Hydrogenation and Neutralization of Carboxylic Styrene–Butadiene Latex to Form Thermoplastic Elastomer with Excellent Thermooxidation Resistance

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ABSTRACT: Hydrogenation of carboxylic styrene–butadiene rubber latex was carried out using hydrazine and hydrogen peroxide with ferrous sulfate as a catalyst without pressurized hydrogen and an organic solvent. A mixed inhibitor was used during hydrogenation to prevent gel formation. Various hydrogenation conditions were studied. Ferrous sulfate is better than is cupric sulfate as a catalyst. The hydrogenation degree can reach over 90%. The hydrogenated product was characterized by IR and DSC. The hydrogenated products behave as a 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 the hydrogenation of polybutadiene segments. Ionomers were obtained by neutralization of the hydrogenated product with metallic ions and characterized by IR, DSC, and TEM. The ionomers also behave as thermoplastic elastomers with mechanical properties better than those of the hydrogenated product without neutralization, due to the existence of ionic domains besides the crystalline domains. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 1375–1384, 2002

Key words: hydrogenation; carboxylic styrene–butadiene rubber latex; thermoplastic elastomer; ionomer; crystalline domain

INTRODUCTION

Polybutadiene-based polymers are widely applied as rubbers, adhesives, coatings, plastic modifiers, etc., due to their high strength and good elastic properties. However, a main disadvantage of these materials is their poor aging properties, caused by the oxidation of the residual double bonds in the vulcanized polybutadienes. An improved method is to hydrogenate the residual double bonds. The conventional hydrogenation process is performed in polymer solutions by a noble metal catalyst using pressurized hydrogen.[1,2] However, some obvious problems exist in this process, such as the safety of the pressurized hydrogen, high cost of the hydrogenation equipment and the catalyst, which is difficult to recover, as well as low efficiency resulting from the limited solubility of the polymer and solvent-induced environmental problems.

A new direction in this area is to hydrogenate rubber in the 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 (the so-called diimide reduction technique) without using any pressure vessel, organic solvent, or hydrogen gas. Later, Parker et al.[3] 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, since 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 relatively new class of rubbers. Their properties are similar to those of vulcanized elastomers without using any vulcanizing agent or vulcanizing process, but they can be processed like thermoplastics due to their physical crosslinking formed by glassy domains, crystalline domains, or ionic domains.[4]

Parker and Roberts[5] proposed a diimide reduction mechanism for the hydrogenation of latex in which the diimide hydrogenating agent was generated from the hydrazine/hydrogen peroxide system at the surfaces of the particles. Carboxylated surfactants adsorbed at the latex particle surfaces play an important role by forming hydrazinium carboxylates with hydrazine and copper ions. The diimide intermediates generated are stabilized by the Cu^{2+} and effectively reduce the carbon–carbon double bonds.

He et al.[6] 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 was 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 increased after the hydrogenation. Sarkar et al.[7] reported the effects of various reaction conditions for the hydrogenation of SBR latex, namely, reaction time and temperature, pH of the latex, and concentration of the hydrogen peroxide, hydrazine, and catalyst on the hydrogenation degree calculated from NMR spectroscopy and denoted the increase of the glass transition temperature with an increasing hydrogenation degree due to the development of crystalline segments.

We studied the hydrogenation of SBR 1502 latex and found that the hydrogenation degree can reach over 95% and the tensile strength of the molded product can reach about 12 MPa, but the permanent set is as high as 100%. This article deals with the hydrogenation of carboxylic SBR latex followed by neutralization of carboxylic acid groups, in order to obtain a thermoplastic elastomer not only with excellent thermooxidation resistance but also with good elastic properties (high ultimate elongation and low permanent set), through utilizing two kinds of domains, that is, crystalline domains and ionic domains.

EXPERIMENTAL

Materials

Carboxylic SBR latex (XSBRL) with a solid content of 54% and the weight ratio of styrene:butadiene:acrylic acid of 42.0:56.4:1.6 was supplied by the pilot plant of the Lanzhou Chemical Co. (Lanzhou, China). Fifty percent hydrazine hydrate, 30% hydrogen peroxide, ferrous sulfate, cobalt sulfate, nickel sulfate, copper sulfate, silver nitrate, n-heptanol, n-octanol, sodium hydroxide, sodium chloride, potassium hydroxide, zinc acetate ($2H_2O$), magnesium acetate ($2H_2O$) , lead acetate ($3H_2O$), sulfuric acid, benzene, and ethanol were chemically pure. The actual concentration of hydrazine and hydrogen peroxide were determined by titration. Antioxidants such as styrenated phenol, hydroquinone, sodium N,N-dimethyldithiocarbamate, and p-$tert$-butylpyrocatechol were of reagent grade. Carbon tetrachloride, potassium iodide, sodium thiosulfate, and starch were analytical reagents.

Hydrogenation of XSBRL via Diimide Reduction Method

XSBRL was diluted with an equal amount of water. A mixed inhibitor composed of sodium N,N-dimethyldithiocarbamate and p-$tert$-butylpyrocatechol was added. After stirring for 1 h, hydrazine hydrate and ferrous sulfate as a catalyst were added and stirred for 0.5 h. Then, the mixture was heated to 47°C. Hydrogen peroxide was dropped in with a velocity so that the temperature of the mixture was not increased quickly. During addition of hydrogen peroxide, if too many bubbles were formed, one drop of n-octanol used as an antifoaming agent was added. After finishing the addition of hydrogen peroxide, the reaction mixture was kept at the reaction temperature for 2 h.

Preparation of Hydrogenated Carboxylic SBR (HXSBR)

The hydrogenation product of XSBRL was added to four times of its volume of 2.5% NaCl solution

with stirring. Then, an amount of dilute sulfuric acid was added to the uniform mixture to coagulate the hydrogenated rubber (HXSBR). 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 lamp and in a 50°C vacuum drier successively.

Neutralization of the HXSBR

HXSBR with a hydrogenation degree of 91.2% was dissolved in a mixed solvent of benzene/ethanol. An 0.1M methanol solution of NaOH or KOH or a 1% methanol solution of zinc acetate, magnesium acetate, or lead acetate in an equivalent amount was added into the HXSBR solution with vigorous stirring and the neutralization reaction was carried out at 50°C for 1–2 h. The neutralized product was dried under an infrared lamp and in a 50°C vacuum drier successively.

Determination of Gel Content of XSBR and HXSBR

Since XSBR or HXSBR contains carboxylic acid groups which lower its solubility in a nonpolar solvent, the solvent for XSBR or HXSBR was improved by adding a small amount of a polar solvent such as n-heptanol into the nonpolar solvent, carbon tetrachloride. The optimum volume ratios of CCl_4/n-heptanol in the mixed solvent was determined to be 50/4 and 50/6 for XSBR and HXSBR, respectively. The procedure is as follows: A 0.2-g finely cut sample was accurately weighed and 50 mL of the mixed solvent was added and stirred thoroughly for 1 day in the dark. The gel-containing solution was filtered on an accurately weighed 400-mesh stainless steel-made filter cup. After drying, the residue with the filter cup was weighed:

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

where G_2, G_0, and G_1 are the weights of the dried residue with the filter cup, the filter cup, and the sample, respectively.

Determination of Hydrogenation Degree of HXSBR

The double-bond content of XSBR or HXSBR cannot be accurately determined by the IR spectrum, since the absorption at 740 cm^{-1} for cis-1,4 double bonds is overlapped by the absorption at 750 and 700 cm^{-1} for phenyl groups of styrene units and also the absorption at 724 cm^{-1} for the polyeth-

ylene segments formed from hydrogenation of 1,4-polybutadiene segments. The double-bond content of XSBR or HXSBR can be determined by the ^{1}H-NMR spectrum, but with an increasing hydrogenation degree, the integral heights at 5.3δ and 5.0δ for polybutadiene segments become smaller and smaller. Thus, we used an improved iodometric method for determining the double-bond content or hydrogenation degree, which was consistent with that determined by ^{1}H-NMR in most cases, where the hydrogenation degree was not very high. The improved iodometric method was carried out as follows:

A sample of 0.1 g XSBR or 0.5 g HXSBR was accurately weighed and placed in an iodometric flask. Fifty milliliters of the mixed solvent 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 first. Twenty-five milliliters of 0.1M ICl(6) was accurately measured into the iodometric flask and a small amount of a 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 15% KI was added to the flask and shaken for 2 min. Fifty milliliters of distilled water was added and the solution was titrated with 0.1M standard $Na_2S_2O_5$, using a 1% starch solution as an indicator. A blank test was carried out under the same conditions:

Double-bond content (DB) (%)

$$= 2.705(V_0 - V)M/G$$

where V_0 and V are the milliliters of $Na_2S_2O_5$ used for titration of the blank and the sample, respectively; G, the weight of the dried sample or the weight of the dried sample minus the weight of the dried gel; and M, the molar concentration of $Na_2S_2O_5$:

Hydrogenation degree (%)

$$= (1 - DB_{HXSBR}/DB_{XSBR}) \times 100$$

Characterization and Testing

IR spectra were taken on an IR-435 spectrophotometer after the sample was dissolved in the mixed solvent and the polymer solution was coated onto KBr crystal. DSC curves were performed on a Perkin–Elmer 7 differential scanning calorimeter with a heating rate of 5°C/min in the temperature range of 25–100°C. The morphology

Table I   Effect of Types of Inhibitors on the Hydrogenation Reaction

Inhibitor[a]	Gel Content (%)	Hydrogenation Degree (%)
None	91.5	
Sodium *N,N*-dimethyl dithiocarbamate	29.1	28.9
Styrenated phenol	25.4	34.4
Hydroquinone	31.8	36.4
Mixed inhibitor (sodium *N,N*-dimethyldithiocarbamate + *p-tert*-butylpyrocatechol)	10.8	73.8

The hydrogenation conditions are $N_2H_4/C{=}C$ = 1.4 molar ratio, H_2O_2/N_2H_4 = 1.5 molar ratio, amount of $FeSO_4$ used = 1.7 $\times 10^{-3}$ mmol/g of dried latex weight, and 52°C.

[a] Amount of inhibitor used was 2.2% based on dried latex weight.

of the sample was observed on a JEM CX100-II electron transmission microscope. The sodium ionomer was stained with OsO_4 vapor for 24 h before observation.

A 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. The error in the measurement of the tensile strength is ±0.05 MPa

RESULTS AND DISCUSSION

Hydrogenation of XSBRL

Hydrogenation of XSBRL via the diimide reduction process induces gel formation in the absence of an inhibitor as shown in Table I. This phenomenon 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.

Thus, various inhibitors were tried to add to the hydrogenation system to capture the free radicals and to reduce the gel content. Table I shows that, without addition of an inhibitor, the gel content reaches about 92%, but in the presence of 2.2 wt % styrenated phenol based on the rubber, the gel content was decreased to 25% and the hydrogenation degree of the product increased to about 34%. However, if a mixed inhibitor composed of sodium *N,N*-dimethyldithiocarbamate and *p-tert*-butylpyrocatechol is used, the gel content can decrease to about 10% and the hydrogenation degree increase to about 74%.

The effect of the amount of the mixed inhibitor on the gel content and hydrogenation degree of XSBR is illustrated in Figure 1. The gel content

decreases abruptly with addition of the mixed inhibitor, but remains almost constant with further increase of the inhibitor. The hydrogenation degree of the product increases with increase of the amount of the mixed inhibitor and a maximum hydrogenation degree occurs at 2.2% of the mixed inhibitor. 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 formation of diimide, resulting in a decreasing hydrogenation degree.

The metallic ion commonly used as a catalyst in the diimide reduction process of SBR latex is Cu^{2+}. However, the Fe^{2+} ion seems to be the best metallic ion in catalyzing the hydrogenation of XSBR latex, as indicated in Table II. Not only is the gel content the lowest, but also the hydrogenation degree is the highest. The gel content increases in the following order of cations as a cat-
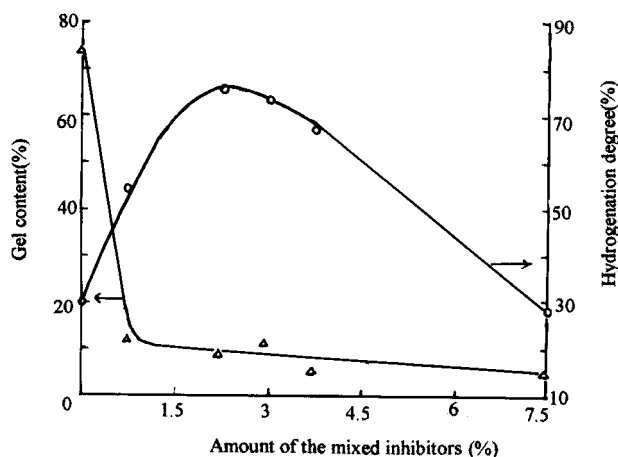

Figure 1   Effect of amount of the mixed inhibitor on the hydrogenation degree and gel content ($N_2H_4/C{=}C$ = 1.4 molar ratio, H_2O_2/N_2H_4 = 1.25; 52°C).

Table II   Effect of Types of Catalyst on Hydrogenation Reaction

Catalyst	Gel Content (%)	Hydrogenation Degree (%)
Fe^{2+}	10.8	73.8
Co^{2+}	12.4	54.6
Ni^{2+}	53.4	46.7
Cu^{2+}	30.6	32.8
Ag^+	5.3	58.7

Amount of catalyst used is 1.7×10^{-3} mmol/g of dried latex weight. The hydrogenation conditions are the same as in Table I.

alyst: $Ag^+ < Fe^{2+} < Co^{2+} < Cu^{2+} < Ni^{2+}$, whereas the hydrogenation degree of the product decreases in the order $Fe^{2+} > Ag^+ > Co^{2+} > Ni^{2+} > Cu^{2+}$.

The oxidation potential of the cations decreases as follows: $Fe^{2+} > Co^{2+} > Ni^{2+} > Cu^{2+} > Ag^+$. It is of interest to note that the hydrogenation degree decreases in the same order of the decreasing oxidation potential of the cations, except the monovalent Ag^+. The latter gave the hydrogenated product with the lowest gel content, but a hydrogenation degree lower than that catalyzed by Fe^{2+}.

Figure 2 indicates the effect of the $FeSO_4$ amount on the hydrogenation degree and the gel content. With an increasing $FeSO_4$ amount, the gel content first remains almost unchanged, but increases quickly over 2.1×10^{-3} mmol/g $FeSO_4$,
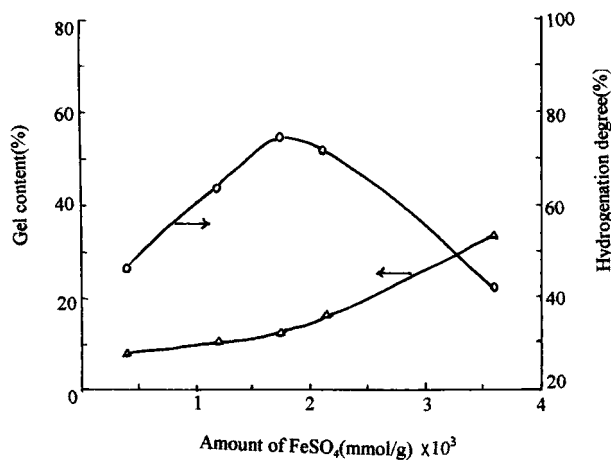
Figure 2   Effect of amount of ferrous sulfate used as catalyst on the hydrogenation degree and gel content ($N_2H_4/C{=}C$ = 1.4 molar ratio, H_2O_2/N_2H_4 = 1.25 molar ratio; 52°C).
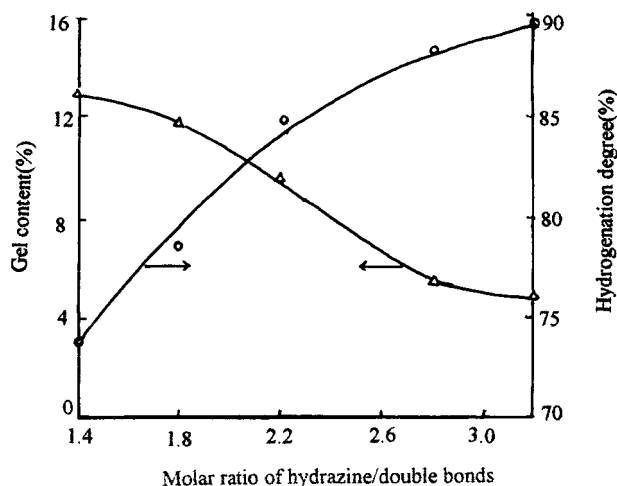
Figure 3   Effect of molar ratio of $N_2H_4/C{=}C$ on the hydrogenation and gel content (H_2O_2/N_2H_4 = 1.4 molar ratio; 48°C).

whereas a maximum hydrogenation degree occurs at about 1.7×10^{-3} mmol/g $FeSO_4$.

Fe^{2+} cannot only act as a catalyst for the diimide formation from hydrogen peroxide and hydrazine, but can also capture free radicals. Excess Fe^{2+} may catalyze the radical formation reaction between hydrogen peroxide and αC of $—COO^-$, resulting in gel formation and decrease of the hydrogenation degree.

The amounts of hydrazine hydrate and hydrogen peroxide used are the main parameters in determining hydrogenation degree. Figure 3 shows that, with an increasing hydrazine amount, the hydrogenation degree increases, whereas the gel content decreases. When the molar ratio of $N_2H_4/C{=}C$ reaches about 2.8, the gel content of the product decreases to about 5% and the hydrogenation degree increases to near 90%. This is because there are two possible reactions between hydrazine and hydrogen peroxide:

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

$$NH{=}NH + \rangle C{=}\langle \rightarrow N_2 + \rangle CHCH\langle \qquad (1)$$

$$NH_2NH_2 + 2H_2O_2 \rightarrow N_2 + 4H_2O \qquad (2)$$
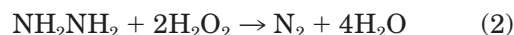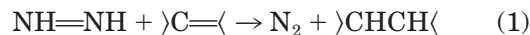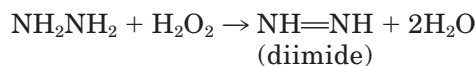
In the presence of double bonds of polybutadiene segments and metallic ion as a catalyst, reactions (1) predominate, that is, diimide is produced and reacts with the double bonds, resulting in increasing the hydrogenation degree, whereas when

amount of double bonds of polybutadiene segments is less and amount of hydrogen peroxide is higher, reaction (2) predominates and forms more nitrogen. The more the N_2H_4, the more diimide that is produced, which increases the hydrogenation degree and inhibits the decomposition of H_2O_2 and thus decreases the formation of the gel.

Figure 4 indicates that, with an increasing molar ratio of H_2O_2/N_2H_4, the hydrogenation degree increases almost linearly, but the gel content remains nearly constant at first and then increases abruptly over the molar ratio of 1.5. This phenomenon may be ascribed to the two competitive reactions between hydrazine and H_2O_2, that is, reactions (1) and reaction (2). When the molar ratio of $H_2O_2/N_2H_4 = 1$, only about a 60% hydrogenation degree can be reached. However, as the molar ratio increases to about 1.6, the hydrogenation degree increases to over 90%. Some hydrazine was consumed in the side reaction (2). Excess H_2O_2 may decompose to form free radicals, which can induce the crosslinking reaction between double bonds, resulting in enhancing the gel formation.

The effect of the reaction temperature on the hydrogenation process is illustrated in Figure 5. When the reaction temperature is lower than 45°C, both the gel content and the hydrogenation degree are low. Only when the reaction temperature is increased over 45°C do both the hydrogenation degree and the gel content increase obviously with the temperature. At lower temperature, the activity of the reactant molecules is
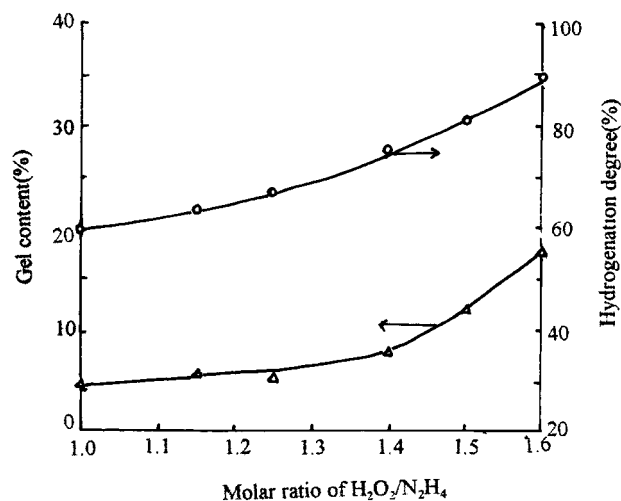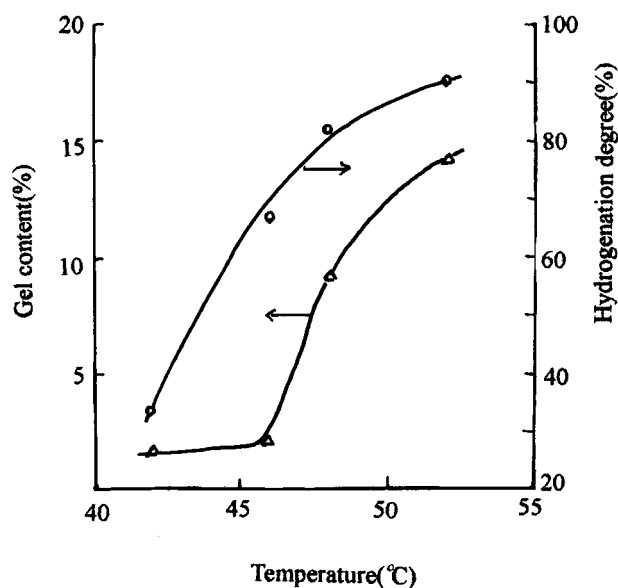

Figure 5 Effect of hydrogenation temperature on the hydrogenation degree and gel content ($N_2H_4/C{=}C = 1.8$ molar ratio, $H_2O_2/N_2H_4 = 1.5$ molar ratio).

lower. As the reaction temperature increases, both the probability of collision and activity of the reactant molecules increase, resulting in enhancing 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. Under the optimum hydrogenation conditions, the product obtained can possess a hydrogenation degree of about 91% and a gel content <5%.

Characterization of the HXSBR

Figure 6 exhibits the IR spectra of (a) XSBR and (b) HXSBR. In spectrum (a), absorption peaks at 1675, 970, 910, 740, and 700–760 cm^{-1} belong to the COOH groups, *trans*-1,4 double bonds, 1,2 double bonds, *cis*-1,4 double bonds, and phenyl groups, respectively. However, the absorption peaks at 740 cm^{-1} is overlapped by that at 700–760 cm^{-1} for phenyl groups. In the IR spectrum (b) of HXSBR with a hydrogenation degree of 91.2%, 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 denotes that most of the double bonds were hydrogenated and transformed into polyethylene segments $(CH_2)_n$ ($n > 4$).
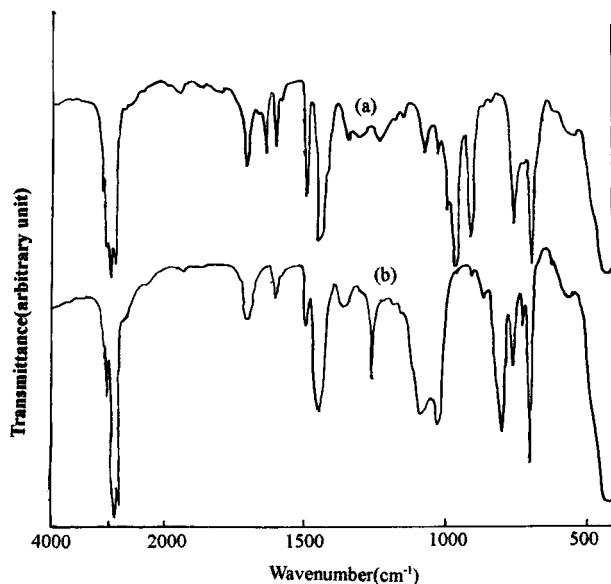

Figure 4 Effect of molar ratio of H_2O_2/N_2H_4 on the hydrogenation degree and gel content ($N_2H_4/C{=}C = 1.8$ molar ratio; 48°C).

Figure 6 IR spectra of (a) XSBR and (b) HXSBR.

Figure 7 represents the DSC curve of HXSBR, which indicates an endothermic peak at 37.7°C. This can be interpreted as the melting of crystalline polyethylene segments of widely varying size and purity formed from the hydrogenation of 1,4-polybutadiene segments, as shown by the similar DSC curve of hydrogenated SBR reported by Parker et al.[3]

Mechanical and Thermooxidation Properties of the HXSBR

Table III shows the mechanical properties of the XSBR and HXSBR with different hydrogenation degrees. It can be seen that XSBR without hydrogenation and vulcanization exhibits very low tensile strength, but after hydrogenation, its tensile strength and ultimate elongation increase significantly, whereas its permanent set keeps a reasonably low value. Thus, it behaves as a thermoplastic elastomer and can be reprocessed. Both the tensile strength and ultimate elongation increase with the hydrogenation degree. But the permanent set remains almost unchanged. The improvement of the 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 XSBR rubber and to the hydrogen bonds formed between COOH groups of different molecules. The hydrogenated XSBR rubber is much more resistant to thermal aging than is XSBR, as

shown in Table III. After thermal treatment at 150°C for 65 h in air, the XSBR sample became brittle, but the HXSBR samples maintained most of the mechanical properties, especially the sample with a 91% hydrogenation degree maintained about 96% of its original tensile strength and about 91%of its ultimate elongation. The higher the hydrogenation degree, the better is the thermooxidation resistance.

Characterization of Ionomers Prepared by Neutralization of HXSBR

Figure 8 shows the IR spectra of (a) the sodium ionomer and (b) the zinc ionomer. The absorption peak at 1675 cm^{-1} for COOH groups, existing in the IR spectrum of HXSBR [Fig. 6(b)] disappears in the spectra of the ionomers. Meanwhile, a wide absorption peak at 1614–1540 cm^{-1} and that at 1400–1450 cm^{-1} appear in the IR spectra of Zn-HXSBR and NaHXSBR, respectively, which indicates the existence of carboxylate groups. Since the ionic potential of Zn^{2+} is higher than that of Na$^+$, the absorption of COO$^-$ for the ZnHXSBR shifts to a higher wavenumber.

DSC curves of the two ionomers (Fig. 9) denote the endothermic peaks at 38.3 and 41.4°C and ΔH of 6.08 and 2.02 J/g for NaHXSBR and ZnHXSBR, respectively. The difference probably is due to the different types of crosslinkages. For NaHXSBR, the physical crosslinkage of macromolecules is ascribed to the association of ions, whereas for ZnHXSBR, the crosslinkage of macromolecules is due to the ionic crosslinkage.

TEM micrographs of the sodium ionomer and lead ionomer (Fig. 10) display the microphase separation of the ionic domains. The sample of the
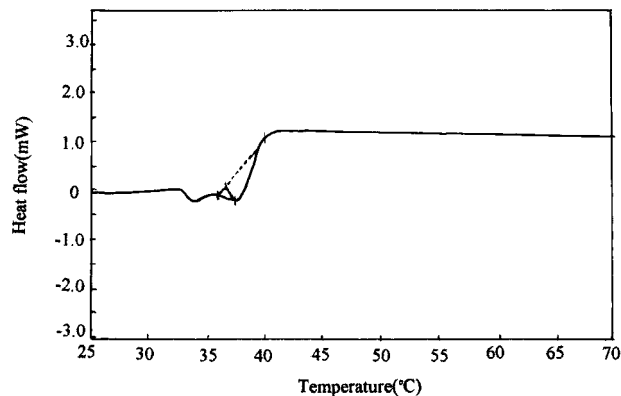

Figure 7 DSC curve of HXSBR with the hydrogenation degree of 91.2%.

Table III   Mechanical Properties and Thermooxidation Resistance of XSBR and Its Hydrogenated Product (HXSBR)

Measurement	XSBR	HXSBR (80.1%)[a]	HXSBR (91.2%)
Original			
Tensile strength (MPa)	0.14	5.1	6.9
Ultimate elongation (%)	220	680	800
Modulus at 300% (MPa)		1.4	2.2
Permanent set (%)	8	21	25
Aged at 150°C for 65 h in air			
Tensile strength (MPa)	Brittle	4.2	6.6
Ultimate elongation (%)		560	730
Modulus at 300% (MPa)		1.2	2.1
Permanent set (%)		19	24

[a] The number in the parentheses is the hydrogenation degree of HXSBR.

sodium ionomer was stained with OsO_4 before observation under an electron transmission microscope. The dark spots represent the ionic domains stained by the OsO_4 distributed in the bright HXSBR continuous phase containing only a few double bonds. The TEM micrograph of the lead ionomer without OsO_4 staining also exhibits dark spots because the heavy lead ions can absorb the electron beams.

Mechanical Properties of Different Ionomers

Different ionomers were prepared by neutralization of HXSBR with different metallic ions. Table IV lists the mechanical properties of the different ionomers. All the ionomers exhibit higher tensile strength, a higher 300% modulus, and somewhat lower ultimate elongation than those of the un-neutralized HXSBR. This may be attributed to the additional physical crosslinkage formed by
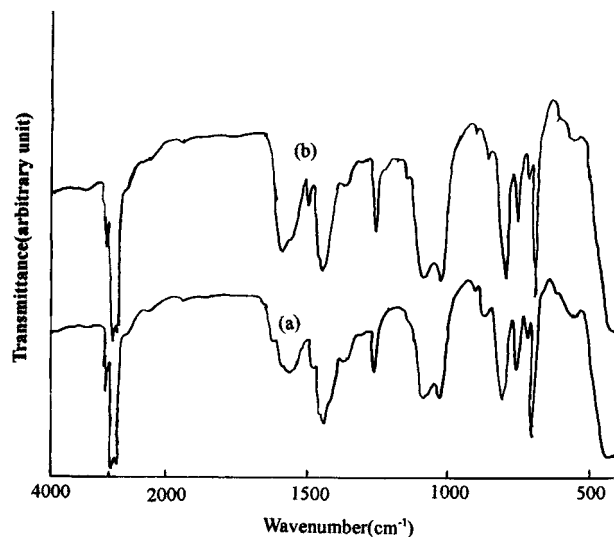

Figure 8   IR spectra of (a) the sodium ionomer and (b) the zinc ionomer of HXSBR with hydrogenation degree of 91.2%.
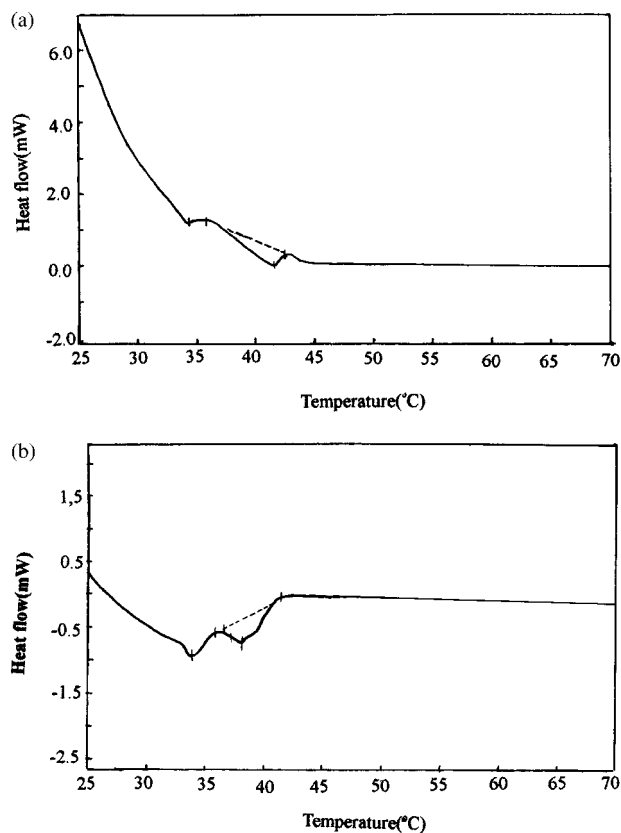

Figure 9   DSC curves of (a) the sodium ionomer and (b) the zinc ionomer of HXSBR with hydrogenation degree of 91.2%.
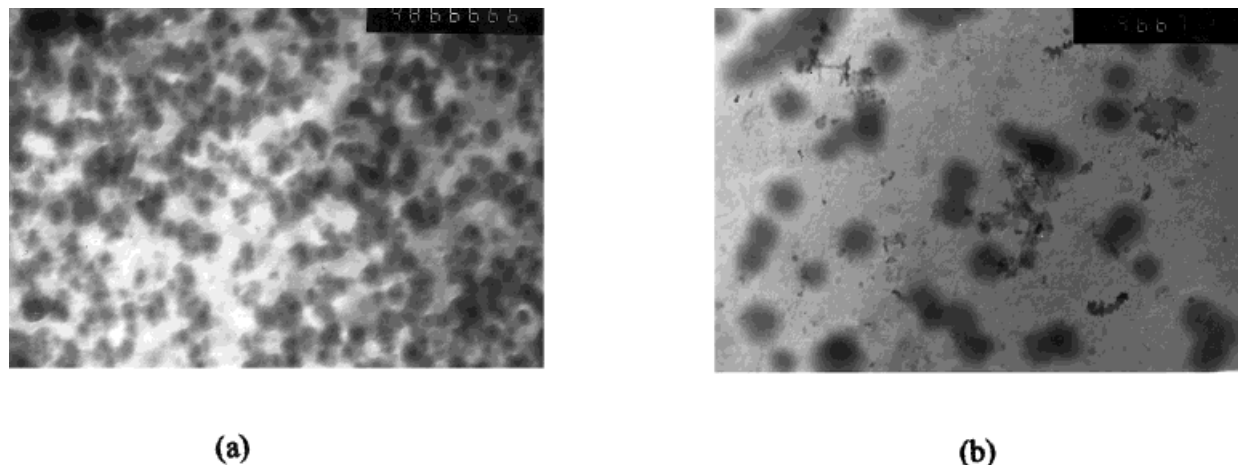
Figure 10 TEM micrographs of (a) the sodium ionomer of HXSBR with magnification of 48,000 and (b) the lead ionomer of HXSBR with magnification of 19,000 of HXSBR.

the ionic domains besides those formed by the crystalline domains of HXSBR. The permanent set of the ionomers are nearly the same as that of the unneutralized HXSBR. The ionomers can be reprocessed. The results imply that the ionomers also behave like the thermoplastic elastomers with mechanical properties better than those of HXSBR.

The tensile strength of ionomers increases in the following order of cations: $K^+ < Mg^{2+} < Na^+ < Zn^{2+} < Pb^{2+}$. For ionomers neutralized with divalent metallic ions, $Mg^{2+} < Zn^{2+} < Pb^{2+}$, and for ionomers neutralized with monovalent ions, $K^+ < Na^+$.

Martsura and Eisenberg[9] indicated that the ionic potential (ratio of charge to ion size) of the metallic ions is an important factor influencing the mechanical properties of ionomers. The higher the ionic potential of a metallic ion, the larger is the repulsive force between the cations and the more difficult it becomes to form ionic domains. Ionic potentials for the divalent cations, such as Pb^{2+}, Zn^{2+}, and Mg^{2+} are 1.67, 2.70, and 3.03, respectively. Thus, the tendency for forming ionic domains is $Pb^{2+} > Zn^{2+} > Mg^{2+}$. Besides, the existence of an external d-level electron makes Pb^{2+} and Zn^{2+} more covalent.[10] These two cations exhibit a lower electrostatic attraction than does Mg^{2+} and it is easier to interchange their ionic bonds. When stress was applied to the ionomer, cation exchange between neighboring groups through dissociation and reformation of ionic bonds may occur, so as to prevent the formation of local stress and, hence, premature failure. Thus, the tendency for cation exchange decreases in the order $Pb^{2+} > Zn^{2+} > Mg^{2+}$. The results of the tensile strength (Table IV) are consistent with the order of the tendency to form ionic domains and cation exchange.

In the case of univalent cations, the tensile strength of the ionomers decreases with a decreasing ionic potential, that is, Na^+ (1.3) > K^+

Table IV   Mechanical Properties of Different Ionomers Obtained from HXSBR

Ionomers	Tensile Strength (MPa)	Ultimate Elongation (%)	300% Modulus (%)	Permanent Set (%)
HXSBR	6.9	800	2.2	25
NaHXSBR	7.3	720	2.4	28
KHXSBR	7.1	760	2.2	26
MgHXSBR	7.2	740	2.3	26
ZnHXSBR	7.4	710	2.5	28
PbHXSBR	7.6	680	2.8	30

Hydrogenation degree is 91.2%.

(0.75). This is contrary to the divalent cations in the formation of crosslinks. The former forms weak crosslinks through association of oppositely charged ions, while the latter forms chemically bonded crosslinks through ionic bonds.[11] For univalent cations, the higher the ionic potential, the more dispersed the ionic domains and, therefore, the greater the strength of the ionomer.

CONCLUSIONS

XSBRL can be hydrogenated via the diimide reduction process to HXSBR with a hydrogenation degree about 91% and a gel content about 5%. It is important to use a mixed inhibitor composed of sodium *N,N*-dimethyldithiocarbamate and *p-tert*-butylpyrocatchecol during hydrogenation to prevent the formation of a large amount of gel. Optimum hydrogenation conditions were obtained. It is better to use ferrous sulfate as a catalyst than cupric sulfate. The hydrogenation degree can reach over 90%. The hydrogenated product showed polyethylene segments in the IR spectrum and an endothermic peak for melting crystalline polyethylene segments. It behaves as a thermoplastic elastomer with good thermooxidation resistance without vulcanization. After neutralization of HXSBR with different metallic ions to form ionomers, the ionomers exhibit carboxylate groups in the IR spectrum and microphase separation of ionic domains in the matrix under the TEM. The ionomers also behave like thermoplastic elastomers. Their mechanical properties are better than those of the unneutralized HXSBR. The tensile strength of the ionomers decreases in the order of cations: For the divalent cations, $Pb^{2+} > Zn^{2+} > Mg^{2+}$, and for the monovalent cations, $Na^+ > K^+$.

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