

Dichlorocarbene Modification of Styrene–Butadiene Rubber

M. T. RAMESAN, ROSAMMA ALEX

Rubber Research Institute of India, Kottayam-686 009, Kerala, India

Received 20 March 1997; accepted 2 September 1997

ABSTRACT: Dichlorocarbene-modified styrene–butadiene rubber (SBR) prepared by the alkaline hydrolysis of chloroform using cetyltrimethylammonium bromide as a phase-transfer agent resulted in a product that showed good mechanical properties, excellent flame resistance, solvent resistance, and good thermal stability. The activation energy for this chemical reaction calculated from the time–temperature data on the chemical reaction by the measurement of the percentage of chlorine indicated that the reaction proceeded according to first-order kinetics. The molecular weight of the polymers, determined by gel permeation chromatography, showed that chemical modification was accompanied by an increase in molecular weight. The chemical modification was characterized by proton NMR, FTIR studies, thermogravimetric analysis, and flammability measurement. Proton NMR and FTIR studies revealed the attachment of chlorine through cyclopropyl rings to the double bond of butadiene. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 153–160, 1998

Key words: dichlorocarbene; modification; styrene–butadiene rubber; thermal; flammability

INTRODUCTION

Chemical modification of general-purpose rubbers plays an important role in imparting special properties to them. The properties of unsaturated elastomers can be modified by reactions involving their double bonds.¹ It was found that the reaction of double bonds with various reagents could result in improvement of flame retardancy, oil resistance, and other properties.² The reaction of carbene with olefins to form a cyclopropane derivative had attracted much attention during the past years.^{3–6} The addition of halocarbenes to *cis*-1,4-polyisoprene (NR)^{7–10} and *cis*-1,4-polybutadiene was reported by Pinazzi and Levesque¹¹ and Barentsvich et al.¹² They found that carbene addition had a significant influence on the properties of polydienes. Various other modifications of natural rubber and polybuta-

diene using *para*-toluene sulfonyl chloride have been carried out.^{13–16} The studies revealed that a copolymer containing modified and unmodified blocks arranged in a sequential manner was formed as a result of the modification.

Styrene–butadiene rubber (SBR) is a versatile elastomer, which finds application in various products. However, it has poor heat, flame, and solvent resistance. In this article, an attempt was made to improve the resistance of SBR toward heat, flame, and solvents by dichlorocarbene modification through the alkaline hydrolysis of chloroform using cetyltrimethylammonium bromide (CTAB) as a phase-transfer agent without destroying the technical properties of SBR. The activation energy of the chemical reaction was calculated and the modification was characterized by proton NMR, FTIR, and chemical analysis. The thermal stability and flammability of modified products were evaluated by thermogravimetry (TGA) and the limiting oxygen index (LOI), respectively.

Correspondence to: R. Alex.

Table I Composition of SBR-1500

Chemical Constituents (%)	Min	Max
Styrene	21.5	25.5
Volatile matter		0.75
Organic acid	4.75	7
Soap		0.5
Ash		1.5
Antioxidant	0.5	1.5
<i>cis</i> -1,4	—	18
<i>trans</i> -1,4	—	65
1,2 (vinyl)	—	17

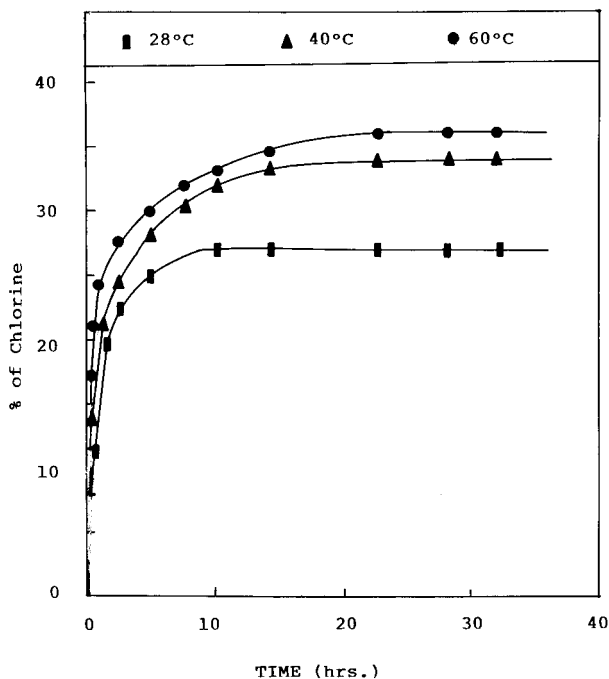
EXPERIMENTAL

SBR (Synaprene 1500) was obtained from Synthetics and Chemicals Ltd., Bareilly, U.P., India, and its composition is given in Table I. All other chemicals were of analytical grade. The modification of SBR was done by the alkaline hydrolysis of CHCl_3 using a phase-transfer agent, according to the method first suggested by Makosza and Wawrzyniewicz¹⁷ and later developed by Joshi et al.¹⁸ SBR was dissolved in toluene, the phase-transfer catalyst was added to this, and the mixture was allowed stir. To this, CHCl_3 was added dropwise followed by an NaOH solution (50%). The reaction product was separated from the solution and washed with hot water and cold water, until free of chlorine. The product was coagulated with isopropyl alcohol and reprecipitated from the toluene solution. The concentration of reagents, the temperature, and the time of reaction are given in Table II. The modification was monitored by the determination of the chlorine percentage at different times using chemical analysis.

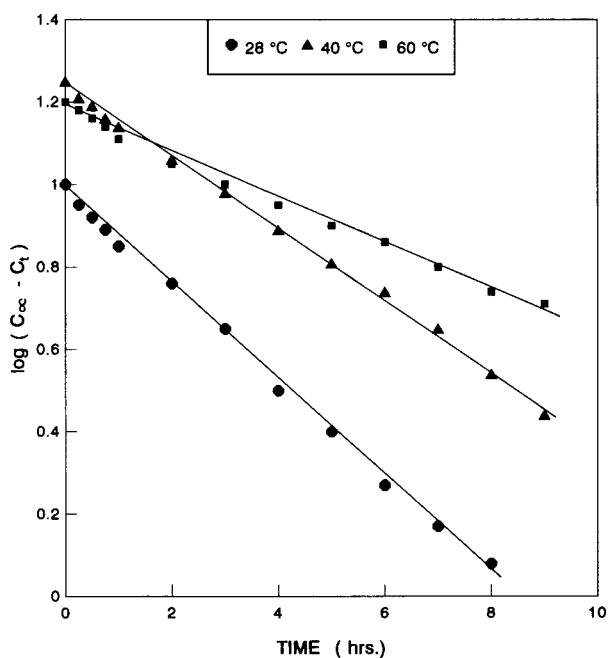
The $^1\text{H-NMR}$ spectrum of SBR and modified SBR in CDCl_3 (10% w/v solution) was recorded with a 90-MHz JEOL EX90 FT NMR spectrometer with tetramethylsilane as the internal reference. IR spectra of samples were recorded with

Table II Concentration of Reagents for Dichlorocarbene Modification

SBR (g)	10
Toluene (mL)	200
CHCl_3 (mL)	30
NaOH 50% (mL)	35
CTAB	0.85
Time (h)	1–36
Temperature ($^\circ\text{C}$)	28/40/60

**Figure 1** Plots of percentage of chlorine versus time, at temperatures of 28, 40, and 60°C.

a Shimadzu-8101 M Fourier transform infrared spectrophotometer, using thin films of polymer. The thin films were prepared by dissolving the polymer in chloroform and then the concentrated

**Figure 2** Plots of $\log(C_\infty - C_t)$ versus time for dichlorocarbene-modified SBR.

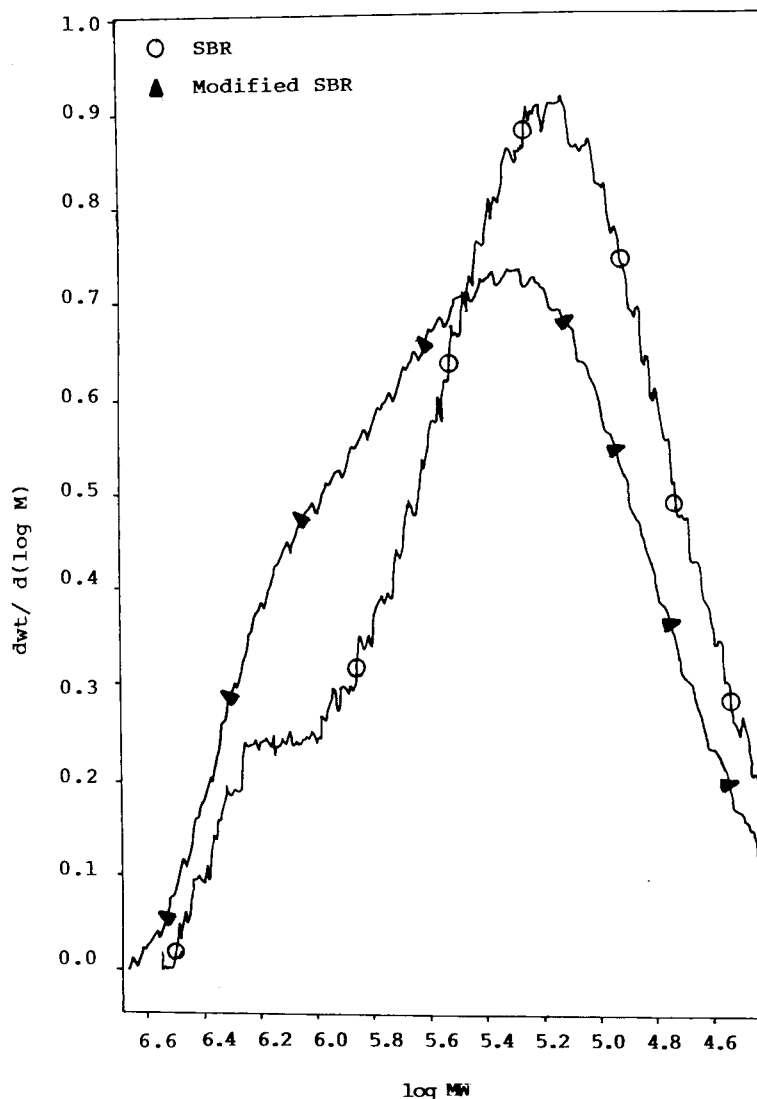


Figure 3 Molecular weight distribution curves of SBR and dichlorocarbene-modified SBR.

solution (5%) was directly cast onto a leveled glass plate.¹⁹ Molecular weight determination was carried out by a Waters 510 gel permeation chromatography (GPC) instrument attached to a 410 diffraction refractometer. HPLC-grade toluene was used as a solvent with a flow rate set to

1 mL/min. The GPC columns were calibrated with polystyrene standards. TGA was carried out with a Shimadzu-50 thermogravimetric analyzer at a heating rate of 10°C/min in a dry nitrogen atmosphere.

The flame resistance was measured with a

Table III Molecular Weights of Modified SBR

Materials	\bar{M}_n (Daltons)	\bar{M}_w (Daltons)	\bar{M}_z (Daltons)	Polydispersity
SBR	125,550	359,502	996,026	2.8634
6% Cl	142,260	421,251	1,225,600	2.9611
20% Cl	164,980	525,782	1,241,151	3.1869

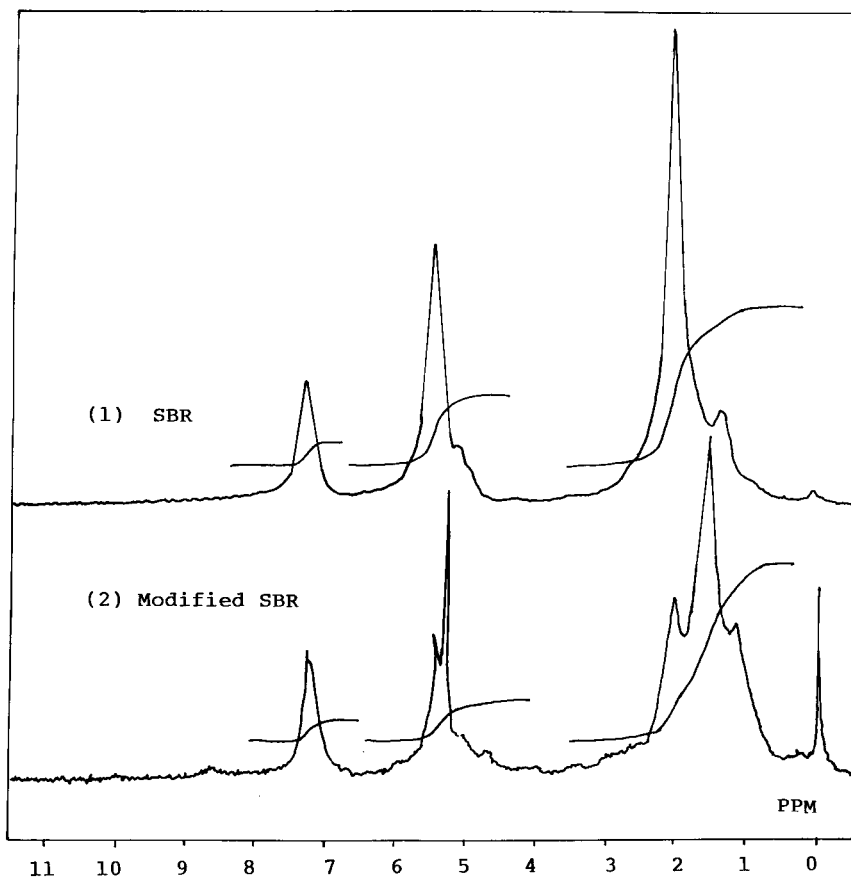


Figure 4 FT ^1H -NMR spectra of (1) pure SBR and (2) dichlorocarbene-modified SBR (representative polymer) 26% Cl.

Stanton Redcroft FTA flammability unit as per ASTM D-2863-77. Samples for tensile tests were prepared by pressing the modified rubber at 180°C for 5 min with a pressure of 50 kg/cm^2 in a hydraulic press so as to obtain sheets of 3 mm thickness. The tensile strength of the samples was tested with a Zwick universal testing machine (Model 1474) at a temperature of $25 \pm 2^\circ\text{C}$ and at a crosshead speed of 50 mm/min, according to ASTM D-412-80 using dumbbell-shaped test pieces. All other physical tests were carried as per relevant ASTM standards.

RESULTS AND DISCUSSION

Effect of Time and Temperature on Chlorination

Figure 1 shows the percentage of chlorine versus time at temperatures of 28, 40, and 60°C . The dichlorocarbene addition is fast in the initial stages but decreases at later stages of the reaction. The rate of reaction almost levels off after 12

h of reaction. The rate of reaction and the chlorine content increases with the temperature of the reaction. As far as the first 15 min of the reaction are concerned, the reaction is extremely fast at 60°C .

Figure 2 shows the change in percentage of chlorine $\log(c_\infty - c_t)$ versus time, where c_∞ is the maximum chlorine percentage obtained at a particular temperature and c_t is the percentage of chlorine at any time t . Linearity of the plots shows that the modification reaction proceeds according to first-order kinetics. Rate constants (k) of the reactions calculated are $3.24 \times 10^{-5}\text{ s}^{-1}$, $2.05 \times 10^{-5}\text{ s}^{-1}$, and $1.23 \times 10^{-5}\text{ s}^{-1}$ at 28, 40, and 60°C , respectively. The activation energy of the reaction calculated from the linear plot of $\log k$ versus $1/T$ (where k is the rate constant and T is the temperature in K) is found to be 35.89 kJ/mol.

Gel Permeation Chromatography

The molecular weight distribution curves of SBR and modified SBR (<20%) determined by GPC

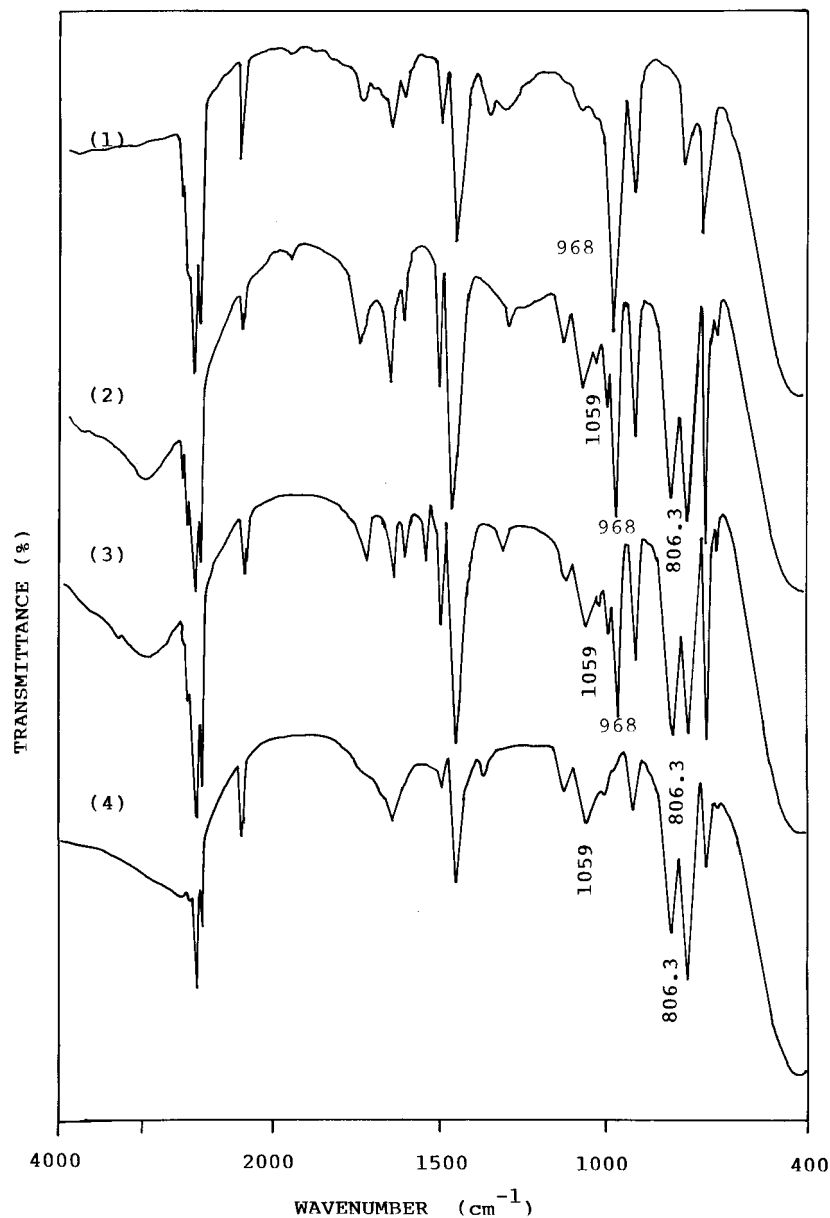


Figure 5 FTIR spectra of thin films of (1) pure SBR, (2) dichlorocarbene-modified SBR of 16%, (3) 26%, and (4) 36% chlorine.

are given in Figure 3. From the figure, it is evident that high molecular weight fractions are formed in modified SBR as a result of the modification. The molecular weight ranges from 2.5×10^4 to 5.01×10^6 in both modified and pure SBR. The high molecular weight fraction above a molecular weight of 10^6 is higher for the modified samples (as seen from the area under the molecular weight distribution curve). The increase in \bar{M}_n (number-average molecular weight), \bar{M}_w (weight-average molecular weight), and \bar{M}_z (z -average or sedimentation-average molecular weight) with very little

change in the polydispersity given in Table III shows that dichlorocarbene modification is accompanied by an increase in molecular weight due to the addition of chlorine through the cyclopropyl ring as a side chain.

FT $^1\text{H-NMR}$ Characterization

FT $^1\text{H-NMR}$ spectra recorded for SBR and dichlorocarbene-modified SBR are given in Figure 4. SBR and representative modified SBR exhibit signals for the hydrogen region of benzene at 7.3–7

Table IV IR Absorption Peak Height Ratios

Time (h)	Chlorine (%)	1653/806 cm^{-1}	968/806 cm^{-1}	910/806 cm^{-1}	698/806 cm^{-1}
1	16	0.307	1.199	0.631	1.78
12	26	0.115	0.957	0.620	1.75
24	36	1653 absent	968 absent	0.619	1.71

ppm. Pure SBR displays signals at 2 and 1.4 ppm due to the methylene hydrogens ($-\text{CH}_2-$) and at 5.6 ppm (s) due to the unsaturated methine hydrogen ($-\text{CH}=\text{}$) of butadiene. Modified SBR displays a triplet for methylene hydrogens, in the region of 1.1–2 ppm. These additional signals can be attributed to the cyclopropyl ring. The doublet in the region 5.8 to 5.2 ppm shown by the modified SBR can be due to the hydrogen of the carbene bearing carbon and the hydrogen of the carbon attached to the benzene ring.

FTIR Characterization

Figure 5 shows the IR spectra of the thin films (cast from CHCl_3) of SBR [Fig. 5(1)] and modified SBR at 1 h [Fig. 5(2)], 12 h [Fig. 5(3)], and 24 h [Fig. 5(4)]. The modified SBR shows characteristic C—Cl absorption peaks at 806 and 1059 cm^{-1} due to the cyclopropane ring.²⁰ It is likely that the *cis*-butadiene takes part in the reaction initially, as $:\text{CCl}_2$ more readily attacks the *cis* double bond. As the reaction time increases, there is a reduction in the intensity of the absorption at 968 cm^{-1} which is due to the *trans* $-\text{CH}=\text{}$ and at 1653 cm^{-1} which is due to *cis* $-\text{CH}=\text{}$. The absorption at 698 cm^{-1} is due to the presence of an aromatic ring, whose concentration remains unaffected with modification. The absorption at 910 cm^{-1} (vinyl 1,2 content) remains almost unaffected after modification. There is a shift of 698 cm^{-1} absorption to 702 cm^{-1} due to the increase in chlorination; this may be attributed to steric hindrance of the cyclopropane ring. The peak ratio of absorption at 1653/806 cm^{-1} , 968/806 cm^{-1} , 910/806 cm^{-1} , and 698/806 cm^{-1} is shown in Table IV. With increase in the duration of the chemical reaction, there is a progressive reduction in the double-bond concentration and corresponding increase in the concentration of C—Cl bonds, whereas the styrene concentration remains almost unchanged. Hence, it can be inferred that it is the double bond^{4,21,22} of butadiene that takes

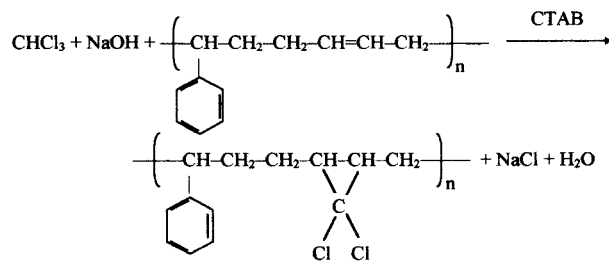
part in the chemical reaction. The proposed reaction is shown in Scheme 1.

Thermogravimetric Analysis

The thermograms of SBR, modified SBR, and chloroprene rubber (Neoprene W) are given in Figure 6. The decomposition pattern is compared with a commercial chloroprene rubber. Pure SBR (curve 1) shows a single-stage decomposition at a temperature of initiation of 454°C. As the chlorination increases, there is a considerable change in the decomposition pattern. The decomposition of chlorinated SBR (at a higher percentage of Cl) takes place in two steps (curves 2 and 3): The first decomposition begins at 286°C, and the second, at 454°C. The time taken for a 50% weight drop for chloroprene rubber and chlorinated SBR are presented in Table V. It is clear from the table that the time taken for a commercial chloroprene rubber for a 50% weight drop is lower than that of dichlorocarbene-modified SBR. This indicates that the chlorinated SBR has a superior thermal stability to that of commercial chloroprene rubber.

Flammability Behavior

The limiting oxygen index (LOI) (which is a direct measure of the flame resistance of the materials) of pure SBR, modified SBR, and commercial chloroprene rubber are given in Table VI. When halogen-containing elastomers are ignited, they could



Scheme 1 Proposed pattern of dichlorocarbene modification.

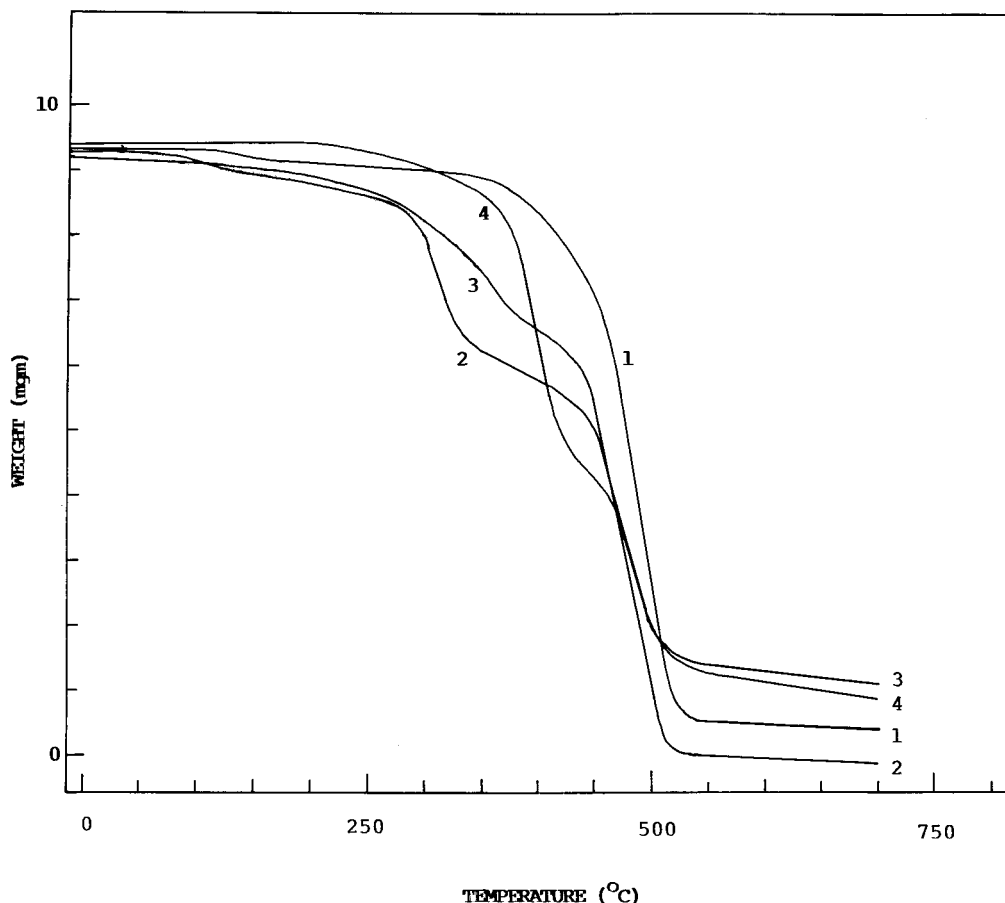


Figure 6 Thermograms of (1) pure SBR, (2) modified SBR of 16% chlorine, (3) modified SBR of 26% chlorine, and (4) commercial chloroprene rubber.

exhibit an intumescence effect, due to which the char formed thermally insulates the polymer from the flame and thus inhibits combustion. From the table, it is clear that modified SBR shows better flame resistance than does unmodified SBR. Moreover, the LOI value for SBR with a chlorine content of 36% is almost the same as that of commercial chloroprene rubber. Thus, modified SBR can be recommended as a substitute for building materials, since materials with an LOI value² greater than 20.8 are considered to be safe for

indoor applications, because these materials will be self-extinguishing even if ignited.

Physical Properties

Chemical modification changes SBR from a soft elastomeric material to a hard thermoplastic material. Modified SBRs with high percentage of chlorine (>20%) were insoluble in solvents including DMF and THF. Thus, at higher levels of chlorination, it is possible that there are side reactions involving crosslinking. The physical proper-

Table V Time for 50% Weight Drop

Material	Curve	Time for 50% Weight Drop (min)
Chloroprene	1	39.8
Modified SBR (16% Cl)	2	44.8
Modified SBR (26% Cl)	3	43.3
Modified SBR (36% Cl)	4	43.3

Table VI Limiting Oxygen Index (LOI) Values

Materials	Chlorine (%)	LOI (%)
SBR	—	19
Modified SBR	16	24
Modified SBR	26	28
Chloroprene	40	28.4

Table VII Physical Properties

Materials	Tensile Strength (MPa)	Elongation at Break (%)	Shore D Hardness
Modified SBR (16% Cl)	5.29	106.6	15
Modified SBR (26% Cl)	28.57	1.3	45
Modified SBR (36% Cl)	20.49	0.9	60

ties are shown in Table VII. At levels of chlorination of < 16%, the material shows comparatively low tensile strength and elongation. As chlorination increases, tensile strength increases to a maximum and then decreases at still higher levels of chlorination. The elongation at break decreases progressively, and at very high levels of chlorination, it behaves like a thermoplastic polymer.

CONCLUSIONS

The dichlorocarbene modification of SBR can be carried out by the alkaline hydrolysis of CHCl_3 using CTAB as a phase-transfer catalyst. The chlorine content increases with temperature of the reaction and the reaction follows first-order kinetics. The basic decomposition pattern and thermal stability of the samples are superior to those of commercial chloroprene rubber. The presence of chlorine in the samples enables them to be safely used as a flame-resistant material for indoor applications. The modified materials are thermoplastics with higher tensile strength and hardness than those of unmodified SBR. The modified SBRs have excellent solvent resistance compared to other chlorine-containing elastomers like chloroprene, even at low levels of chlorination (16–20%), where they exhibit rubbery properties. Further studies on more efficient chemical modifications of SBR are in progress.

The authors are thankful to Dr. M. R. Sethuraj, Director, and Dr. N. M. Mathew, Joint Director, Rubber Research Institute of India, for their support and encouragement in this work.

REFERENCES

1. D. N. Schulz and S. R. Turner, *Rubb. Chem. Technol.*, **55**, 809 (1982).
2. S. T. M. Sang, *J. Rubb. Res. Inst. Malaysia*, **26**, 48 (1978).
3. M. Jones, Jr. and R. A. Moss, Eds., *Carbenes*, Vol. II, Wiley, New York, 1975.
4. M. Jones, Jr. and R. A. Moss, Eds., *Carbenes*, Vol. I, Wiley, New York, 1973.
5. D. L. S. Barahms and W. P. Dailey, *Chem. Rev.*, **96**, 1585 (1996).
6. L. M. Pande and G. C. Joshi, India Pat. 132,396 (July 20, 1974) (to India Ministry of Defense), *Chem. Abstr.*, **82**, 32205 (1975).
7. J. Lal and W. M. Saltman, *J. Polym. Sci. A*, **4**, 1637 (1966).
8. C. Pinazzi and G. Levesque, *J. Polym. Sci. C*, **16**, 4695 (1969).
9. C. Pinazzi, J. P. Vilette, and Pleurdean, *Eur. Polym. J.*, **9**, 1127 (1972).
10. A. Koneitzny and U. Beithan, *Angew. Makromol. Chem.*, **61**, 74 (1978).
11. C. Pinazzi and G. Levesque, *Compt. Rend.*, **260**, 3393 (1965).
12. E. N. Barentsvich, L. S. Breshler, E. L. Rabinerzon, and A. E. Kalas, *Vysokmol. Soedin, Ser A*, 1289 (1979); *Chem. Abstr.*, **89**, 76116 (1978).
13. G. G. Cameron and R. B. Muir, *J. Polym. Sci.*, **14**, 661 (1976).
14. A. Brydon, G. G. Cameron, and R. B. Muir, *Makromol. Chem.*, **178**, 1739 (1977).
15. A. T. Bullock, G. G. Cameron, and R. B. Muir, *Eur. Polym. J.*, **13**, 505 (1977).
16. A. K. Wong and P. K. Seow, *J. Rubb. Res. Inst. Malaysia*, **28**, 1 (1980).
17. M. Makosza and M. Wawrzyniewicz, *Tetrahedron Lett.*, **53**, 4659 (1969).
18. G. C. Joshi, L. M. Pande, A. K. Mukherjee, K. K. Ganguli, P. K. Tiwari, and S. C. Raman, in *Proceedings of the Symposium on High Polymers*, Kanpur, India, 1972.
19. T. Miyazawa, K. Fukushima, and Y. Ideguchi, *J. Polym. Sci. B*, **1**, 385 (1963).
20. S. A. Liebman and B. J. Gudzinowicz, *Anal. Chem.*, **33**, 931 (1961).
21. H. Mayr and U. W. Heigl, *Angew. Chem. Int. Ed. Engl.*, **24**, 579 (1985).
22. L. W. Jenneskens, L. A. M. Turkenburg, W. H. De Wolf, and F. Bickelhaupt, *Recl. Trav. Chim. Pays-Bas.*, **104**, 184 (1985).