

# Influence of hydrogenation and styrene content on the unaged and aged properties of styrene-butadiene copolymer

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The influence of hydrogenation and styrene content on the properties of styrene butadiene copolymer (SBR) has been studied. There is an increase in glass transition temperature ( $T_g$ ) associated with the reduction of double bonds by hydrogenation. The hydrogenated polymers demonstrate higher tensile strength, elongation at break and modulus values. The superior mechanical properties of HSBRs are due to the generation of polyethylene crystallites. The thermo-oxidative stability of saturated polymer is much higher than that of its unsaturated analogue. The samples with higher styrene content show higher modulus, but lower tensile strength and elongation at break, due to lower crystallinity. The thermo-oxidative stability of HSBR increases with increase in styrene content. © 1999 Kluwer Academic Publishers

## 1. Introduction

The hydrogenation of polymers containing olefinic units play an important role in the development of polymer science and is one of the oldest polymer modification reactions [1, 2]. Recent advances in polymer technology have prompted a re-investigation of hydrogenation of unsaturated polymers. Hydrogenation of diene elastomers improves both chemical as well as physical properties of the existing polymers. Hydrogenated styrene-butadiene rubber (HSBR) can be prepared not only in the latex form, but also is an unique thermoplastic elastomer [3]. Properties of such elastomers would obviously depend considerably on degree of saturation and proportion of styrene units. Preliminary reports are available on the hydrogenation of styrene-butadiene rubber latex [3, 4]. But the literature survey indicates a lack of a detailed investigation on the effect of level of hydrogenation and styrene content on properties of HSBR, particularly after aging.

The present investigation is principally aimed at a systematic study of the effect of level of hydrogenation and styrene content on the aged and unaged properties of unvulcanized SBR.

## 2. Experimental

### 2.1. Materials

SBR latex with 17% styrene content, used as a substrate for hydrogenation was obtained from Nippon Zeon Co. Ltd., Japan. SBR lattices with styrene content 23 and 28% were procured from Apcotex Lattices Ltd., India. Hydrogenated styrene-butadiene rubber (HSBR) was prepared by diimide reduction of SBR latex [4]. The solid rubber was dried in vacuum before any test.

### 2.2. Moulding of the samples

The HSBR and SBR samples were compression moulded in an electrically heated Moore Press between two aluminium foils at 150 °C for 4 min at a pressure of 4 MPa to get sheets of  $1.75 \pm 0.05$  mm thickness.

### 2.3. Dynamic mechanical thermal analysis

The dynamic mechanical spectrum of the aged and unaged materials were obtained using Dynamic Mechanical Thermal Analyser (DMTA MKII) from Polymer Laboratories Ltd., UK. All the samples ( $43.5 \times 13.3 \times \sim 1.8$  mm) were analysed in a dual cantilever bending mode with a strain of 64  $\mu\text{m}$  (peak to peak displacement) in the temperature range from  $-50$  to  $70$  °C. Frequencies selected were 0.1, 1 and 10 Hz. The testing rate was 2 °C/min.

### 2.4. Wide angle X-ray diffraction spectroscopy

The aged and unaged samples were subjected to a Iron filtered  $\text{Co-K}\alpha$  radiation generated from Philips PW 1719 X-ray generator at an operating voltage and current of 40 kV and 20 mA respectively. The diffraction pattern of the samples was recorded with Philips X-ray diffractometer (PW-1710). Samples of the same thickness and area were exposed. The diffractions were recorded in an angular range from  $10^\circ 2\theta$  to  $50^\circ 2\theta$  at a scanning speed of  $3^\circ/\text{min}$ . The crystalline and amorphous components were separated by curve fitting considering the relatively high noise level of the diffractograms; the base line was taken as a straight line in the  $2\theta$  range from  $10^\circ$  to  $40^\circ$  and no further corrections

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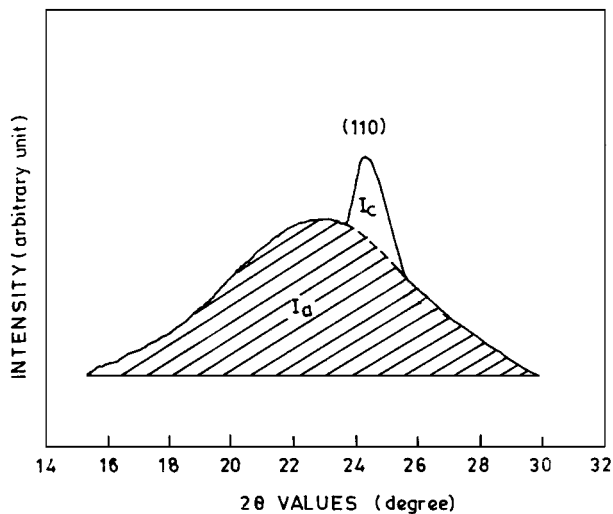


Figure 1 Typical X-ray diffractograms of HSBR with 94% saturation.

were applied. The amorphous peak of the different samples was found to be centered at  $2\theta = 22.7 \pm 0.1$ , the lower limit being for the HSBR with 94% saturation and upper one for the control SBR. The amorphous reflection contributions were subsequently resolved with curve fitting by a non-linear least square method under the assumption that the intensity peak profile could be approximated by a Gaussian function [5]. An illustration of the separation of the diffraction trace into its components is shown in Fig. 1 for HSBR with 94% saturation. The degree of crystallinity was determined from the ratio of areas under the crystalline peak and amorphous halo according to Equation 1. The error in the crystallinity determinations, is estimated to be  $\pm 0.5\%$ .

$$\text{Crystallinity (\%)} = \frac{I_c}{I_c + I_a} \times 100 \quad (1)$$

where  $I_c$  = area under crystalline peak and  $I_a$  = area under amorphous halo.

## 2.5. Infra-red spectroscopy

Infra-red spectral analyses were performed in a Perkin Elmer 843 double beam recording spectrophotometer. The samples were analysed as thin films. The spectra were taken with  $5.4 \text{ cm}^{-1}$  resolution in the range of wave numbers from  $4000$  to  $400 \text{ cm}^{-1}$  at a noise level of  $0.1\%$  transmittance.

## 2.6. Measurement of physical properties

The tensile strength, elongation at break and modulus at 100 and 300% elongation were measured on dumb-bell specimens [(BS-E) type, cut with a hollow punch from the test slab] according to ASTM D412-93 in Zwick-1445 Universal Testing Machine at a strain rate of  $500 \text{ mm/min}$  at  $30 \pm 2^\circ\text{C}$ . The average of three data points was taken and the experimental error was  $\pm 5\%$  (deviation from the median value).

## 2.7. Aging tests

Oxidative aging of the samples was carried out in a Test Tube Aging Tester (Seisaku SHO Ltd., Toyaseiki,

Japan) for varying lengths of temperature and time. The time of aging was varied from 2 to 48 h and the temperature from  $75$  to  $150^\circ\text{C}$ .

## 2.8. Gel content

Percent gel content of unaged and aged samples were measured gravimetrically by immersing the samples in toluene at  $30^\circ\text{C}$  for 72 h, the equilibrium swelling condition.

## 3. Results and discussion

### 3.1. Effect of hydrogenation on unaged properties of SBR

#### 3.1.1. Dynamic mechanical properties

Dynamic mechanical properties of the control and the hydrogenated samples are displayed in Fig. 2. The control SBR show a strong transition at  $-37^\circ\text{C}$ , while the HSBR samples with 74 and 94% saturation register peaks at  $-28$  and  $-18^\circ\text{C}$  respectively (Fig. 2a). This peak temperature is ascribed to the glass transition

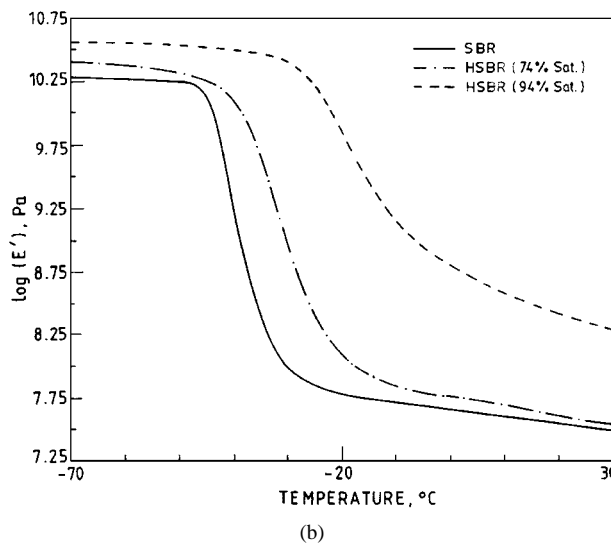
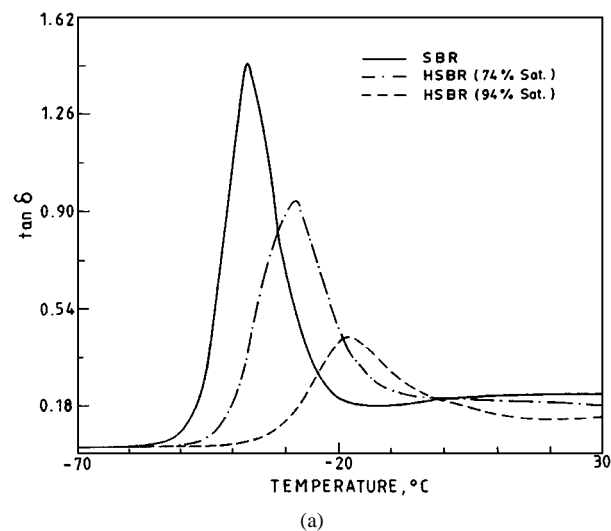


Figure 2 (a) Temperature dependence of loss tangent ( $\tan \delta$ ) for SBR and HSBRs with 74 and 94% saturation at a frequency of 10 Hz, (b) Temperature dependence of storage modulus ( $E'$ ) for SBR and HSBRs with 74 and 94% saturation at a frequency of 10 Hz.

TABLE I Effect of degree of hydrogenation on dynamic mechanical properties of SBR and HSBR with 17% styrene content

Samples	Degree of hydrogenation (%)	$T_g$ (°C)	$\tan \delta$ at $T_g$	$E'$ (Pa)		Degree of crystallinity (%)
				at $T_g$	at 30 °C	
SBR	0	-37	1.42	$0.44 \times 10^9$	$0.31 \times 10^8$	—
HSBR	74	-28	0.94	$0.50 \times 10^9$	$0.33 \times 10^8$	3.5
HSBR	94	-18	0.42	$0.89 \times 10^9$	$1.9 \times 10^8$	8.4

temperature ( $T_g$ ). It is clear that with increase in the saturation level, the glass transition temperature of the amorphous rubber phase increases. There is an increase in  $T_g$  of 19 °C at 94% hydrogenation as compared to the control sample. This may be due to the gradual replacement of amorphous segments by crystalline units of HSBR. There is an increase of percent crystallinity from 3.5 to 8.4%, as the hydrogenation level is increased from 74 to 94% (Table I). A similar shift in  $T_g$  values towards high temperature, as observed by DSC experiments was reported earlier by us [4]. It is also seen from Table I that the peak  $\tan \delta$  is decreased from 1.42 for pure SBR to 0.42 for HSBR with 94% saturation because of the increase in crystallinity and appearance of more ordered structure. The storage modulus ( $E'$ ) value of SBR at  $T_g$  increases with increase in saturation due to the same reason given above. The storage moduli of the various samples are plotted against temperature (Fig. 2b). The storage modulus at a temperature much higher than  $T_g$  i.e. 30 °C increases with increase in saturation due to enhanced crystallinity. As shown in Fig. 2b and Table I, there is an increase of storage modulus by approximately 6 times with increasing the saturation level from 0 to 94%.

### 3.1.2. Physical properties

The effect of hydrogenation on the physical properties of HSBR samples with 74, 87 and 94% saturation has been investigated. The stress-strain properties of HSBRs along with the control SBR are depicted in Fig. 3. It is seen that the saturation of the butadiene units changes the physical properties tremendously. A drastic improvement in tensile strength and elongation at break is seen above 74% saturation. Below 74% saturation, the HSBR samples show comparable physical properties as that of the control (not shown in figure for clarity). Table II records the values of tensile strength, elongation at break, work to break and modulus calculated for these samples. It is observed from the data that tensile strength, modulus and elongation at break increase with saturation. Control SBR shows a low tensile strength (0.8 MPa) with low elongation at break

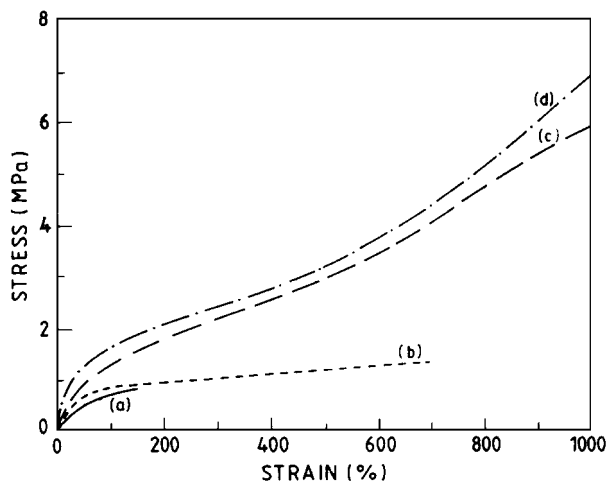


Figure 3 Stress-strain curves for (a) SBR and HSBRs with (b) 74%, (c) 87% and (d) 94% saturation.

(170%), whereas, its 94% saturated counterpart shows a strength of 6.8 MPa with remarkably high elongation at break (981%). The superior mechanical properties exhibited by the HSBR samples are due to appearance of polyethylene crystallites and increased crystallinity as observed by X-ray diffraction method (Table I). The strain induced crystallisation of HSBRs having high saturation level can not be ruled out, as there is an upturn in the stress-strain curve around 250% elongation. It is reported that hydrogenated nitrile rubber samples register a high value of tensile strength due to the above reason [6].

### 3.2. Effect of hydrogenation on the properties of aged SBR

In order to understand the effects of hydrogenation on the properties of rubbers after aging, the behaviour of SBR and its 94% saturated version (HSBR-94) with 17% styrene content was examined. Table III compares the properties of SBR and HSBR-94. It is readily apparent from the data that the inherent oxidation resistance of hydrogenated materials as compared to the control is more pronounced. Upon aging of both the samples

TABLE II Effect of degree of hydrogenation on physical properties of SBR and HSBR with 17% styrene content

Samples	Degree of hydrogenation (%)	Modulus (MPa)		Tensile strength (MPa)	Elongation at break (%)	Work to break (kJ/m <sup>2</sup> )
		100%	300%			
SBR	0	0.73	—	0.8	170	0.5
HSBR	74	0.79	1.00	1.3	692	3.1
HSBR	87	1.28	2.10	5.4	991	12.2
HSBR	94	1.53	2.35	6.8	981	15.5

TABLE III Aged properties of SBR and HSBR containing 17% styrene content

	SBR	HSBR <sup>a</sup>
Aged 24 h air oven @ 75 °C		
Tensile strength (MPa)	0.3 (38%)	6.7 (99%)
Elongation at break (%)	119 (70%)	830 (85%)
Modulus (MPa)		
100%	0.29 (40%)	2.12 (140%)
300%	—	3.13 (133%)
Gel (%)	48	2
Aged 24 h air oven @ 150 °C		
Tensile strength (MPa)	—	4.85 (71%)
Elongation at break (%)	Embrittled	315 (32%)
Modulus (MPa)		
100%	0	2.80 (183%)
300%	—	4.20 (179%)
Gel (%)	92	12

<sup>a</sup>HSBR with 94% saturation of butadiene units.

The values within parenthesis indicate the retention (%) of the respective properties.

for 24 h at 75 °C, only marginal changes in properties are seen with HSBR-94, whereas, in SBR, most of the properties deteriorate drastically. At 150 °C for 24 h of heating, SBR becomes totally brittle, whereas HSBR retains most of its properties. In general, with diene based elastomers, oxidation resistance is related to the amount of allylic hydrogens present. Therefore, as the butadiene units become progressively more saturated, the thermo-oxidative stability increases as expected.

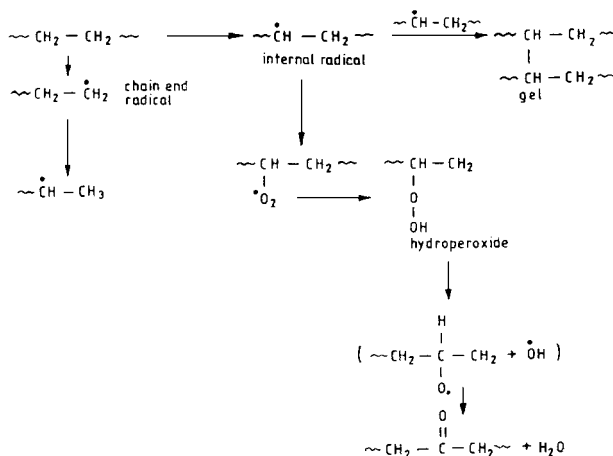
IR studies have been carried out to elucidate the structural changes during aging. There is an increase in intensity at 1710 cm<sup>-1</sup> due to >C=O functionality [7]. The appearance of the peak at 1210 cm<sup>-1</sup> due to -COOR functionality signifies the oxidation (Table IV) [Scheme 1]. In order to quantify the amount of oxidation during aging, an absorbance ratio  $Q (=A_{1710}/A_{699})$  is plotted against aging time at different temperatures, where  $A_{1710}$  and  $A_{699}$  are respective absorbances of >C=O group and styrene unit respectively (Fig. 4). The aromatic ring of the styrene unit is assumed to be unaffected at temperatures below 400 °C and the 699 cm<sup>-1</sup> peak serves here as an internal standard [8]. It is seen from Fig. 4 that, initially there is an increase in absorbance ratio with aging time at all tem-

TABLE IV Peak positions and corresponding absorbances<sup>a</sup> from the IR spectra of HSBR (94% saturated) containing 17% styrene before and after aging

Functional groups	Wave numbers (cm <sup>-1</sup> )	Absorbances <sup>a</sup>	
		Before aging	After aging (12 h @ 150 °C)
>C=O	1710	0.60	0.95
>CH <sub>2</sub>	1465	1.52	1.46
-COOR	1210	—	0.44
Trans -CH=CH-	966	0.47	0.50
Vinyl -CH=CH <sub>2</sub> -	904	0.24	0.28
Cis -CH=CH-	758	0.76	0.81
-(CH <sub>2</sub> ) <sub>n&gt;4</sub>	720	0.80	0.72
Styrene	699	1.00	1.00

<sup>a</sup>All absorbance values are normalised with respect to that of styrene unit.

peratures. The increase is marginal in the case of HSBR-94 samples aged at 75 °C. At 125 and 150 °C, there is a decrease in absorbance parameter after a long time of aging. On prolonged aging, the increased crosslinking hardens the polymer surface preventing the diffusion of oxygen. Also there is a possibility of loss of oxygen containing small fragments into gases. The mechanisms of degradation of hydrogenated styrene-butadiene rubber studied by NMR and thermo-gravimetry have been recently demonstrated [8].



Scheme 1: Mechanism of ageing of ethylene segments of HSBR.

The effect of aging on physical properties of HSBR is evident from Figs 5–9. Tensile strength of HSBR (shown in Fig. 5) remains almost unchanged with

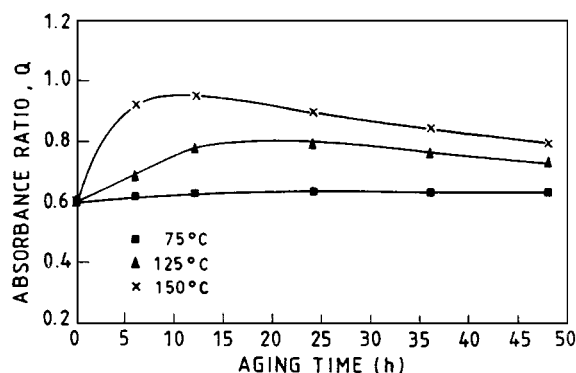


Figure 4 Effect of aging time on the absorbance parameter  $Q (=A_{1710}/A_{699})$  at different temperatures.

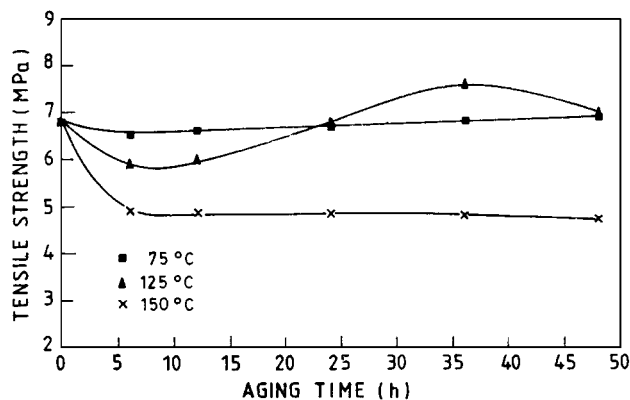


Figure 5 Effect of aging time on tensile strength of HSBR-94 at different temperatures.

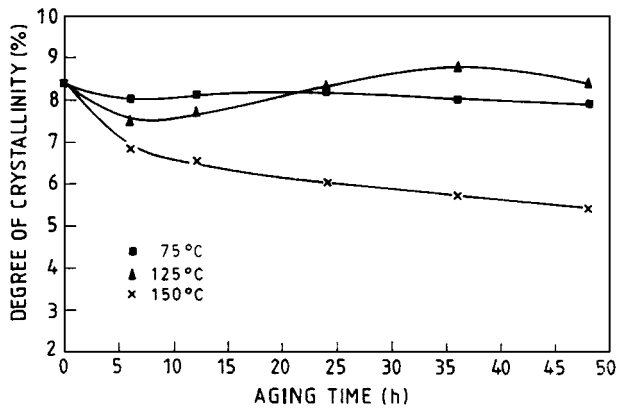


Figure 6 Effect of aging time on degree of crystallinity of HSBR-94 at different temperatures.

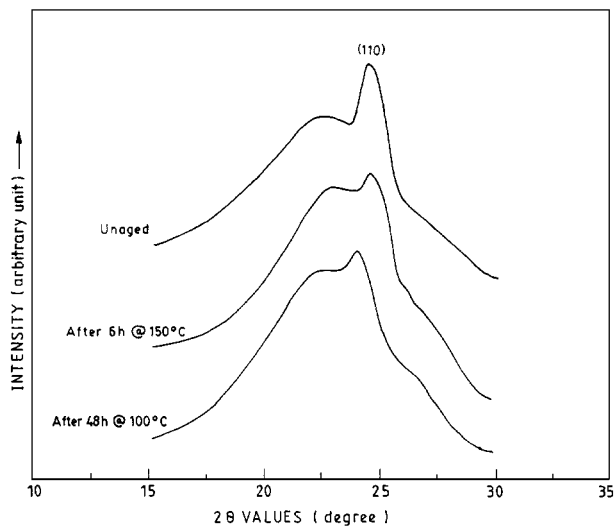


Figure 7 X-ray diffraction patterns of HSBR-94 before and after aging.

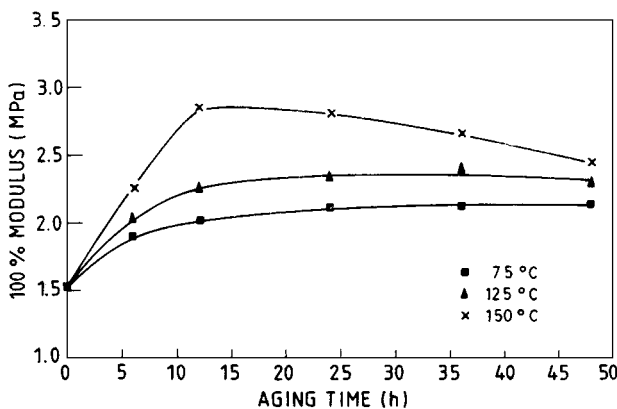


Figure 8 Effect of aging time on 100% modulus of HSBR-94 at different temperatures.

increase in aging time at 75 °C. At 125 °C, the tensile strength decreases first, then registers an increase before a final decrease. At 150 °C, the tensile strength decreases gradually with time. It is interesting to notice that at all temperatures, the tensile strength drops down at the initial stage of aging. The changes in tensile strength with temperature and time of aging are in line with changes in degree of crystallinity (Fig. 6). The degree of crystallinity decreases at higher temperature and for prolonged time of aging. It is again clear from

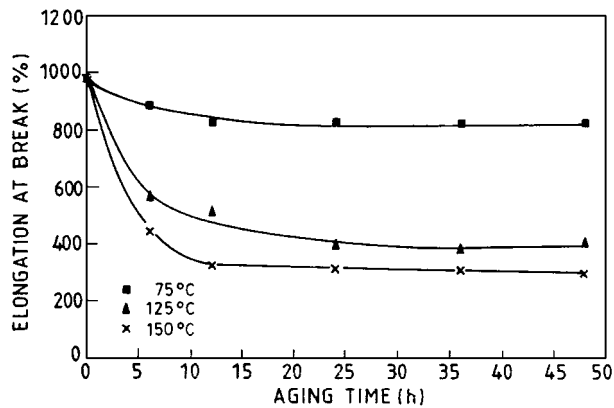


Figure 9 Effect of aging time on elongation at break of HSBR-94 at different temperatures.

the X-ray diffractograms of unaged and aged HSBR-94 samples (Fig. 7). Unaged HSBR-94 shows a major reflection at 24.6° along (110) plane which may be due to the presence of crystalline polyethylene segments. With increase in temperature or time of aging, the intensity of this peak decreases.

The modulus values, however, increase with increase in aging temperature as shown in Fig. 8 in spite of the decrease in crystallinity. The increase in modulus with increase in aging time or temperature is due to the appearance of cross-linked or gelled structure (Scheme 1). Increase in temperature or prolonged time of aging assists gel formation. HSBR-94 forms 12% gel, while the control SBR aged for 48 h at 150 °C forms 92% gel under similar condition due to presence of unsaturation (Table III). At very high aging time or temperature, the gelled network disintegrates, lowering the values of modulus.

The elongation at break value decreases with increase in aging time at all temperatures (Fig. 9) due to the formation of the cross-linked structure and subsequent disintegration.

The rate of change in tensile strength with aging time was found for HSBR-94 from the initial linear region of the plot of percent retention in tensile strength versus time of aging at various temperatures (Fig. 10).

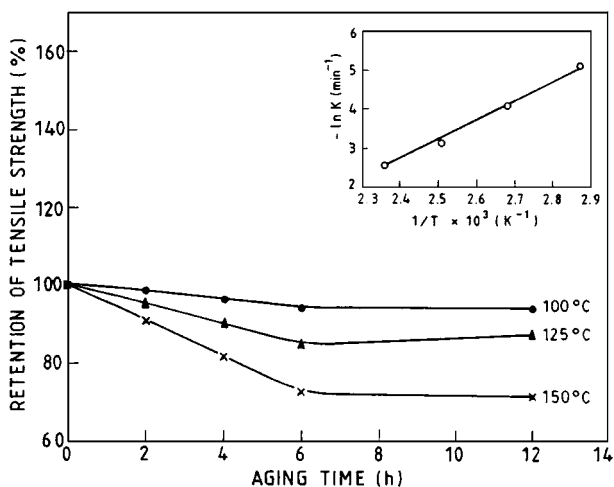


Figure 10 Plot showing retention of tensile strength against aging time. Inset shows Arrhenius plot.

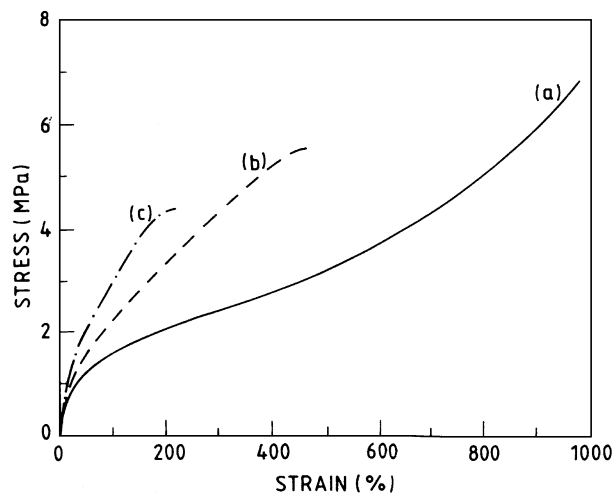
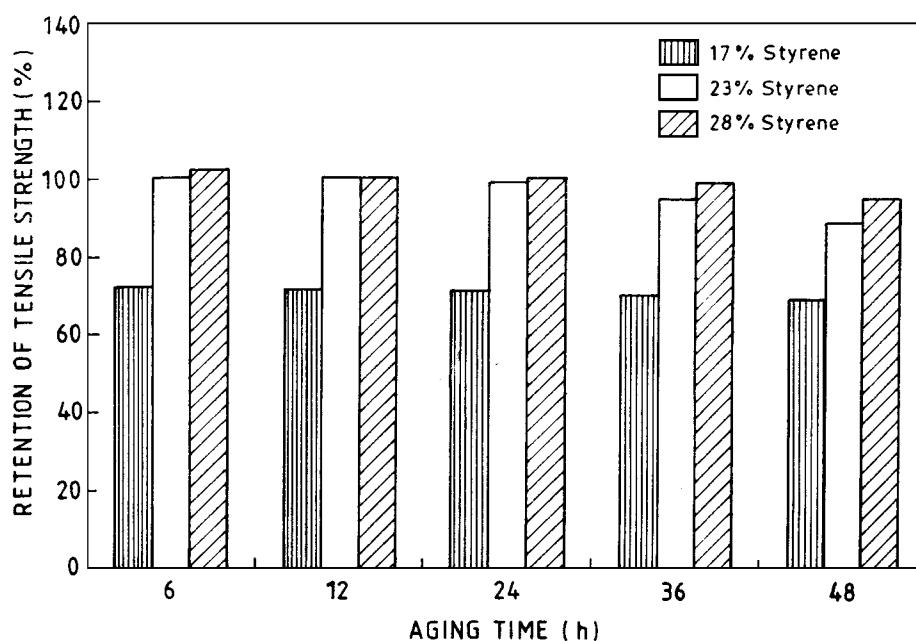


Figure 11 Stress-strain curves for HSBRs having (a) 17% (b) 23% and (c) 38% styrene content and with same saturation level (~94%).

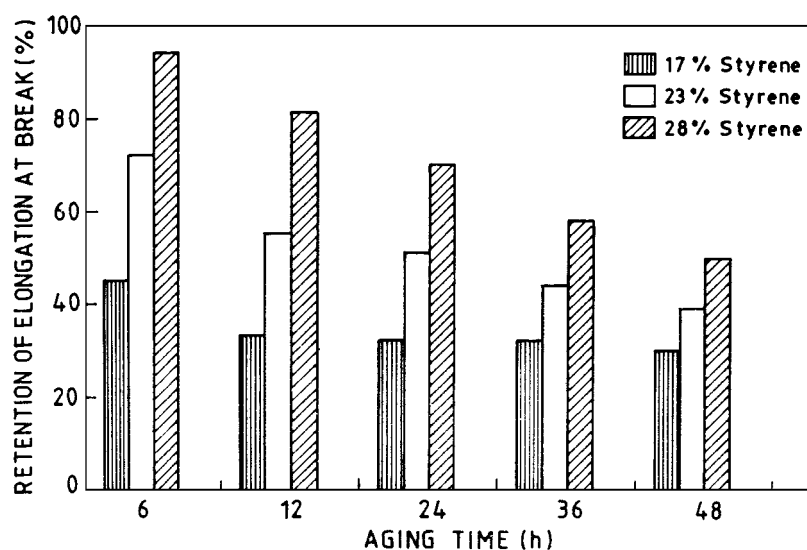
The activation energy for the property deterioration was calculated using the Arrhenius equation. A typical Arrhenius plot is shown as an inset in Fig. 10. The activation energy of deterioration of tensile strength is found to be 40 kJ/mol. It may be mentioned that the activation energy value for the degradation of filled vulcanized EPDM rubber was reported to be 50 kJ/mol in the temperature range of 125–175 °C [9].

### 3.3. Effect of styrene content on the aged and unaged properties of HSBR

An investigation on the influence of styrene content on the physical properties of HSBR was undertaken. The stress-strain properties of the HSBR samples with varying amounts of styrene content are plotted in Fig. 11. The tensile strength of the samples decreases with



(a)



(b)

Figure 12 (a) Plot showing retention of tensile strength against aging time at 150 °C for HSBRs with 17, 23 and 28% styrene content, (b) Plot showing retention of elongation at break against aging time at 150 °C for HSBRs with 17, 23 and 28% styrene content.

TABLE V Effect of styrene content on physical properties of HSBR

Level of hydrogenation (%) <sup>a</sup>	94	94	94
Styrene content (%) <sup>b</sup>	17	23	28
Degree of crystallinity (%) <sup>c</sup>	8.4	4.3	1.6
Tensile strength (MPa)	6.8	5.5	4.2
Elongation at break (%)	989	470	205
Work to break (kJ/m <sup>2</sup> )	15.5	7.4	2.7
Modulus (MPa)			
100%	1.53	2.18	2.77
300%	2.35	4.18	—

<sup>a</sup>As determined by infra-red spectroscopy.

<sup>b</sup>As determined by NMR spectroscopy.

<sup>c</sup>As determined by X-ray diffraction studies.

increase in styrene content. This may be due to decrease in crystallinity. The HSBR sample with 28% styrene level contains only 1.6% crystallinity, whereas the samples with 17 and 23% styrene level contain 8.4 and 4.3% crystallinity respectively, though these samples have almost same saturation level (Table V). Now, higher level of butadiene (lesser styrene level) allows longer sequential runs of hydrogenated butadiene segments (polyethylene segments) to form. In general, the longer the runs, the more complete their saturation and the higher the percent crystallinity. The crystallite size is ultimately limited by a styrene unit (which is too large to be incorporated into the polyethylene crystallites).

Ageing behaviour of HSBR samples with different styrene contents is depicted in Fig. 12. The tensile strength and elongation at break values decrease much more rapidly in HSBR with 17% styrene content compared to HSBRs with higher styrene content. HSBR with 28% styrene content retains 95% of its tensile strength and 50% of elongation after aging at 150 °C for 48 h, whereas, HSBRs with 17% styrene content retains 69% tensile strength and 30% of elongation under the same condition. The thermo-oxidative stability of HSBR samples increases with increase in styrene content while aged at the temperature range studied (75–150 °C).

#### 4. Conclusions

The effect of hydrogenation and influence of styrene content on the aged and unaged properties of styrene-butadiene copolymer has been investigated in this paper.

(1) There is an increase in glass transition temperature associated with the reduction of double bonds by hydrogenation as observed by Dynamic Mechanical Thermal Analysis.

(2) The hydrogenated polymers are found to be superior in terms of mechanical properties. The tensile strength, elongation at break and modulus values increase with increase in saturation level. The superior mechanical properties of HSBRs are due to the appearance of polyethylene crystallites, as evidenced from the X-ray diffractograms.

(3) The thermo-oxidative stability of the hydrogenated polymer is higher than that of the control.

(4) The samples with higher styrene content show higher modulus, but lower tensile strength and elongation at break due to lower crystallinity.

(5) The thermo-oxidative stability of HSBR samples with same saturation level increases with increase in styrene content.

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