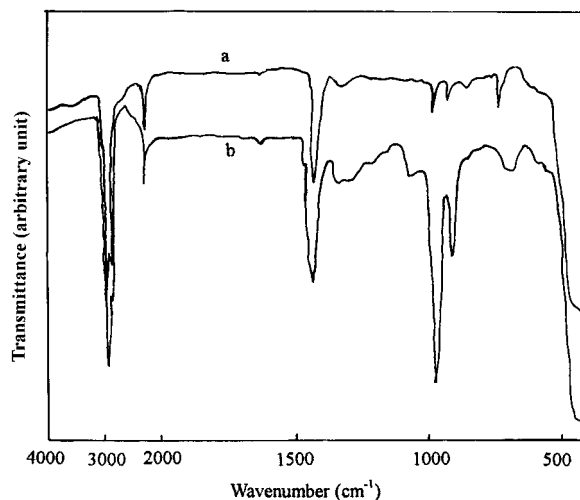
Figure 4 Effect of molar ratio of H_2O_2/N_2H_4 on hydrogenation of NBR latex.

Figure 6 IR spectra of (a) NBR and (b) HNBR.

tween double bonds, resulting in enhancing gel formation.

The effect of reaction temperature on the hydrogenation process is illustrated in Figure 5. When the reaction temperature is <30°C, both the gel content and the hydrogenation degree are low. Only when the reaction temperature is raised to >30°C do both the hydrogenation degree and gel content increase obviously with temperature. At lower temperature, the activity of the reactant molecules is lower. As the reaction temperature rises, both the probability of collision and activity of the reactant molecules increase, resulting in enhancement of the hydrogenation degree of the product. On the other hand, H_2O_2 tends to decompose and produce free radicals at higher temperature. The free radicals induce the crosslinking between double bonds of different polybutadiene segments, thus increasing the gel content of the product.

Characterization of the hydrogenated NBR

The IR spectra of NBR and HNBR are shown in Figures 6 (a) and (b), respectively. In the spectrum shown in Figure 6(a), absorption peaks at 2236, 970, 910, and 740 cm^{-1} belong to the CN groups, *trans*-1,4 double bonds, 1,2 double bonds, and *cis*-1,4 double bonds, respectively. In the IR spectrum shown in Figure 6(b) of HNBR with a hydrogenation degree of 87%, an absorption peak appears at 725 cm^{-1} for polyethylene segments, whereas the absorption peaks at 970 cm^{-1} for *trans*-1,4 double bonds and 910 cm^{-1} for 1,2 double bonds almost disappear. This result indicates that most of the double bonds are hydrogenated and transformed into polyethylene segments $(CH_2)_n$ ($n > 4$). The ^{1}H-NMR spectrum of NBR showed peaks at ~5.3 ppm for the olefinic protons in the 1,4-polybutadiene structure and a small peak near 5.0 ppm for the 1,2 vinyl group content. In contrast, the ^{1}H-NMR of HNBR with 87% hydrogenation degree showed only small peaks at ~5.3 ppm and almost no peak near 5.0 ppm.

Figure 5 Effect of temperature on the hydrogenation of NBR latex.
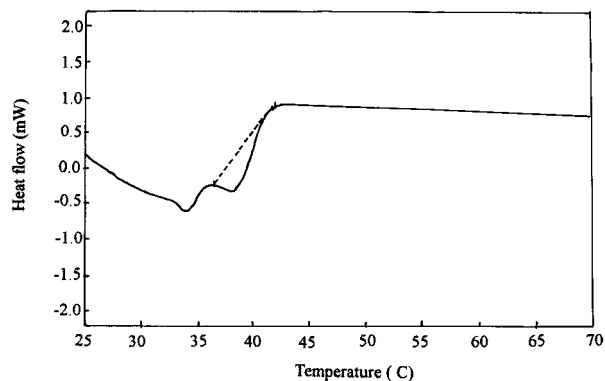
Figure 7 DSC curve of HNBR with hydrogenation degree of 87%.

TABLE II
Mechanical Properties of NBR and HNBR Before and After Thermoaging under Air at 150°C for 65 h

Property	NBR		HNBR (78.4%)[a]		HNBR (86.2%)[a]	
	Unaging	Aging	Unaging	Aging	Unaging	Aging
Tensile strength (MPa)	0.3	Brittle	3.2	2.7	4.9	4.8
Ultimate elongation (%)	760	Brittle	370	320	480	460
Permanent set (%)	320	Brittle	19	16	12	10

[a] The percentages in parentheses denote the hydrogenation degree.

The DSC curve of the HNBR with hydrogenation degree of 87%, indicates an endothermic peak at 38.47°C, whereas no endothermic peak appears in the DSC curve of NBR (see Figure 7). This result can be interpreted as the melting of crystalline polyethylene segments of widely varying size and purity formed from hydrogenation of 1,4-polybutadiene segments[3] in the former case.

Mechanical and thermooxidation properties of the hydrogenated NBR

The mechanical properties of the NBR and HNBR with different hydrogenation degrees are summarized in Table II. NBR without hydrogenation and vulcanization exhibits very low tensile strength. In contrast, after hydrogenation, the tensile strength and ultimate elongation increase significantly, whereas the permanent set keeps a reasonably low value. HNBR behaves as a thermoplastic elastomer. Both the tensile strength and ultimate elongation increase with the hydrogenation degree, but the permanent set remains almost unchanged. The improvement of mechanical properties is due to the crystalline domains formed by the polyethylene segments, which are produced from the hydrogenation of 1,4-polybutadiene units in the NBR rubber. HNBR is much more resistant to thermal aging than NBR, as shown in Table II. For the thermal aging test, specimens were put into a 150°C oven with air for 65 h. The mechanical properties of the specimens after the thermal aging test were determined using the tensile tester at room temperature. After the aforementioned thermal treatment, the NBR sample became brittle but the HNBR samples maintained most of the mechanical properties. In particular, the NHBR sample with 87% hydrogenation degree maintained ~98% of its original tensile strength and ~96% of its ultimate elongation., The higher the hydrogenation degree, the better is the thermooxidation resistance.

Oil resistant property of the hydrogenated NBR

The oil resistance of the hydrogenated NBR without vulcanization is good with respect to the mineral lu-

bricant oils. After immersing the HNBR sample with hydrogenation degree of 87% in the mineral lubricant oil at room temperature for 2 months, changes in weight, volume, tensile strength, ultimate elongation, and hardness are +3.3, +4.9, −0.6, −3.8, and −4.0%, respectively. The presence of polar nitrile groups is responsible for the oil resistance of the thermoplastic HNBR.

CONCLUSIONS

NBR latex can be hydrogenated via the diimide reduction process to HNBR with a hydrogenation degree of ~87% and a gel content of 15%. It is important to use an inhibitor, p-tert-butyl-pyrocatchecol, during hydrogenation to prevent the formation of a large amount of gel. Optimum hydrogenation conditions were obtained. The hydrogenated product showed polyethylene segments in the IR spectrum and an endothermic peak for melting the crystalline polyethylene segments in the DSC curve. HNBR behaves as an oil-resistant, thermoplastic elastomer with good thermooxidation resistance.

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