ELSEVIER

Polymer 41 (2000) 907–915

polymer

Diimide reduction of carboxylated styrene–butadiene rubber in latex stage

M. De Sarkar, P.P. De, A.K. Bhowmick*

Rubber Technology Centre, Indian Institute of Technology, Kharagpur-721 302, India

Received 22 October 1998; received in revised form 1 March 1999; accepted 25 March 1999

Abstract

Carboxylated styrene–butadiene rubber (XSBR) is selectively hydrogenated by diimide reduction technique in latex stage using hydrazine hydrate, hydrogen peroxide and Cu^{+2} as catalyst. The products are characterised by IR and NMR spectroscopy. Dynamic Mechanical Properties and Transmission Electron Micrographs of the hydrogenated products confirm the existence of ionic aggregates involving carboxyl (–COOH) groups of the substrate and externally added Cu^{+2} ions. Longer reaction time and higher amount of catalyst are required for hydrogenation of XSBR compared to that of SBR. An increase in the amount of carboxyl group decreases the extent of reaction. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Hydrogenation; Carboxylated styrene–butadiene rubber; Diimide

1. Introduction

Chemical modification of polymers by hydrogenation is an active field of research as it leads to polymers with unusual and novel monomer sequence, which are otherwise inaccessible or difficult to prepare by conventional polymerisation [1]. Hydrogenation simply reduces the degree of unsaturation in diene polymers. Nevertheless, it leads to significant changes in the chemical and physical properties of polymers [2]. Hydrogenation of polymers can be achieved by both catalytic and non-catalytic methods. Non-catalytic hydrogenation of unsaturated polymers is usually carried out using diimide generated in-situ. The diimide reduction could efficiently be run in emulsion by oxidation of hydrazine hydrate using metal catalyst [3]. Nitrile rubber (NBR), polybutadiene rubber (BR), styrene–butadiene rubber (SBR) have been successfully hydrogenated by diimide reduction technique in the latex stage [4,5]. The influence of the level of hydrogenation and styrene content on preparation and properties including degradation of styrene–butadiene rubber latex has been reported by us [6–8]. The hydrogenated SBR films show high tensile strength and thermoplastic elastomeric behaviour, caused by the polyethylene crystallites that exist even in unstretched films under ambient conditions.

It is well known that introduction of functional group into conventional elastomer is one of the strategies for altering physical characteristics or designing rubber molecules to suit specific functions. Carboxyl groups, when introduced into elastomers, give elevated elasticity range, impart strength to rubber through ionic bonds and give superior filming properties, increased resistance to hydrocarbon solvents and susceptibility to cross-linking or vulcanization by polyvalent reagents [9]. Hence, the presence of carboxyl group should influence the reaction conditions of hydrogenation and properties of the resultant rubber. Reports are available on catalytic hydrogenation of diene elastomer with carboxyl functionality [10,11]. But, no attempt has so far been made to hydrogenate carboxylated styrene–butadiene rubber in latex stage where both the styrene group and carboxyl functionality interfere in the double bond reduction. It has been demonstrated earlier [12] that hydrogenation of carboxylated nitrile rubber can be carried out without decarboxylation only with $[Pd(CH_2COO)(C_6H_5\text{-}COC_5H_4N)_2]$ catalyst, whereas other catalyst systems lead to decarboxylation of the rubber and subsequent loss of properties. We have therefore, undertaken a study to explore the utility of diimide reduction for latex stage hydrogenation of carboxylated SBR. This paper reports the application of diimide for hydrogenation of carboxylated styrene–butadiene rubber in water emulsion and the physical properties of the modified rubbers.

2. Experimental

2.1. Materials

Carboxylated styrene–butadiene rubber lattices with

---

* Corresponding author. Tel.: +91-3222-55221, ext. 4972; fax: +91-3222-55303.

PII: S0032-3861(99)00269-4

Table 1
Microstructural analysis from NMR studies solid content and pH of styrene–butadiene and carboxylated styrene–butadiene rubber

Sample	A	B	C	D
Styrene (mol%)	17.3	20.9	20.2	18.1
Butadiene (mol%)				
Trans	68.4	60.1	61.2	59.5
Cis	11.4	21.9	20.1	22.3
Vinyl	20.2	18.0	18.7	18.2
Methacrylic acid (mol%)	0	1.2	3.6	4.3
Solid content (%)	32.9	37.2	35.3	39.0
pH	9.28	2.95	2.88	2.65

different acid contents were received from the Goodyear Tyre and Rubber Co. Ltd., USA. The microstructural analyses of these polymers are shown in Table 1. Hydrazine hydrate, hydrogen peroxide, cupric sulphate catalyst, surfactant (sodium lauryl sulphate) and methanol were received from the standard sources.

2.2. Latex reduction process

The original carboxylated styrene–butadiene rubber latex was first adjusted to pH 10 with sufficient amount of dilute (3%) KOH solution. Then the desired amount of latex was charged into an appropriate sized reaction flask equipped with stirrer, hydrogen peroxide inlet tube, rubber septumed inlet for syringed addition of antifoam, condenser and an outlet connected to a bubbler containing water. The reaction flask was immersed into a constant temperature bath. To the stirred latex was then added the calculated molar amount of copper sulphate solution mixed with equal weight of surfactant and a few drops of antifoam agent followed by the addition of desired molar amount of 80% aqueous hydrazine. At a desired temperature, a required volume of 30% hydrogen peroxide was introduced drop-wise over a specific period of time. Small amount of antifoam was added as necessary to minimize foaming. The latex was post-reacted for several hours while cooling to room temperature. The hydrogenated polymer was coagulated into acidified isopropanol, washed several times, filtered and dried under vacuum for 48 h.

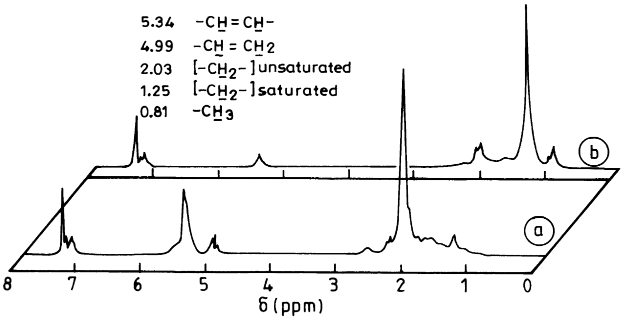


Fig. 1. ^{1}HNMR spectra for (a) XSBR containing 1.2% methacrylic acid and (b) the same with 80% saturation.

2.3. Characterisation

FT NMR spectra were recorded in 300 MHz Bruker Advance DPX NMR Spectrophotometer by taking the soluble fraction of the polymer in $CDCl_3$.

IR spectra were collected in Perkin–Elmer (model 843) spectrophotometer using thin latex cast films. The spectra were taken with 5.4 cm^{-1} resolution at a noise level of 0.1% transmittance.

Dynamic mechanical thermal analysis of pure and hydrogenated polymer were performed using Dynamic mechanical thermal analyser (DMTA MK II) from Polymer Laboratories Ltd., UK. All the samples were analysed in a dual cantilever bending mode with a strain of 64 μm (peak to peak displacement) in the temperature range of −70°C to 100°C. Frequencies selected were 0.1, 1 and 10 Hz. The heating rate was 2°C/min.

Transmission electron microscopy was carried out using TEM (model C-12, Philips). The latex cast samples were stained with OsO_4 for better contrast.

Physical properties (tensile strength, elongation at break and modulus values) were measured on latex cast films in Zwick 1445 Universal Testing machine at a strain rate of 500 mm/min at 30 ± 2°C following ASTM D-412-93.

Elemental analysis was performed in Perkin–Elmer Series II CHN Analyser (model 2400).

Wide angle X-ray diffraction spectra were recorded with Philips X-ray diffractometer (PW-1710) using Iron filtered Co-K_α radiation at a scanning speed of 3° per minute.

3. Results and discussion

3.1. Structural aspects

Fig. 1 shows representative ^{1}HNMR spectra of the control and the 80% hydrogenated XSBRs. Major peaks are obtained in the aliphatic (0.5–2.8 ppm) and olefinic (4.6–5.8 ppm) regions. The signals of olefinic protons due to 1,4 unsaturation are centred at 5.3 ppm, while those due to 1,2 unsaturation are centred at 4.9 ppm. With the progress in hydrogenation, the olefinic peak area decreases considerably; consequently, two new peaks appear at $\delta = 0.8$ and 1.2 ppm attributed to $-CH_3$ and saturated $-CH_2-$ units, respectively. It is clear from Fig. 1 that the peak due to 1,2 unsaturation is absent from 80% saturated sample indicating its faster rate of hydrogenation compared to that of 1,4 unsaturation. As the vinyl double bonds occur in a pendent position of the polymer chain, it should be more accessible to the diimide reagent. There is no change in the intensity of aromatic peaks in the region of 6.8–7.2 ppm due to styrene reflecting the stability of aromatic ring towards diimide reduction. The degree of hydrogenation has been calculated from the ^{1}HNMR spectra from the change in the integral of the peaks representing protons in hydrogenated rubber. The results are comparable with those obtained from

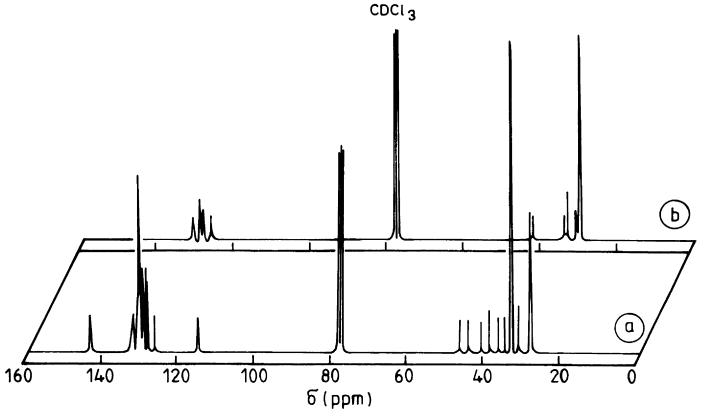


Fig. 2. ^{13}CNMR spectra for (a) XSBR containing 1.2% methacrylic acid and (b) the same with 80% saturation.

the IR analyses. A similar correspondence between these two measurements was reported in our earlier studies on hydrogenation of styrene–butadiene rubber [6,8].

The ^{13}CNMR spectra of pure and hydrogenated XSBRs are shown in Fig. 2. The peak assignments in the region of (0–160 ppm) of pure XSBR are given in Table 2. On hydrogenation, the peaks in the olefinic region (114–143 ppm) decrease.

IR spectra of the pure and the hydrogenated XSBRs are shown in Fig. 3. The spectra of the control XSBR in the region of 600–1050 cm^{-1} (Fig. 3(a)) indicate peaks at 699 cm^{-1} due to styrene units, 757 cm^{-1} due to 1,4 *cis*, 909 cm^{-1} due to 1,2 vinyl and 967 cm^{-1} due to 1,4 *trans* butadiene units. As the level of hydrogenation increases, the peaks due to butadiene units decrease. A new peak at 722 cm^{-1} due to –CH$_2$– rocking vibration [(–CH$_2$–)$_{n>4}$] appears in the spectra of hydrogenated XSBRs. The absorption peak at 699 cm^{-1} shows no change in the intensity reflecting the stability of the aromatic ring towards diimide reduction. In the control XSBR, a peak appears at 1694 cm^{-1} due to >C=O stretching vibration as shown as an inset in Fig. 3. The sharp peak shape and the frequency of >C=O absorption suggest that most –COOH groups present in XSBR are hydrogen bonded. On hydrogenation the peak broadens, as it begins to split into three absorption bonds. The broad absorption band can be deconvoluted by curve fitting. For the peak shape, a Gaussian instead of Lorenzian profile is assumed in our fitting procedure. As suggested by Maddams [13], Lorentzian profile is generally better than Gaussian approach; but for closely overlapping peaks, the use of Gaussian shape may be appropriate.

Table 2
^{13}CNMR assignments for pure XSBR containing 1.2% methacrylic acid

Peak chemical shift (ppm)	Polymer[a]	Carbon type[b]
Saturated carbon region		
27.4	BD	C_{CH_2}
30.2	BD	
30.4	BD	
32.8	BD	
34.0	BD	V_{CH_2}
35.7	S	S_{CH_2}
38.2	BD	T_{CH_2}
40.1	BD	T_{CH_2}
43.6	BD	V_{CH}
45.7	S	S_{CH}
Unsaturated carbon region		
114.2	BD	V_{CH_2}
125.9	S	C_4
127.8	BD	T_{CH}, C_{CH}
128.0	S	C_3, C_5
128.2	S	C_2, C_6
128.4	BD	T_{CH}, C_{CH}
129.5	BD	C
130.0	BD	T
131.3	BD	C, T
142.8	BD	V_{CH}

[a] BD, butadiene; S, styrene.

[b] T, *trans*; C, *cis*; V, vinyl; S, styrene; C_1, carbon 1 on styrene ring.

The broad carboxyl peak for HXSBR can be deconvoluted into three peaks, one at original 1694 cm^{-1} position and the other two approximately at 1720 and 1680 cm^{-1}, respectively. The shift in the position of the >C=O band to the higher frequency side corresponds to the reduction of the average strength of hydrogen bonds, whereas the peak due to lower frequency side at 1680 cm^{-1}, may be attributed to the ionic aggregates or clusters involving –COOH groups and Cu^{+2} ions.

The amount of carboxylic group and the presence of any nitrogen containing compounds which may be formed during reduction process involving –COOH groups of the substrate and added hydrazine hydrate ($N_2H_4 \cdot H_2O$) has been checked by Elemental Analysis. There is no decrease in oxygen content indicating no decarboxylation and no trace of nitrogenous compounds formed during hydrogenation process.

The dynamic mechanical properties of XSBR before and after hydrogenation are depicted in Fig. 4. The temperature dependence of the mechanical loss tangent (tan δ) of the control and the 80% hydrogenated XSBR is shown in Fig. 4(a). The loss tangent curve of XSBR has a single peak at −31°C, which is ascribed to the glass transition

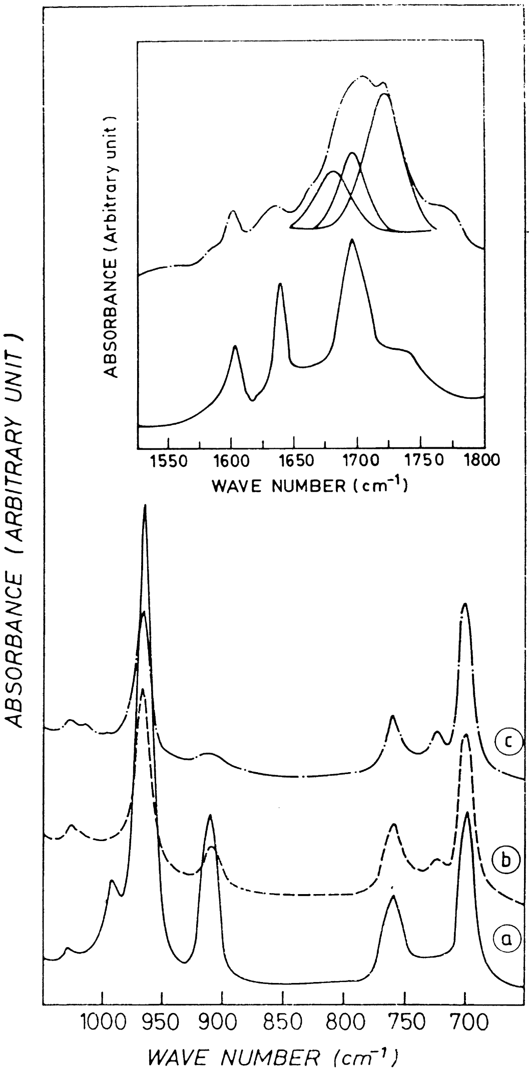


Fig. 3. IR spectra of (a) XSBR and HXSBR with (b) 60% and (c) 80% saturation.

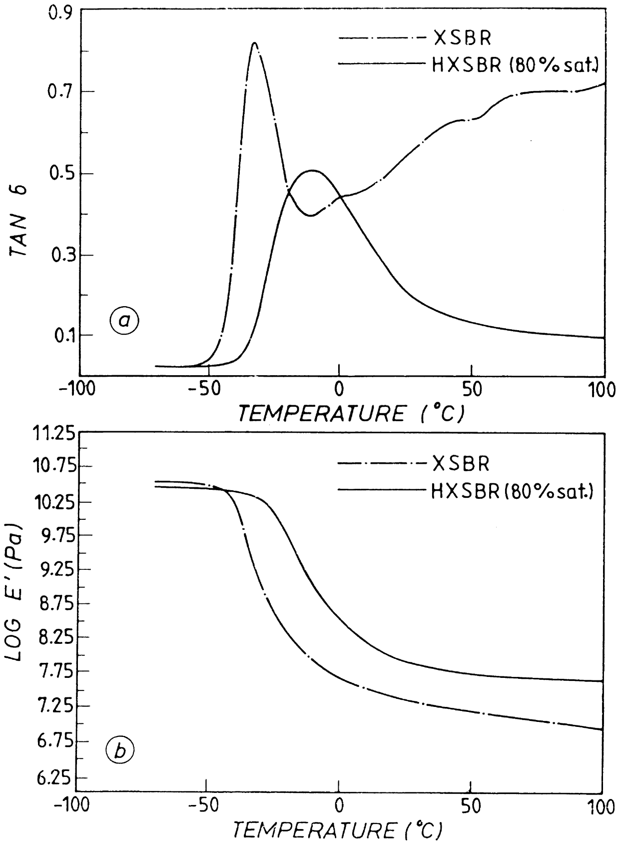


Fig. 4. Temperature dependence of (a) loss tangent (tan δ) and (b) storage modulus (E') for control XSBR and HXSBR with 80% saturation at a frequency of 10 Hz.

temperature. On hydrogenation, this peak shifts to a higher temperature with a lowering of peak tan δ value and the peak width increases. XSBR with 80% saturation shows single peak at around -11°C. A similar shift in T_g towards higher temperature side (from -37 to -28°C) was observed for HSBR with 74% saturation [14] which was due to the gradual replacement of amorphous segments by polyethylene like crystalline units and appearance of more ordered structure in HSBR. HSBR with 74% saturation was found to contain 3.5% crystallinity [14]. However, in contrast to HSBR, HXSBR does not show any crystallinity, as evidenced from wide-angle X-ray diffraction studies, even at 80% saturation level. The increase in T_g value of HXSBR may be due to restriction of the mobility of the segmental chains due to partial complexation involving the externally added Cu^{+2} ion and –COOH groups present in the substrate. When aqueous solution of $CuSO_4$ is added to the XSBR latex as a catalyst, the Cu^{+2} may form a distorted octahedral complex with four –COOH groups of the substrate (Fig. 5). Similar type of structure was reported to be seen in [Cu_2 (acrylate)] [15]. Associated sulphate ions of the catalyst or from the surfactant may also occupy the other two sites. Though hydrogenated products were thoroughly dried under vacuum, it was possible that two water molecules may be retained in a coordinated form.

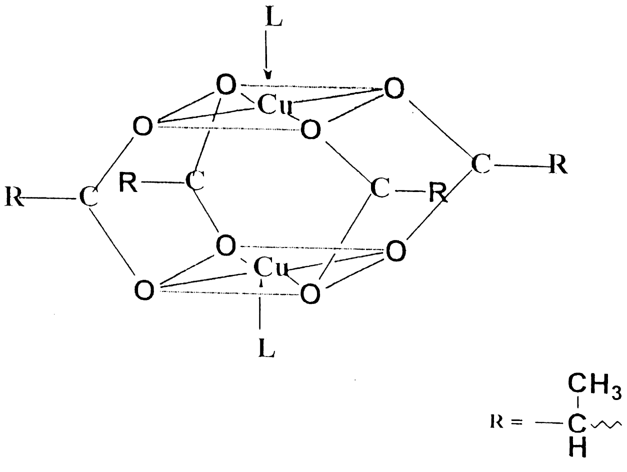


Fig. 5. Structure of Dicopper-acid complex.

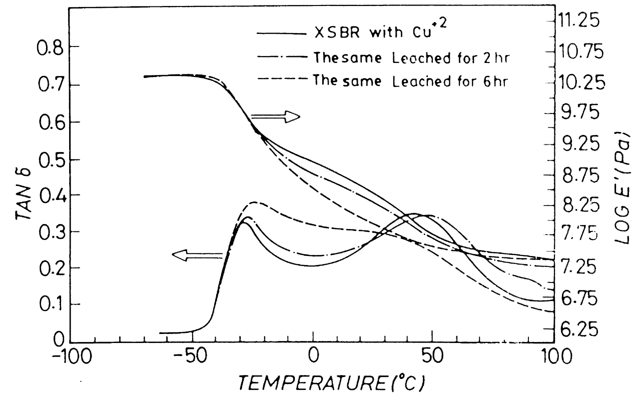


Fig. 6. Dynamic mechanical properties for XSBR under different conditions (—) XSBR with added Cu^{+2}, (—·—) the same leached for 2 h and (- - -) the same leached for 6 h.

The polymer entrapped ligand-bound Cu^{+2} ion could be released by acid-leaching[with 1(N) HCl; 80(C]. Fig. 6 shows the dynamic mechanical properties of the control XSBR samples with added Cu^{+2} and those of the samples after acid-leaching. The peak at around 60°C present in XSBR with Cu^{+2} is due to the presence of ionic clusters. After acid-leaching the particular peak disappears gradually. The position of the glass transition temperature does not change appreciably on addition of Cu^{+2} ion, though the peak height increases on acid-leaching.

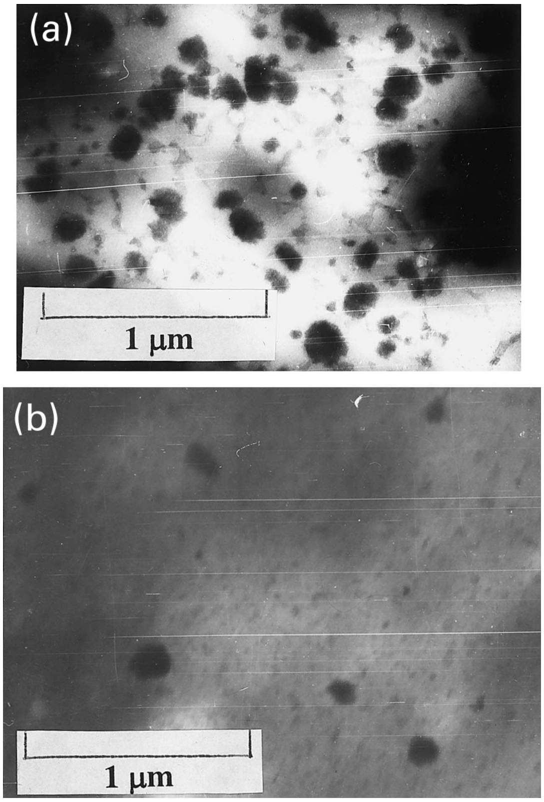


Fig. 7. Transmission electron micrographs of (a) XSBR with Cu^{+2} and (b) HXSBR with 80% saturation (30 000 ×).

The presence of ionic multiplets involving Cu^{+2} and –COOH groups can again be evidenced from the storage modulus (Fig. 4(b)), which increases with increase in concentration of Cu^{+2} and also from the transmission electron micrographs. The clusters varying from 75–100 nm size are observed for the control XSBR with few drops of aqueous $CuSO_4$ solution (Fig. 7(a)). The HXSBR with 80% saturation show much smaller dimensions of the clusters (Fig. 7(b)).

3.2. Effect of reaction parameters

The hydrogenation reaction has been carried out by varying different parameters such as time, temperature, concentration of hydrazine hydrate and catalyst. The effect of these parameters on the level of hydrogenation has been investigated with 25 gm XSBR latex with 3.6% acid containing 0.125 mol double bond and the results are compared with no acid containing SBR [6]. Both SBR and XSBR lattices contain comparable level of double bonds and styrene.

3.3. Effect of reaction time

The effect of reaction time has been studied at 50 ± 2°C in the presence of 0.188 mol hydrazine hydrate (1.5 times to that of molar olefin content), 0.188 mol hydrogen peroxide and 0.020 mmol $CuSO_4 \cdot 5H_2O$. It is observed from Fig. 8 that the level of hydrogenation increases with increase in reaction time due to the reduction of double bonds. However, the extent of hydrogenation levels off after 7 h, showing only a marginal change thereafter. But for SBR, a maximum reduction of 80% is achieved at 45 ± 2°C for 1 h. of reaction time [6].The higher reaction time needed for XSBR may be due to the partial complexation involving Cu^{+2} and –COOH groups. Also, the average latex particle size increases due to the formation of ionic clusters. As a result, the distance for diffusion of the diimide molecules from the surface to react with the double bonds residing at the innerside of the latex particle increases.

The longer the diffusion distance, the longer is the lifetime needed for the diimide before reaching a double bond and greater the disproportionation/decomposition of diimide itself according to Eqs. (1) and (2):

$$NH{=}NH \rightarrow N_2 + H_2 \qquad (1)$$

$$2NH{=}NH \rightarrow NH_2{-}NH_2 + N_2 \qquad (2)$$

Hence, longer reaction time is necessary for XSBR compared to that of SBR to achieve same level of hydrogenation.

3.4. Effect of reaction temperature

The hydrogenation reaction has been studied from 30 to 70°C in the presence of 0.188 mol hydrazine and hydrogen peroxide, 0.020 mmol $CuSO_4 \cdot 5H_2O$ catalyst for 7 h. The

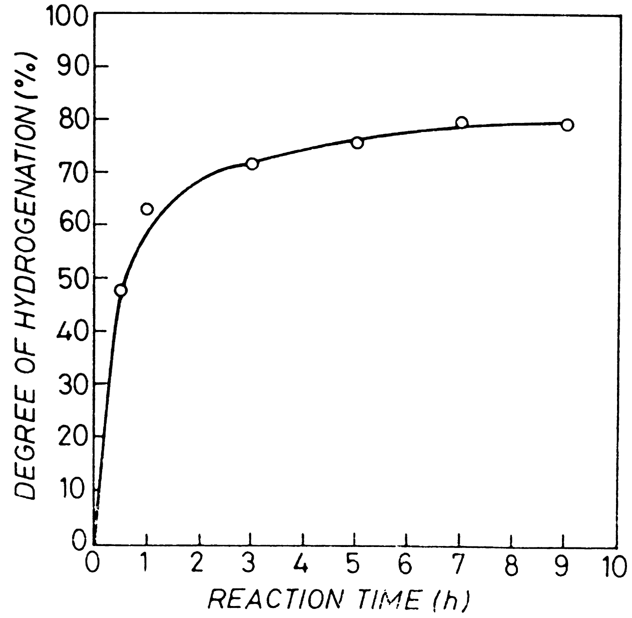


Fig. 8. Effect of reaction time on the degree of hydrogenation of XSBR (temperature 50 ± 2°C; 0.188 mol hydrazine; 0.188 mol hydrogen peroxide and 0.020 mmol $CuSO_4 \cdot 5H_2O$ catalyst).

extent of hydrogenation increases with increase in temperature up to 50 ± 2°C; at that temperature maximum conversion (80%) is achieved (Fig. 9). After 50°C; the degree of hydrogenation decreases, because of the possibility of crosslinking involving the double bonds and decomposition of the reactants at higher temperature. Similar observation has been made for SBR, where maximum conversion is achieved at 45 ± 2°C [6].

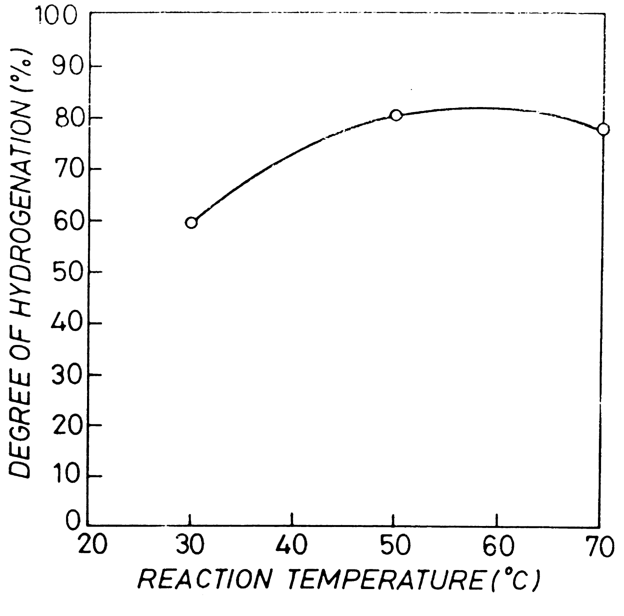


Fig. 9. Effect of reaction temperature on the degree of hydrogenation of XSBR. (Time 7 h; 0.188 mol hydrazine; 0.188 mol hydrogen peroxide and 0.020 mmol $CuSO_4 \cdot 5H_2O$ catalyst).

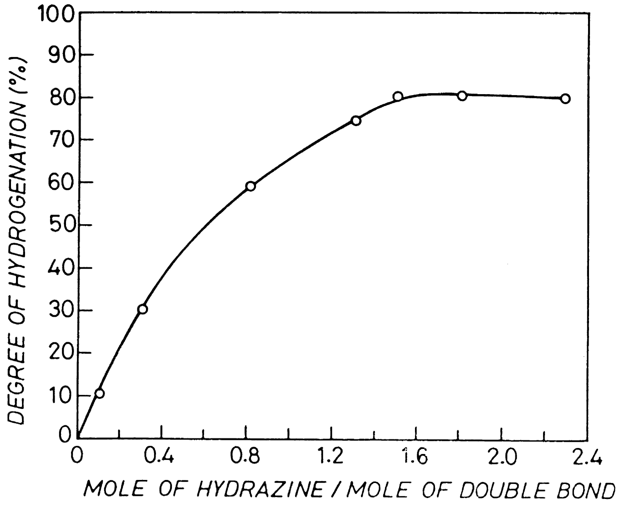


Fig. 10. Effect of hydrazine concentration on the degree of hydrogenation of XSBR. (Temperature 50 ± 2°C; time 7 h; 0.188 mol hydrogen peroxide and 0.020 mmol $CuSO_4 \cdot 5H_2O$ catalyst.)

3.5. Effect of concentration of hydrazine hydrate

The effect of hydrazine hydrate concentration has been studied in the presence of 0.020 mmol catalyst at 50 ± 2°C for 7 h reaction time. The degree of hydrogenation is plotted against the ratio of moles of hydrazine to moles of double bond initially present (Fig. 10). It can be seen that the maximum level of hydrogenation is achieved when 1.5 mol of hydrazine per mole of butadiene units is used. After reaching a maxima, degree of hydrogenation does not increase. Similar observation was reported earlier [6]; the addition of excess hydrazine with respect to surfactant concentration results in no visible effect on appearance or stability of the latex. However, an exothermic heat of mixing is

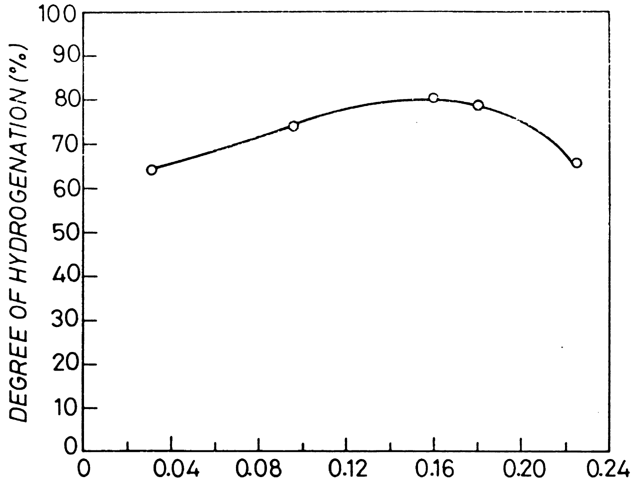


Fig. 11. Effect of catalyst ($CuSO_4 \cdot 5H_2O$) concentration on the degree of hydrogenation of XSBR. (Time 7 h; temperature 50 ± 2°C; 0.188 mol hydrazine and 0.188 mol hydrogen peroxide.)

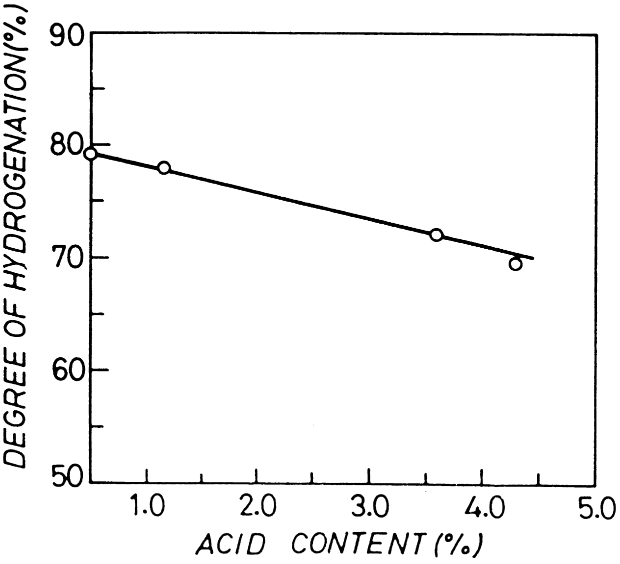


Fig. 12. Effect of acid content on degree of hydrogenation. (Time 3 h; temperature 50 ± 2°C, hydrazine hydrate and hydrogen peroxide at a molar ratio of 1.5 times and at a catalyst concentration of approximately 10^{-4} times to that of olefin content of XSBR.)

observed. It has been shown earlier [16] that a large excess (at least two folds) of diimide precursors with respect to multiple bond to be reduced is necessarily required in order to compensate for the loss of *anti* (*trans*) diimide which are inactive for reduction and also the concurrent disproportionation of diimide according to Eqs. (1) and (2) shown earlier. In Fig. 10, it is observed that the degree of hydrogenation increases linearly with increase in concentration of hydrazine even if the equivalent of hydrazine used is less than/or equal to one.

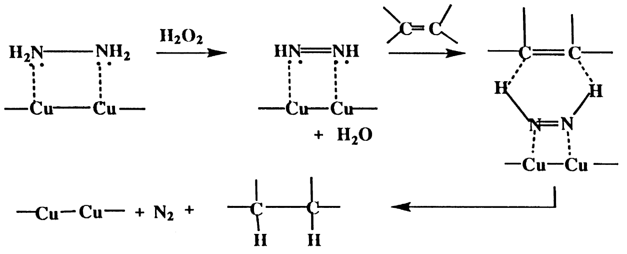
3.6. Effect of concentration of copper sulphate catalyst

The effect of catalyst concentration on the hydrogenation percent has been studied for a period of 7 h at 50 ± 2°C in the presence of 0.188 mol hydrazine and 0.188 mol hydrogen peroxide. It is clear from Fig. 11 that the catalyst concentration plays an important role on the extent of hydrogenation. The reduction of double bonds increases with increase in catalyst concentration. A maximum of 80% hydrogenation is achieved at 0.020 mmol of catalyst (1.65×10^{-4} times the concentration of original molar olefin content). The level of hydrogenation decreases thereafter. The optimum catalyst concentration required for 25 gm (0.125 mol double bond) SBR is 0.0064 mmol in the presence of 0.20 mol hydrazine, 0.26 mol hydrogen peroxide at 9.36 pH at 45 ± 2°C for a 4 h reaction. Maximum hydrogenation of 94% was achieved at that condition. Higher amount of catalyst is required for XSBR to optimize compared to that of SBR. It is also interesting to note that the variation of degree of hydrogenation with respect to the catalyst concentration is larger in the case of SBR [6].

In the actual reduction process, the copper ion is able to greatly accelerate the formation of diimide from the $NH_2{\cdot}NH_2/H_2O_2$ redox system [16]. Copper ion, when added to the system can be present in three locations: (a) in water medium; (b) at the polymer surface; (c) inside the latex. Localizing copper ion in water phase will lead only to decomposition reactions of diimides as shown earlier (Eqs. (1) and (2)). Copper ion when added to the system can be distributed over the surface of latex particles by means of strong complexation with carboxylate soap anions ($RCOO^-Na^+$). The reaction can be represented as:

$$2CuSO_4{\cdot}5H_2O + RCOO^-Na^+ \rightarrow Cu_2(RCOO)_4 + Na_2SO_4 + 5H_2O \quad (3)$$

From the above equation, it is seen that the active site is actually bimetallic copper and resides within the surfactant surface layer of polymer particles as the bridged species [4]. As the carboxylated copper complex resides at the latex particle surface, where it comes across a large excess of hydrazine in aqueous phase, it is likely that the hydrazine bound between copper centres through lone electron pairs on nitrogen. Subsequent oxidation of bound hydrazine with hydrogen peroxide then directly produces diimide and water, while the active copper site is regenerated. Diimide is the actual hydrogenating species which reduces the double bond [16].



(4)

Thus concentration of copper ion at the particle surface is the key factor which need to be controlled. To reach a high degree of hydrogenation, the copper ions should reside only at the surface of the latex particle.

For XSBR, there is a possibility of few Cu^{+2} ions to get attached inside the latex particle via complexation. The entrapment of Cu^{+2} within the latex is evidenced from their dynamic mechanical properties and electron micrographs. Thus, the total number of copper ions which could be present at the surface is somehow limited by a competing complexation reaction between Cu^{+2} and –COOH at a particular time. For XSBR, more catalyst (almost three times) is required to get maximum level of hydrogenation, as compared to the amount for SBR. It can be noticed that for XSBR (Fig. 11) and also for SBR [6], the degree of hydrogenation is low at higher copper ion concentration. The rate of formation of diimide would be faster at higher concentration of the catalyst which inturn enhances the diimide disproportionation as compared to that of reduction. At even higher copper ion concentration, some free copper

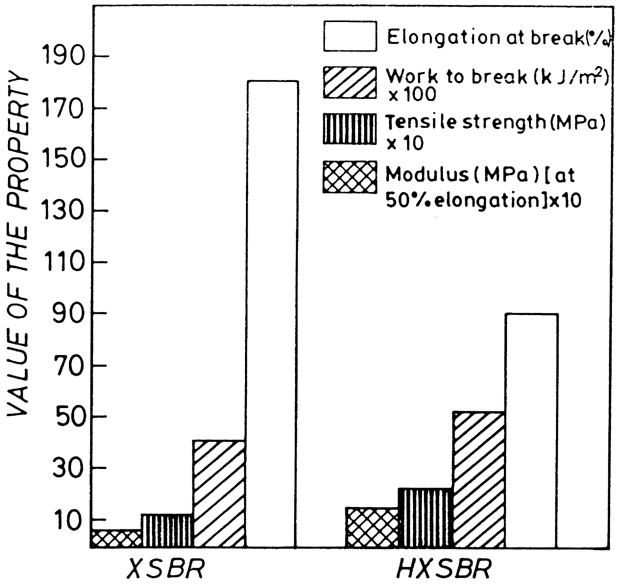


Fig. 13. Plot showing the variation of tensile strength (F_{max}), modulus at 50% elongation, elongation at break and work to break for XSBR and HXSBR with 94% saturation.

ions may also be present in the water medium; this would make the $NH_2 \cdot NH_2/H_2O_2$ reaction to occur mostly in water phase. As a result, the double bond reduction will be decreased.

3.7. Effect of acid content on the level of hydrogenation

The effect of acid content on the level of hydrogenation has been studied for styrene–butadiene rubber with 0, 1.2, 3.6 and 4.3% methacrylic acid using hydrazine hydrate and hydrogen peroxide at a molar ratio of 1.5 times to that of olefin content of XSBR and at a catalyst concentration of approximately 10^{-4} times to that of olefin at 45–50°C for 3 h. All four lattices contain almost the same amount of styrene (18–20%) and molar olefin content. It has been seen from Fig. 12 that with an increase in the acid content, the level of hydrogenation decreases slightly. Similar observation was reported by Bhattacharjee et al. [10] for hydrogenation of liquid carboxylated rubber using palladium complex $[Pd(CH_3COO)(C_6H_5COC_5H_4N)_2]$ as catalyst. The XSBR samples with 1.2, 3.6 and 4.3% acid have a non-uniform distribution of a carboxyl group for every 430, 145 and 122 carbon atom, respectively. With increase in acid content, the chance of complexation involving –COOH group and the added Cu^{+2} increases. As a result, the availability of Cu^{+2} on the surface which is a prime requirement for hydrogenation to occur in the latex stage, decreases. Another fact is that, for XSBR with higher –COOH content, the chance of formation of a network like structure involving inter- or intra-chain –COOH groups increases and subsequently, the rigidity increases. As a result, the diffusion of diimide inside the latex particles decreases, which reduces the extent of hydrogenation in turn. It has been reported [17] that the hydrogenation zone (thickness) from the particle surface inward, where diimide molecules can diffuse before disproportionation reactions among themselves, is about 20 nm.

3.8. Effect of hydrogenation on physical properties of carboxylated styrene–butadiene rubber

Fig. 13 shows a comparison of the physical properties (tensile strength, modulus at 50% elongation, work to break and elongation at break) of the control XSBR (4.3% acid) with its 80% saturated counterpart. It is seen that there is an increase in the tensile strength and modulus values whereas the elongation at break value shows a decrease. HSBR (0% acid) with 87% saturation shows a remarkable increase in the tensile strength from 0.5 to 5.4 MPa and elongation at break from 170 to 991% [14]. The remarkable improvement in mechanical properties for HSBR with 87% saturation was explained by taking into account its 5.6% crystallinity. But HXSBR samples do not show any crystallinity. The increase in tensile strength of HXSBR with 80% hydrogenation may be due to the presence of ionic bonds between the –COOH and Cu^{+2} ions and hence gelling. The ionic clusters can function as cross-links at room temperature. Presence of these ionic cross-links may provide HXSBR with high tensile strength.

4. Conclusions

Carboxylated styrene–butadiene rubber can be selectively hydrogenated by diimide reduction technique. During the reduction, both the carboxyl groups and styrene units do not undergo any change. Gradual reduction of ^{1}HNMR peaks in the range of 4.6–5.8 ppm and ^{13}CNMR peaks in the range of 114–142 ppm indicate the hydrogenation. The results of dynamic mechanical thermal analysis and electron micrographs confirm the existence of ionic aggregates/clusters involving –COOH group of the substrate and externally added Cu^{+2} ions. The effect of reaction conditions on hydrogenation has also been studied. With increase in reaction time, temperature, concentration of hydrazine hydrate and the copper sulphate catalyst, the extent of hydrogenation increases in the initial stages. It is observed that higher reaction time and higher amount of catalyst are required for XSBR compared to those of SBR. An increase in the amount of carboxyl group decreases the extent of reaction.

Acknowledgements

The authors gratefully acknowledge the support of Mr Dane K. Parker, The Goodyear Tyre and Rubber Co. for providing the samples of XSBR and for helpful suggestions in various stages of this investigation. One of the authors (M. De Sarkar) is grateful to the CSIR, New Delhi, India, for providing a Senior Research Fellowship.

References

[1] Mudilige DC, Rempel GL. Molecular Catalyst, A: Chemical 1997;123:15.

[2] Bhowmick AK, Stephens HL. Handbook of elastomers—new developments and technology. New York: Marcel Dekker, 1988.

[3] Wideman LG. To the Goodyear Tyre and Rubber Co. US 4, 452, 950, 1984.

[4] Parker DK, Roberts RF, Schiessl HW. Rubber Chem Technol 1992;65:245.

[5] Parker DK, Roberts RF, Schiessl HW. Rubber Chem Technol 1994;67:288.

[6] De Sarkar M, De PP, Bhowmick A K. J Appl Polym Sci 1997;66:1151.

[7] De Sarkar M, De PP, Bhowmick AK. J Appl Polym Sci 1999;71:1581.

[8] De Sarkar M, Mukunda PJ, De PP, Bhowmick AK. Rubber Chem Technol 1997;70:855.

[9] Brown HP, Gibbs CF. Indus Engng Chem 1955;47(5):1006.

[10] Ishii M. Idemitsu Petrochemical Co. Ltd. Japan, Jpn Kokai, Tokyo, Koho, JP62, vol. 151, 1987. p. 404.

[11] Wills CL, Pollick, LA, Goodwin, DE. Shell Internationale Research Maatschppij BV, Eur Pat Appl EP, 360, 356, 1990.

[12] Bhattacharjee S, Bhowmick AK, Avasthi BN. J Polym Sci Polym Chem 1992;30:1961.

[13] Maddams WF. Appl Spectrosc 1980;34:245.

[14] De Sarkar M, De PP, Bhowmick AK. J Mater Sci 1999.

[15] Edmondson BJ, Lever ABP. Inorg Chem 1965:1608.

[16] Aylward F, Sawistowska MH. Chem Ind (London) 1962;484 17 March.

[17] He Y, Daniels ES, Klein A, El-asser MS. J Appl Polym Sci 1997;64:2047.