Cure Modification of Natural Rubber Containing Benzothiazole Accelerators by Some Modified Thiocarbamyl Sulfenamides

R. N. Datta, S. C. Debnath, J. W. M. Noordermeer

Rubber Technology, Faculty of Chemical Technology, University of Twente, P.O. Box 217, 7500AE Enschede, The Netherlands

ABSTRACT: The effects of *N*-cyclopentamethylene thiocarbamyl-*N'*-(cyclohexyl,thiocyclohexyl)sulfenamide (CPCTS) and *N*-oxydiethylene thiocarbamyl-*N'*-(cyclohexyl,thiocyclohexyl)sulfenamide (ODCTS) as cure modifiers on the vulcanization of natural rubber (NR) containing benzothiazole accelerators were studied. CPCTS and ODCTS were used separately with 2-mercaptobenzothiazole and *N*-oxydiethylene benzothiazole sulfenamide to determine their effects on these accelerators. CPCTS and ODCTS retarded the accelerators. Enhanced activity was found with respect to the torque, scorch, modulus, and tensile strength and was believed to be due to the formation of different intermediate components during the early stage of the vulcanization of NR. Reactions likely responsible for acceleration and retardation were explored. CPCTS and ODCTS provided better cure retardation than *N*-cyclohexyl thiophthalimide. The chemical characterization of the NR vulcanizates correlated with the physical properties obtained at 140°C. Stocks containing CPCTS or ODCTS produced mostly monosulfide linkages, which were affected when *N*-cyclohexyl thiophthalimide was used. This provided information concerning the heat-resistance properties of the vulcanizates. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3835–3847, 2003

Key words: natural rubber; thiocarbamyl sulfenamide; high performance liquid chromatography; cure modification

INTRODUCTION

Scorch safety is a requirement for the processing of a rubber compound. The scorch behavior of 2-mercaptobenzothiazole (MBT) can be moderated by the chemical transformation of the compound into N-substituted 2-benzothiazole sulfenamide, which has been recognized as an accelerator with inhibitor activity.[1–3] In 1968, *N*-cyclohexyl thiophthalimide (CTP) emerged as an effective retarder that could delay the process of the vulcanization of natural rubber (NR).[4] Other structurally related compounds containing bivalent sulfur linked to nitrogen have been reported to be effective retarders.[5–9]

Benzothiazole sulfenamides activated by thiuram compounds usually result in a higher cure rate and modulus but less processing safety, which can be retained by the incorporation of CTP.[10] Unfortunately, CTP generates phthalimide, which sometimes causes blooming on the vulcanizates. In an earlier study by Das et al.,[11] it was shown that phthalimide reduced the modulus and tensile strength of NR vulcanizates during aging. In this investigation, an attempt was made to formulate a compound that would produce thiuram accelerators during vulcanization and could

scavenge MBT, thus delaying the process of vulcanization. In the structure of CTP, a cycloalkylthio moiety is attached to nitrogen to incorporate an S—N bond that is reactive toward accelerators, especially MBT.[4] The S—N bond can be introduced into a suitable thiocarbamyl sulfenamide, the curing efficiency of which is similar to that of thiuram ultra-accelerators, through the —NH functionality; as a result, the retarding and accelerating activity of the resultant compound can be observed. A binary combination of this compound and a benzothiazole accelerator gives an optimum balance of the scorch delay and cure rate and no undesirable side effects. *N*-Cyclopentamethylene thiocarbamyl-*N'*-cyclohexyl sulfenamide (CPCS) and *N*-oxydiethylene thiocarbamyl-*N'*-cyclohexyl sulfenamide (ODCS) were selected as representative thiocarbamyl sulfenamide accelerators that were chemically modified as shown in Scheme 1.

To determine the dual activity of some other modified thiocarbamyl sulfenamides accelerated by dibenzothiazyl disulfide, some similar studies were made previously.[12] In this investigation, the effects of *N*-cyclopentamethylene thiocarbamyl-*N'*-(cyclohexyl,thiocyclohexyl)sulfenamide (CPCTS) and *N*-oxydiethylene thiocarbamyl-*N'*-(cyclohexyl,thiocyclohexyl)sulfenamide (ODCTS) on thiazole accelerators were studied. The thermal and age-resistant properties of the vulcanizates obtained from these systems were included in this study. Also, the various reactions
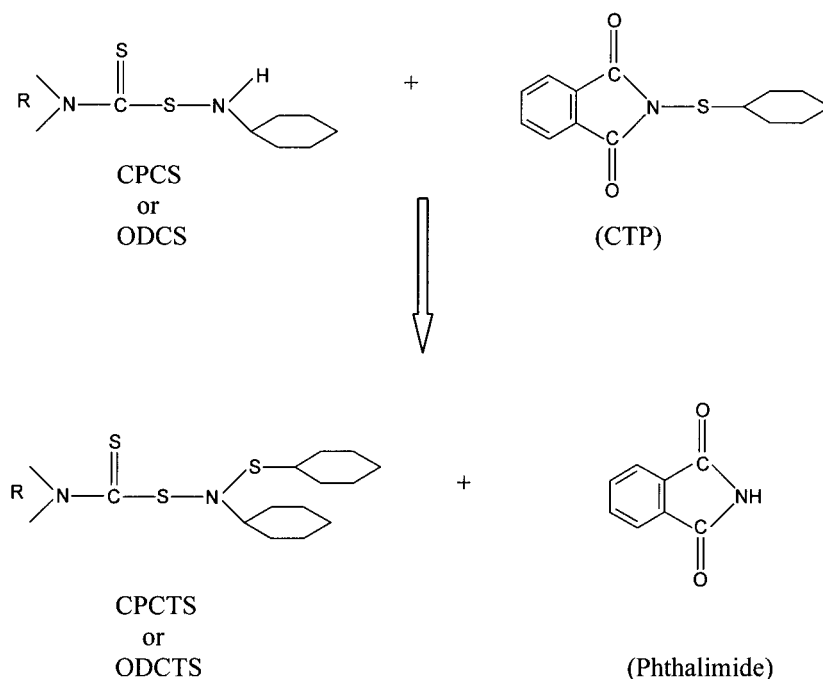
Scheme 1 Formation of CPCTS/ODCTS from the reaction of CPCS/ODCS and CTP (R = cyclopentamethylene or oxydiethylene).

occurring in these systems were explored through high-performance liquid chromatography (HPLC) to determine the mechanism of cure modification. An attempt was made to correlate the physical properties of the vulcanizates with the chemical linkages formed. Gum stocks were deliberately chosen so that any complexity that might arise during the investigation would be avoided.

EXPERIMENTAL

The accelerators and retarders employed in this study are shown in Table I. The vulcanizing ingredients [5 parts per hundred parts of rubber (phr) zinc oxide, 2 phr stearic acid, 0.5 phr sulfur, 9 mmol phr accelerator, and 2 mmol phr retarder] were incorporated into NR on a 203 mm × 104 mm laboratory mill with an 18-min mixing cycle. The stocks were cured under pressure at 140 and 170°C for optimum cure times, and the vulcanizates were kept for 24 h at the ambient temperature before the measurement of the modulus at 200% elongation and the tensile strength according to ASTM D 412-51T with dumbbell-shaped test pieces. The modulus and tensile strength of the vulcanizates and the cure data obtained on a rubber process analyzer (RPA-2000; Alpha Technologies) at 140 and 170°C are provided in Table II.

In the aging experiments, vulcanizates obtained at the optimum cure were aged at 100 ± 1°C in an oven provided with forced air circulation for 96 h. The specimens thus aged were kept for a further period of

24 h at room temperature (21 ± 1°C) before the modulus and tensile strength were measured.

As the temperature increased, the modulus, tensile strength, torque, and so forth of the vulcanizates decreased. Hence, the retention of these physical properties of the vulcanizates obtained at elevated temperatures was considered to be a measure of the heat resistance of the cured products.

The number-average molecular weight (M_n) of different rubber stocks, before vulcanization, was determined from intrinsic viscosity measurements,[21] and an average value of 1.4×10^5 was found in this study. The density of the chemical crosslinks [$(2M_{C,\text{chem}})^{-1}$ (g mol/g of hydrocarbon rubber)] was estimated from the elastic constant (C_1) with the Mullins relationship:[22]

$$C_1 = [\rho R T (2M_{C,\text{chem}})^{-1} + 0.78 \times 10^6]$$
$$[1 - 2.3(M_{C,\text{chem}})M_n^{-1}] \, \text{dyn cm}^{-2}$$

where ρ is the density of the rubber vulcanizates, $M_{C,\text{chem}}$ is the number-average molecular weight of the network chains between chemical crosslinks, 0.78×10^6 is the correction factor (which includes the maximum contribution of chain entanglements), R is the molar gas constant, and T is the absolute temperature. The value of C_1 (dyn cm^{-2}) for an NR gum vulcanizate was determined with the Mooney–Rivlin expression[23] according to the procedure reported by Saville and Watson.[24] The proportions of monosulfide,
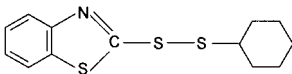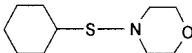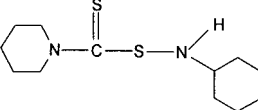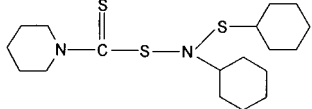
TABLE I
List of Compounds Used
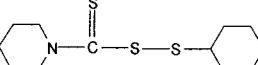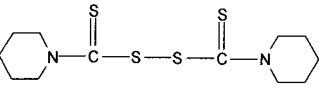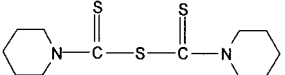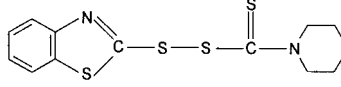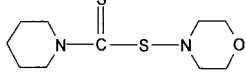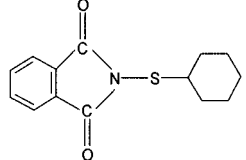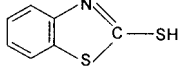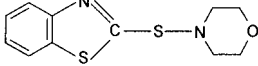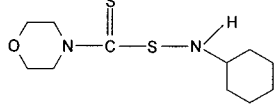
Chemical name	Abbreviation	Structure
2-Cyclohexyldithiobenzothiazole[13]	CDB	
Cyclohexyl thiomorpholine[14,15]	CM	
N-Cyclopentamethylenethiocarbamyl-N′-cyclohexyl-sulfenamide[16]	CPCS	
N-Cyclopentamethylenethiocarbamyl-N′-(cyclohexyl, thiocyclohexyl) sulfenamide[17]	CPCTS	
N-Cyclopentamethylenethiocarbamyl cyclohexyl disulfide[18]	CPTCD	
Bis(cyclopentamethylene)thiuram disulfide[19]	CPTD	
Bis(cyclopentamethylene)thiuram monosulfide[20]	CPTM	
N-Cyclopentamethylenethiocarbamyl-2-benzothiazyl disulfide[11]	CTBD	
N-Cyclopentamethylenethiocarbamyl-N′-oxydiethylene sulfenamide[16]	CTOS	
Cyclohexyl thiophthalimide	CTP	
2-Mercaptobenzothiazole	MBT	
N-Oxydiethylene benzothiazole sulfenamide	OBTS	
N-Oxydiethylenethiocarbamyl-N′-cyclohexyl sulfenamide[16]	ODCS	

TABLE I *Continued*

Chemical name	Abbreviation	Structure
N-Oxydiethylenethiocarbamyl-N'-(cyclohexyl, thiocyclohexyl) sulfenamide[17]	ODCTS	
N-Oxydiethylenethiocarbamyl-2-benzothiazyl disulfide[11]	OTBD	
N-Oxydiethylenethiocarbamyl cyclohexyl disulfide[18]	OTCD	
Bis(oxydiethylene) thiuram disulfide[19]	OTD	
Bs(oxydiethylene) thiuram monosulfide[20]	OTM	
N-Oxydiethylenethiocarbamyl-N'-oxydiethylene sulfenamide	OTOS	

disulfide, and polysulfide crosslinks in the vulcanizates were determined with thiol–amine chemical probes.[25,26] For the estimation of combined sulfur in the vulcanizates, the specimen was thoroughly extracted with a benzene/alcohol (2:1 v/v) mixture at the reflux temperature. This extracted and dry sample (0.045 g) was burnt in an Erlenmeyer flask (M/S Heraeus, Germany) in the presence of oxygen. The resultant sulfur dioxide was oxidized by hydrogen peroxide into sulfate ions, which were determined[27] quantitatively by titration with a standardized barium perchlorate solution with thorin as an indicator.

The identification of the various compounds formed during the reaction of the accelerators and retarder at

TABLE II
Physical Data of Cured Stocks Obtained at 140 and 170°C[a]

Mix no. and composition (mmol)	R_∞ (Nm)	t_2 (min)	t_{90} (min)	Modulus[b] (MPa)			Tensile strength (MPa)		
					Aged for			Aged for	
				Unaged	72 h	96 h	Unaged	72 h	96 h
1. MBT 9	1.45 (1.05)	2.5 (1.0)	24.0 (4.0)	0.28	0.30	0.31	5.65	5.12	4.71
2. MBT 9									
CTP 2	1.30 (0.90)	5.5 (1.5)	28.0 (4.75)	0.18	0.20	0.16	3.34	3.01	2.61
3. MBT 9									
CPCTS 2	2.90 (2.80)	8.0 (2.5)	20.0 (5.5)	0.64	0.68	0.72	13.32	14.13	14.92
4. MBT 9									
ODCTS 2	2.70 (2.45)	10.0 (3.5)	22.0 (6.5)	0.50	0.54	0.56	11.03	11.92	12.32
5. OBTS 9	3.50 (2.90)	28.5 (4.0)	45.5 (6.0)	0.69	0.71	0.73	13.99	13.80	12.85
6. OBTS 9									
CTP 2	3.10 (2.50)	50.5 (6.0)	71.5 (8.0)	0.59	0.62	0.58	13.27	13.12	12.62
7. OBTS 9									
CPCTS 2	3.90 (3.80)	52.0 (8.0)	67.0 (11.0)	0.88	0.90	0.93	16.21	16.71	16.90
8. OBTS 9									
ODCTS 2	3.70 (3.45)	54.0 (9.0)	69.0 (12.5)	0.79	0.82	0.86	14.38	14.85	14.99

[a] Values in parentheses indicate those obtained at 170°C.
[b] Modulus at 200% elongation.
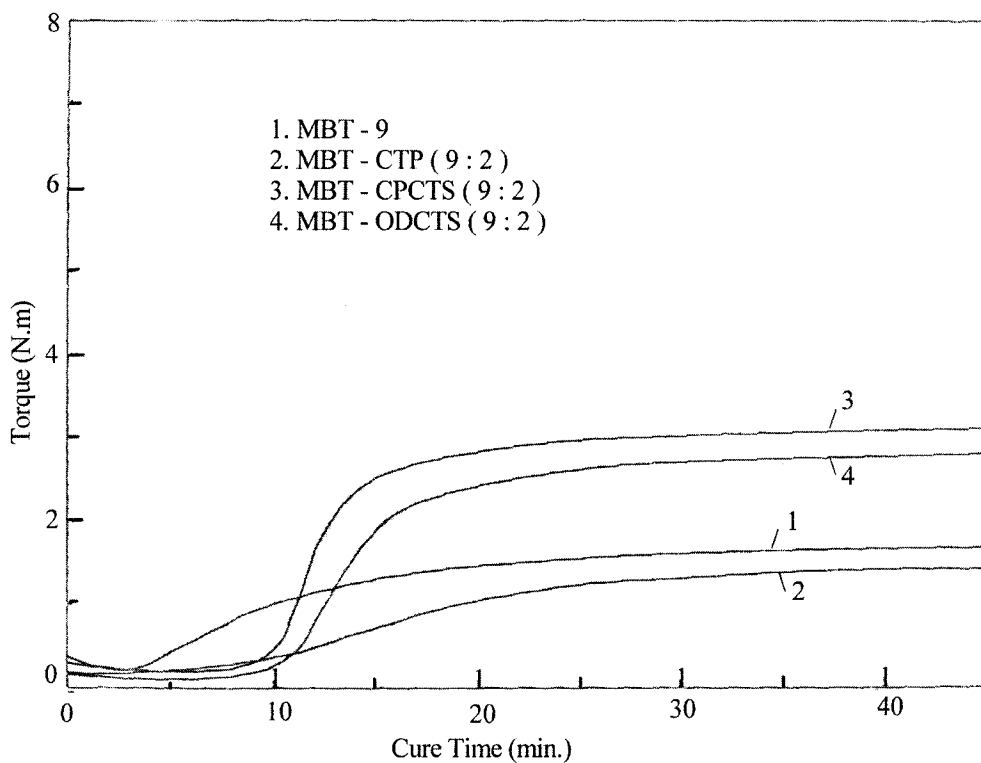
Figure 1 Effect of CTP/CPCTS/ODCTS on MBT-accelerated stocks cured at 140°C.

140°C was performed with an HPLC technique.[28,29] The calculated amounts of the rubber additives corresponding to different molar ratios were heated to 140°C for 2 min. The molten mass obtained in each case was extracted with an acetonitrile/water (70:30 v/v) mixture, and the volume was raised up to 5 cm³.

Figure 2 Effect of CTP/CPCTS/ODCTS on OBTS-accelerated stocks cured at 140°C.

Figure 3 Rheographs of mixes 1, 2, 3, 5, 6, and 7 at 170°C, showing the effects of CTP and CPCTS.

Figure 4 High-performance liquid chromatograms obtained by the heating of the additives at 140°C for 2 min: (a) OBTS–CPCTS (9:2 molar ratio) and (b) OBTS–ODCTS (9:2 molar ratio).

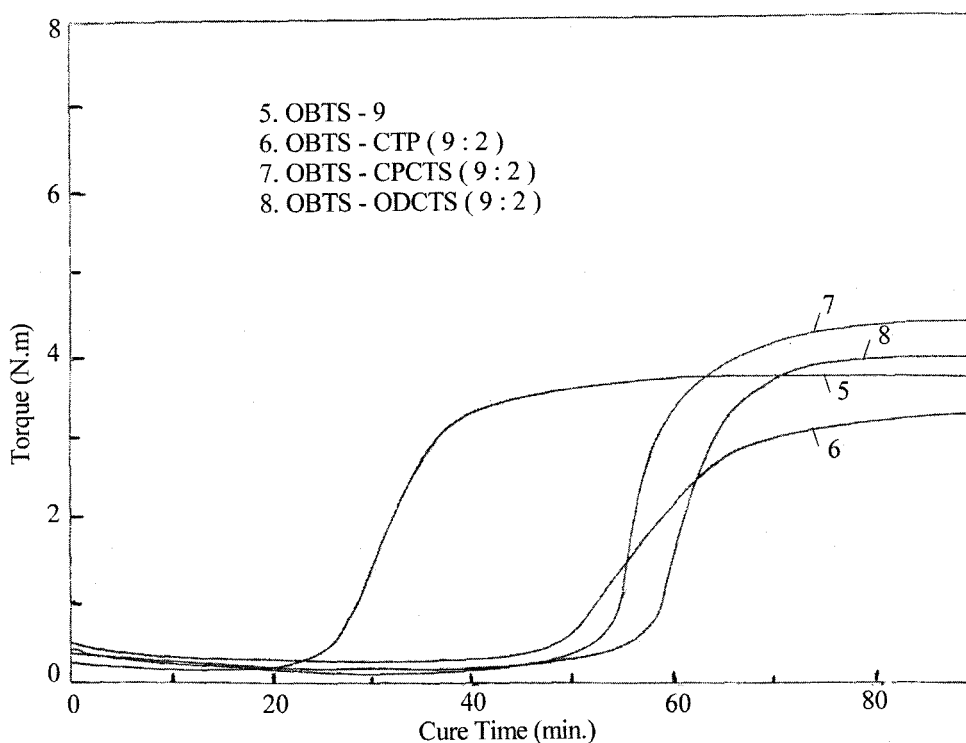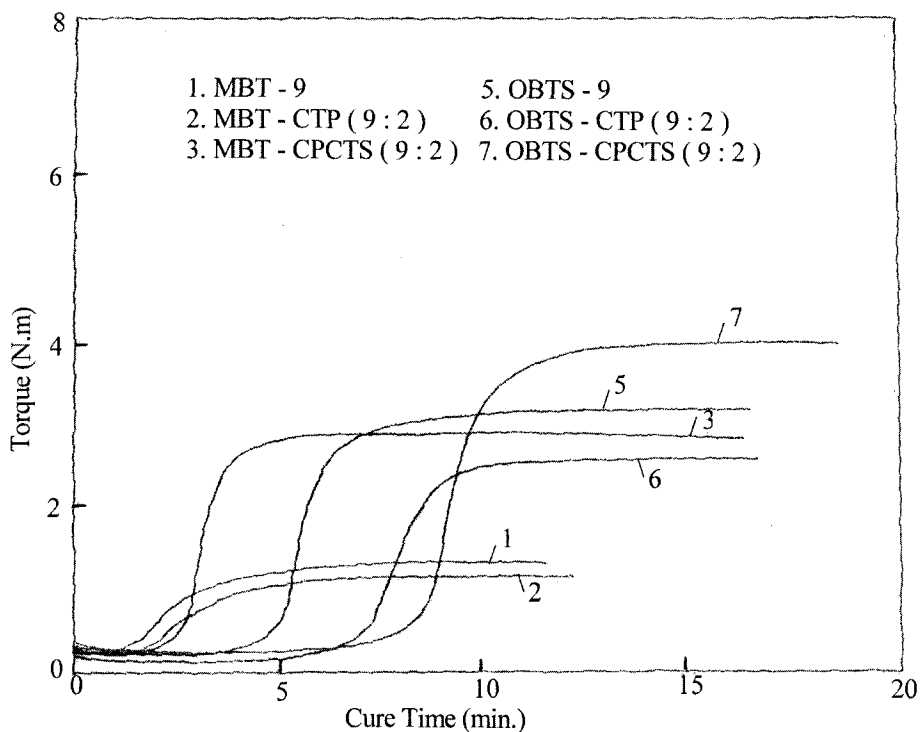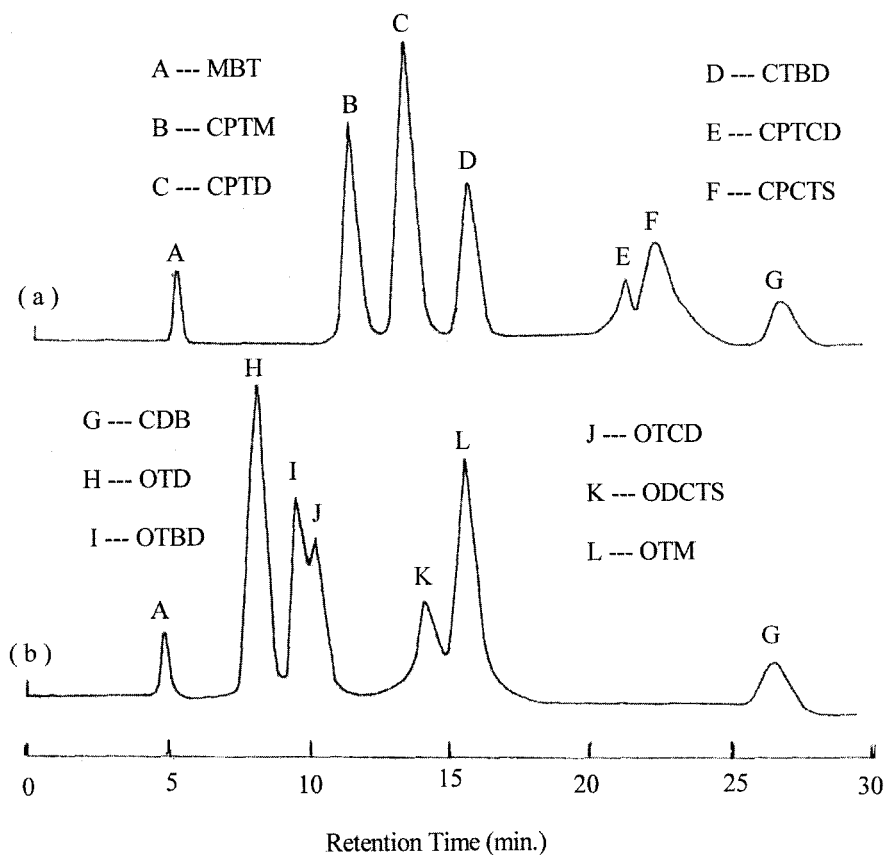**Figure 5** High-performance liquid chromatograms obtained by the heating of the additives at 140°C for 2 min: (a) OBTS–CPCTS (9:2 molar ratio) and (b) OBTS–ODCTS (9:2 molar ratio).
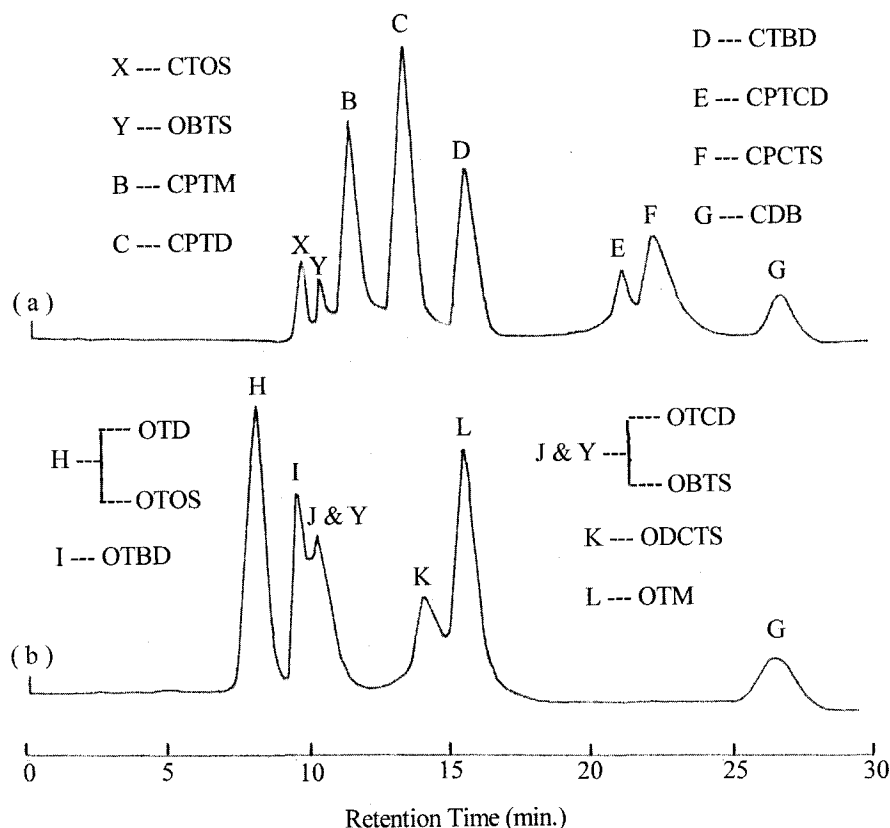
An aliquot of 2 mm^3 of the clear solution was injected into the column, and the chromatograms were obtained. Thin samples of grossly undercured vulcanizates were obtained at 140°C with spacers for the investigation carried out in the presence of rubber. The calculated amount of the resultant mass containing identical amounts of the rubber additives used before in the absence of rubber was processed, and chromatograms were obtained in the same way reported earlier.[28,29]

CPCTS and ODCTS were prepared as follows. A mixture containing 5.22 g (0.02 mol) of CTP and 0.02 mol of the appropriate sulfenamide in 50 cm^3 of isopropyl alcohol was heated at reflux (82–83°C) for 10 h. The obtained solution was stirred at the ambient temperature for 24 h, at which point phthalimide precipitated out; it was removed by filtration. To the filtrate, 70 cm^3 of water containing 4.8 g (0.03 mol) of NaOH was added, and stirring was continued for 30 min. The reaction mixture was extracted with 60 cm^3 of diethyl ether, separated, washed with water until the washing was neutral, and then dried over anhydrous Na$_2$SO$_4$. The ether was removed *in vacuo*, and the solid so obtained was pure according to the following analyses.

CPCTS

mp: 53°C (recrystallized from ethanol). ELEM. ANAL. Found: C, 58.01%; H, 8.16%; N, 7.15%; S, 25.76%. Calcd. for C$_{18}$H$_{32}$N$_2$S$_3$: C, 58.06%; H, 8.60%; N, 7.52%; S, 25.80%. NMR (CCl$_4$, δ): 0.80–2.30 (m, 26H, methylene protons), 3.50–3.90 (m, 6H, N—CH$_2$—, —S—CH, and N—CH merged).

ODCTS

mp: 114°C (recrystallized from ethanol). ELEM. ANAL. Calcd. for C$_{17}$H$_{30}$N$_2$OS$_3$: C, 54.54%; H, 8.02%; N, 7.48%; S, 25.66%. Found: C, 54.14%; H, 8.16%; N, 7.39%; S, 25.51%. NMR (CCl$_4$, δ): 0.95–2.11 (m, 20H, methylene protons), 3.28–4.11 (m, 10H, N—CH$_2$—, —O—CH$_2$— and —S—CH merged).

The ^{1}H-NMR spectrum at 60 MHz was taken with a Varian T-60 A NMR spectrometer.

RESULT AND DISCUSSION

Table II records the data for the cure characteristics of the benzothiazole accelerators, MBT and *N*-oxydiethylene benzothiazole sulfenamide (OBTS), in the presence of CTP, CPCTS, and ODCTS in terms of the
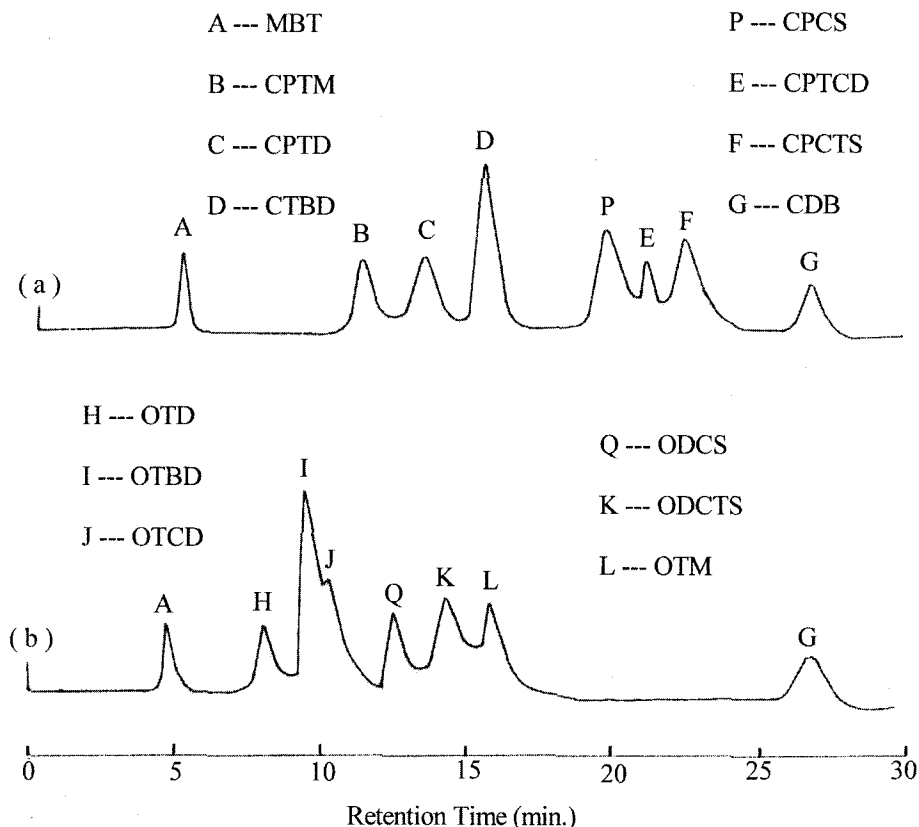
Figure 6 High-performance liquid chromatograms of the extracts obtained from 0.366 g of NR vulcanizates cured at 140°C for 2 min (stock composition: NR, 100; zinc oxide, 5; stearic acid, 2; and sulfur, 0.5): (a) MBT (9 mmol) and CPCTS (2 mmol) and (b) MBT (9 mmol) and ODCTS (2 mmol).

extent of crosslinking (R_∞), the scorch safety time (t_2), and the optimum cure time (t_{90}) obtained at 140 and 170°C. The values in parentheses denote those obtained at 170°C. Of the four combinations (stocks 1–4), the MBT–CPCTS combination gives the maximum torque values and at the same time increases the scorch safety, as evidenced by the t_2 value. MBT–ODCTS (stock 4) in the series occupies the second position with respect to R_∞ but ranks first in terms of t_2; CTP in this respect behaves differently and lowers the torque and the cure rate, as observed earlier (stock 2).[30] These facts are schematically shown in Figure 1. The same thing happens for OBTS-accelerated stocks (mixes 5–8, Fig. 2).

At 170°C, as expected, t_2 and t_{90} are lowered to a great extent, whereas R_∞ varies in an irregular fashion (the results are given in parentheses, Table II). Of the four combinations (stocks 1–4), MBT–CPCTS-accelerated stock exhibits the maximum R_∞ value in the series at this elevated temperature, and the extent of the fall in the torque value is minimum for this combination. Similar is the case for the series (stocks 5–8) containing OBTS: the OBTS–CPCTS combination (stock 7) resists a considerable portion of torque obtained at 140°C. The curing behavior at

the elevated temperature, however, can be clearly followed from Figure 3.

To understand the activation influence of CPCTS/ODCTS on thiazole accelerators in the vulcanization of NR, we performed some HPLC studies.

MBT, in conjunction with CPCTS, is highly reactive, and even in the absence of rubber, we have observed that a vigorous reaction begins when these two components are heated at 140°C for 2 min. The results are depicted in Figure 4(a) and suggest the formation of large amounts of bis(cyclopentamethylene)thiuram disulfide (CPTD), bis(cyclopentamethylene)thiuram monosulfide (CPTM), and N-cyclopentamethylene-thiocarbamyl-2-benzothiazyl disulfide (CTBD). Also, N-cyclopentamethylenethiocarbamyl cyclohexyl disulfide (CPTCD), 2-cyclohexyldithiobenzothiazole (CDB), and so forth could be detected in the mixture after the reaction. Figure 4(b) depicts the chromatogram obtained with the MBT–ODCTS combination. It is evident from the chromatogram that significant amounts of bis(oxydiethylene)thiuram disulfide (OTD), bis(oxydiethylene)thiuram monosulfide (OTM), and N-oxydiethylenecarbamyl-2-benzothiazyl disulfide (OTBD) are formed in the reaction medium. The reactions of OBTS and CPCTS/ODCTS are of the same
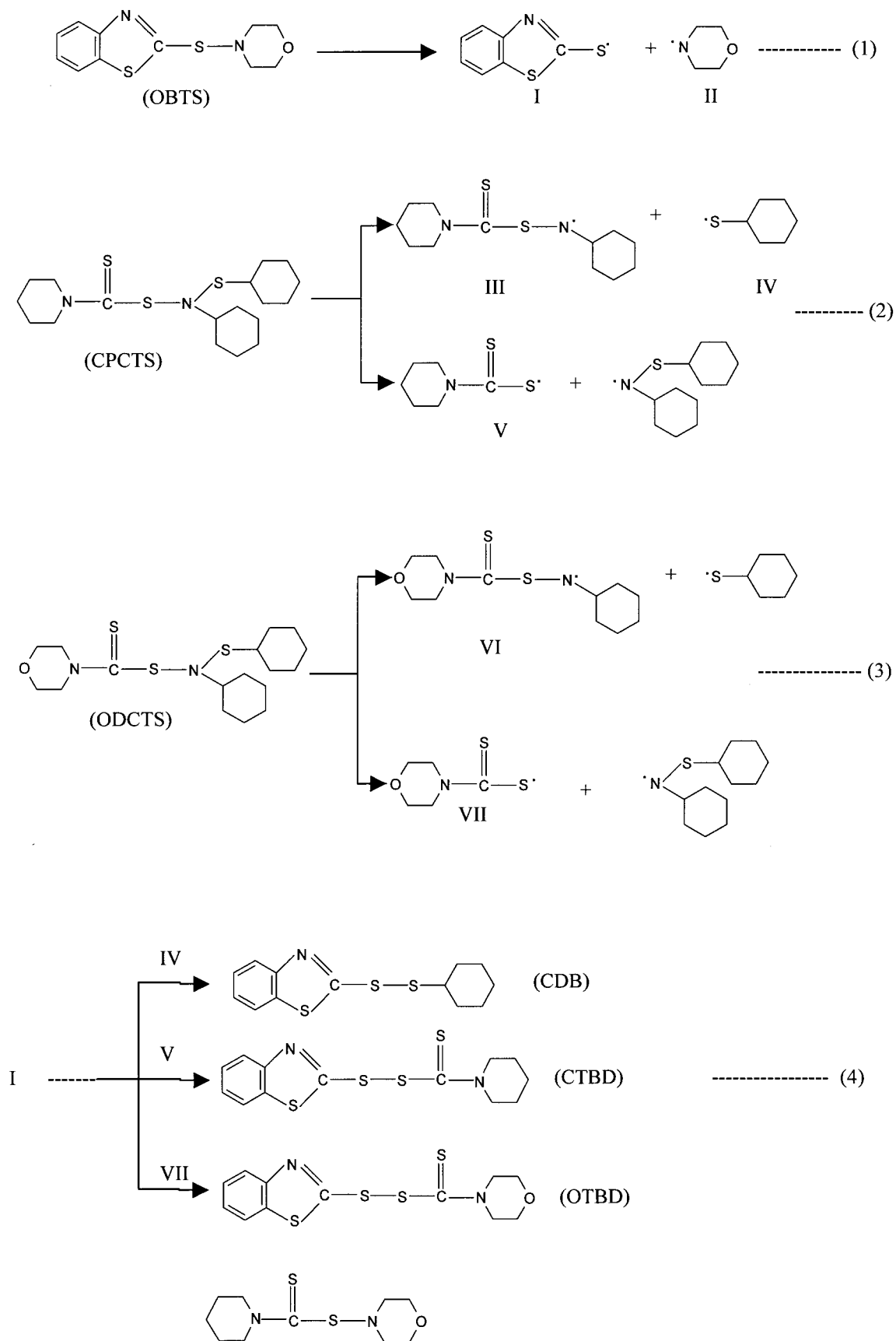
Scheme 2 Formation of various products from the reaction of the accelerators (KaH ≡ rubber).
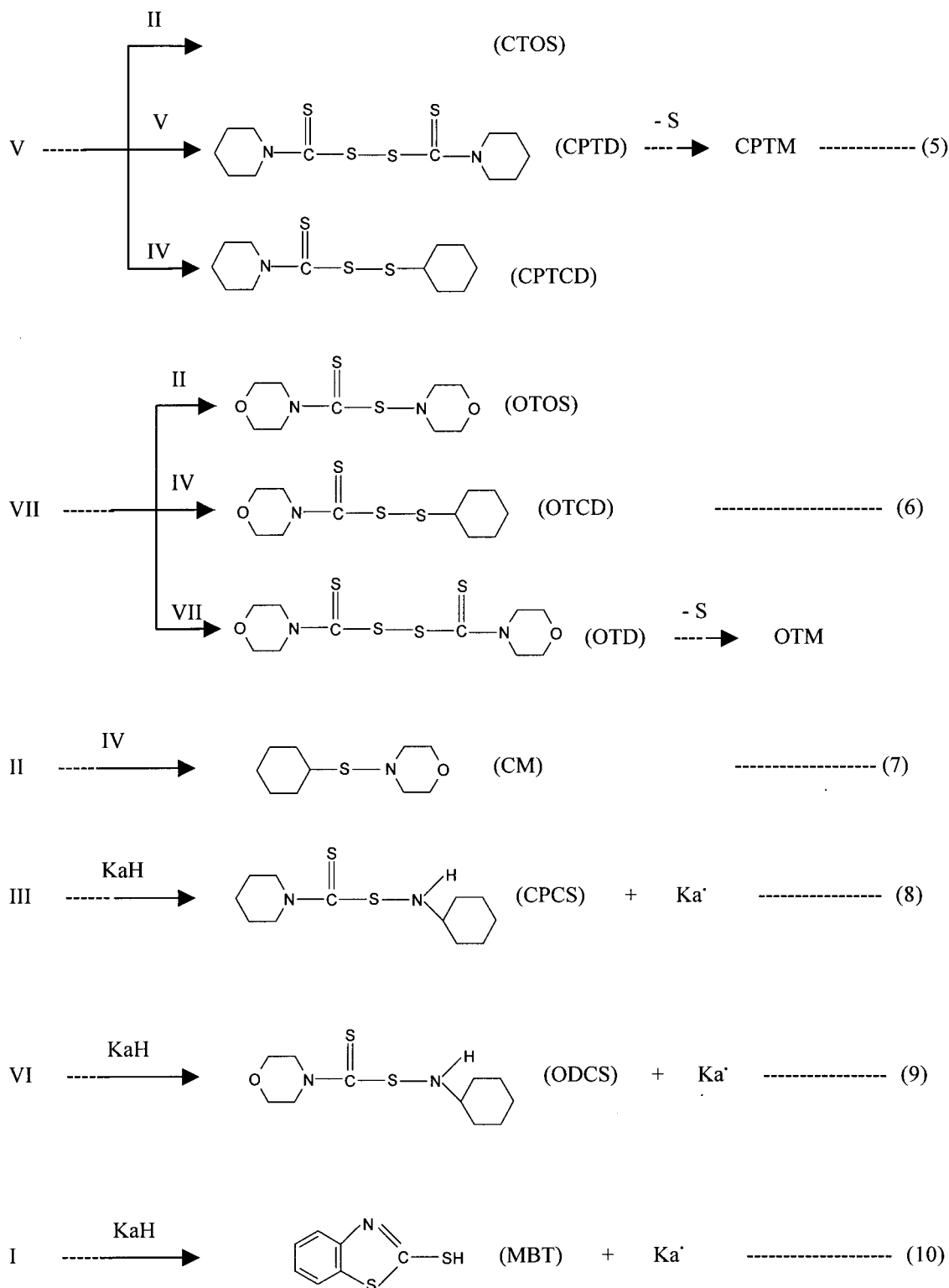
Scheme 2 (*Continued from the previous page*)

kind, and they are depicted in the chromatograms of Figure 5(a,b). However, more meaningful results are expected when these reactions are carried out in the presence of NR at the vulcanization temperature.

Reaction of MBT with CPCTS/ODCTS dispersed in NR

Figure 6(a) depicts a chromatogram obtained with the MBT–CPCTS combination dispersed in NR. The char-

acteristics of the reaction are depicted in the generation of CPCS and in the depletion of CPTD and CPTM. In addition to these, other components (CDB, CTBD, and CPTCD) are formed in the reaction medium. The generation of these compounds, according to the free-radical mechanism[17,31] shown in Scheme 2 (steps 1, 2, 4, 5, and 8), is likely to influence the vulcanization reaction. The concentration of CTBD, as noticed from the chromatogram [cf. Fig. 4(a,b)], remains practically unaltered in comparison with those obtained in the absence of rubber. The facile formation of CPCS in the rubber medium obviously arises from step 8 of Scheme 2. As for the notable decrease in the concentrations of CPTD and CPTM, it can reasonably be said that CPTD and CPTM are also formed in the rubber medium in substantial quantities, but these are rapidly converted into dithiocarbamates in the presence of zinc oxide, which is also present in the medium. Zinc dithiocarbamates quickly react with rubber and form rubber-bound intermediates as well.

A different compound that forms in the reaction of accelerators is likely to influence the vulcanization reaction, which ultimately changes the physical properties of the resulting vulcanizates. From an examination of the physical data given in Table II, it is evident that MBT–CPCTS-accelerated vulcanizates possess higher torque, modulus, and tensile values than those obtained from the MBT–CTP combination (cf. the physical data of stocks 2 and 3). The MBT–CPCTS combination yields a thiuram compound, which actively takes part in the vulcanization reaction. Moreover, the existence of CTBD in the MBT–CPCTS combination is apt to increase the physical properties of the vulcanizates,[11] and this has actually been observed. The increment in the scorch time is due to the formation of CDB, as shown in step 4 of Scheme 2. The reaction of MBT with ODCTS in NR is similar to that observed in the MBT–CPCTS combination. This fact is depicted in Figure 6(b). The longer scorch time for the MBT–ODCTS combination (stock 4, Table II) is due to the formation of, among other products, OTD [Fig. 6(b)], which is less scorchy[17] than CPTD formed from the MBT–CPCTS combination (stock 3, Table II). From a comparison of the physical data of the vulcanizates of mix 2 with mixes 3 and 4 (Table II), it may be inferred that under identical experimental conditions, both CPCTS and ODCTS surpass CTP in many respects.

Reaction of OBTS with CPCTS/ODCTS dispersed in NR

It is apparent from Figure 7(a) that MBT, CDB, CTBD, CPTD, N-cyclopentamethylenethiocarbamyl-N′-oxydiethylene sulfenamide (CTOS), CPTCD, and CPCS are generated from the OBTS–CPCTS combination (steps 1, 2, 4, 5, 8, and 10 of Scheme 2). These products

are known accelerators for sulfur vulcanization of NR. Moreover, CTOS is generated in the system. We could not detect cyclohexyl thiomorpholine (CM; step 7, Scheme 2) in the medium; its reaction with MBT is probably sharp, giving CDB in significant quantities. Considering the products formed in the reaction of the OBTS–ODCTS combination [Fig. 7(b)], we may infer that the reaction is very similar in nature. Here we could detect N-oxydiethylenethiocarbamyl-N′-oxydiethylene sulfenamide (OTOS) in place of CTOS. The existence of CTOS, CTBD, CPTD, and other components in the OBTS–CPCTS reaction is reflected in the enhanced physical properties[11,17] of the vulcanizates (cf. the physical data of mixes 6 and 7, Table II). The combination containing OBTS–ODCTS (stock 8, Table II) has lower physical properties than the OBTS–CPCTS combination (stock 7, Table II), which, as observed previously[17] has a lower crosslinking potential than the related compounds, CTOS and CPTD, formed from the OBTS–CPCTS combination [Fig. 7(a)].

From the foregoing HPLC study, it is evident that both CPCTS and ODCTS react with MBT and OBTS as well as the rubber and thus generate a number of other components that are likely to influence the vulcanization reaction, ultimately leading to the formation of crosslinks, as manifested in physical properties such as the modulus, tensile strength, and torque of the vulcanizates. The results clearly indicate that CPCTS and ODCTS can efficiently act as retarders for benzothiazole-accelerated stock. In addition to this, both CPCTS and ODCTS have the added advantage of generating *in situ* highly effective accelerators. However, CTP, acting as a sulfur sink,[30] lowers the torque in the vulcanization of NR and also reduces the physical data of the vulcanizates.

Effect of CPCTS/ODCTS/CTP on the aging behavior of NR vulcanizates

It is expected that any major flaw occurring in the polymer backbone during oxidative aging will be reflected in the modulus and tensile strength of the vulcanizates. The retention of physical properties, namely, the modulus and tensile strength, will thus provide a measure of the age resistance. The data obtained during aging at 100°C up to 96 h are recorded in Table II.

The vulcanizates obtained from mixes 3, 4, 7, and 8 resist the accelerated aging in terms of the tensile strength up to 96 h. The modulus values of the vulcanizates are found to increase from the beginning. This is not an unusual phenomenon and has been reported by earlier workers.[18,32] The most interesting observation is that the stock containing CTP (mixes 2 and 6) under identical conditions behaves differently. The tensile values of the vulcanizates containing CTP fall
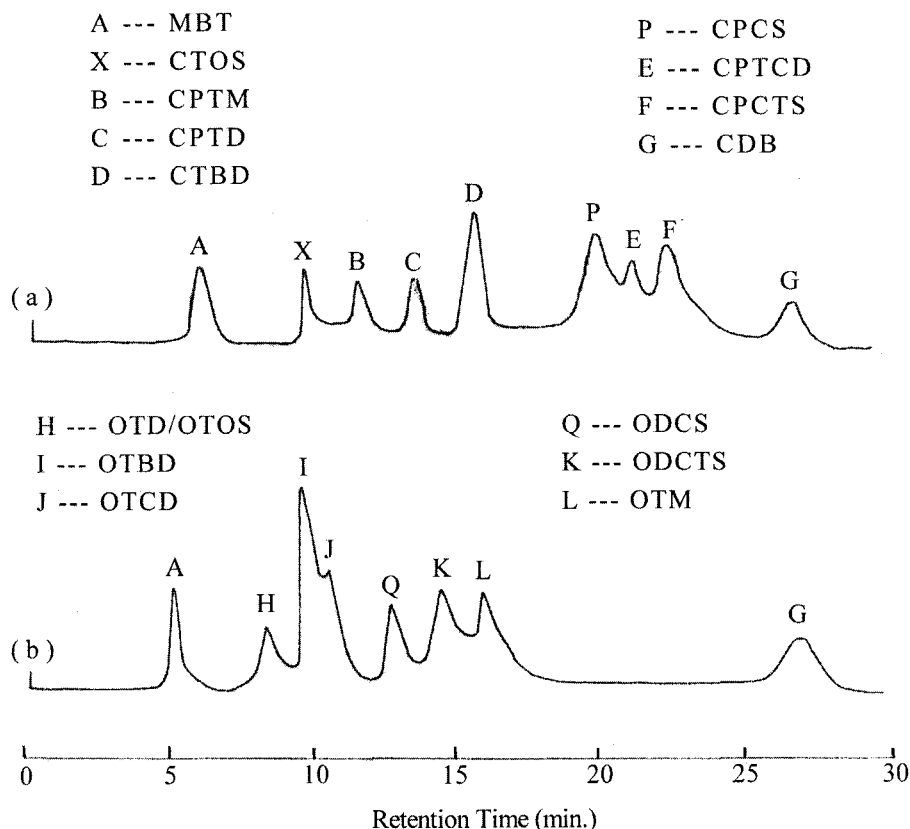
A --- MBT
X --- CTOS
B --- CPTM
C --- CPTD
D --- CTBD

P --- CPCS
E --- CPTCD
F --- CPCTS
G --- CDB

(a)

H --- OTD/OTOS
I --- OTBD
J --- OTCD

Q --- ODCS
K --- ODCTS
L --- OTM

(b)

Retention Time (min.)

Figure 7 High-performance liquid chromatograms of the extracts obtained from 0.366 g of NR vulcanizates cured at 140°C for 2 min (stock composition: NR, 100; zinc oxide, 5; stearic acid, 2; and sulfur, 0.5): (a) OBTS (9 mmol) and CPCTS (2 mmol) and (b) OBTS (9 mmol) and ODCTS (2 mmol).

during aging, whereas the modulus values after an initial increase decrease to some extent. The generation of phthalimide in the reaction medium is the cause[11] of the low values of the modulus and tensile strength on aging. The retention of the physical properties of the stocks containing CPCTS or ODCTS is due to the formation of active accelerators in the reaction medium in the vulcanization of NR.

Structural characterization of the vulcanizates

To determine the cure modification effected by CPCTS and ODCTS in light of the fine network structure of

the vulcanizates, we took stocks 1–4 and 5–8 as representative samples, and we first determined the total crosslinks of the vulcanizates. These linkages were then resolved into monosulfide, disulfide, and polysulfide types. It can be seen in Table III that stocks 3, 4, 7, and 8 generally have E values (sulfur atoms/ chemical crosslink) between those obtained for stocks 1 and 2 and stocks 5 and 6. Thus, it may be inferred that in the stocks containing CPCTS or ODCTS, there is a proper use of sulfur. This might account for the higher modulus, tensile strength, and torque values of the stocks containing CPCTS or ODCTS. It is also evident from Table III that for the vulcanizates ob-

TABLE III
Chemical Characterization of Vulcanizates Obtained at 140°C

Mix no.	$[2\,M_{C,chem}]^{-1} \times 10^4$ g mol/g of rubber	E	Monosulfide linkages $\times 10^4$ (g mol/g of rubber)	Disulfide linkages $\times 10^4$ (g mol/g of rubber)	Polysulfide linkages $\times 10^4$ (g mol/g of rubber)
1	0.292	15.36	0.151	0.080	0.061
2	0.235	10.24	0.132	0.062	0.041
3	0.377	12.27	0.205	0.096	0.076
4	0.351	12.17	0.191	0.088	0.072
5	0.362	16.33	0.171	0.101	0.090
6	0.302	11.50	0.151	0.086	0.065
7	0.447	13.39	0.235	0.117	0.095
8	0.425	13.01	0.221	0.110	0.094

tained at 140°C, the order of the crosslink densities is $3 > 4 > 1 > 2$ and $7 > 8 > 5 > 6$. This agrees with the torque values shown in Table II. The results thus clearly indicate that the cure modification is associated with the enhancement of the crosslink density.

By resolving the total crosslinks into monosulfide, disulfide, and polysulfide linkages, we can obtain information on the variations of the different types of crosslinks formed in the presence of CPCTS, ODCTS, and CTP. The addition of 2 mmol phr CPCTS (stocks 3 and 7) has a positive effect on the formation of monosulfide crosslinks. The incorporation of CTP (stocks 2 and 6), however, has a negative effect with respect to the total and monosulfide crosslinkages. Like CPCTS, ODCTS (stocks 4 and 8) enhances the total number of crosslinks with a significant number of monolinkages. The results thus lend support to the observation that the stocks containing CPCTS or ODCTS produce heat- and age-resistant vulcanizates. In the stocks containing CTP, the proportions of disulfide and polysulfide linkages decrease to some extent (cf. the data of mixes 1 and 5 to those of mixes 2 and 6, respectively; Table III), although an enhancement in the concentration of these can be observed for the stocks containing CPCTS or ODCTS (cf. the data of mix 1 to those of mixes 3 and 4 and the data of mix 5 to those of mixes 7 and 8). The decrease in the tensile strength values for the vulcanizates of mixes 2 and 4 may be correlated to the decrease in the number of polysulfide and disulfide crosslinks.

From the foregoing results, it is apparent that the proportion of each crosslink satisfactorily explains the physical properties of the vulcanizates.

CONCLUSIONS

It is clear that CTP cannot function effectively as a cure modifier in the sulfur vulcanization of NR accelerated by benzothiazoles, although it has been shown to be an effective inhibitor of curing.

A series of compounds (LS—<>) with reactive cyclohexyl thio groups (—S—<>) attached to the leaving group (—L) can be formulated, and these are generally effective cure modifiers of NR for benzothiazole accelerators. —L is an accelerator fragment, which actively takes part in the vulcanization reaction.

In stocks accelerated by benzothiazoles, these compounds (CPCTS and ODCTS) act as scavengers of MBT liberated during the cure with the formation of asymmetric disulfides (CDB), thus delaying the process of vulcanization.

References

1. Morita, E.; Young, E. J. Rubber Chem Technol 1963, 36, 844.
2. Morita, E.; D'Amico, J. J.; Young, E. J. Rubber Chem Technol 1968, 41, 721.
3. Campbell, R. H.; Wise, R. W. Rubber Chem Technol 1964, 37, 635.
4. Leib, R. I.; Sullivan, A. B.; Trivette, C. D., Jr. Rubber Chem Technol 1970, 43, 1188.
5. Coran, A. Y.; Kerwood, J. E. U.S. Pat. 3,427,319 (1969).
6. Coran, A. Y.; Kerwood, J. E.; Trivette, C. D., Jr. U.S. Pat. 3,513,139 (1970).
7. Roos, E.; Abele, M.; Kempermann, T.; Schubart, R. Ger. Pat. 2,005,692 (1971).
8. Roos, E.; Abele, M.; Kempermann, T.; Schubart, R. Belg. Pat. 765,587 (1971).
9. Kempermann, T.; Abele, M. Rubber World 1971, 165, 83.
10. Trivette, C. D., Jr.; Morita, E.; Maender, O. W. Rubber Chem Technol 1977, 50, 570.
11. Das, P. K.; Datta, R. N.; Basu, D. K. Rubber Chem Technol 1988, 61, 760.
12. Datta, R. N. Polym Plast Technol Eng 1989, 28, 261.
13. Son, P. N. Rubber Chem Technol 1972, 45, 1513.
14. Boustany, K. Chimia 1970, 24, 369.
15. D'Amico, J. J.; Morita, E.; Sullivan, A. B.; Boustany, K.; Potts, K. T.; Kane, J.; Mckeough, D. Rubber Chem Technol 1973, 46, 1299.
16. Smith, G. E. P.; Alliger, G.; Carr, E. L.; Young, K. C. J Org Chem 1949, 14, 935.
17. Datta, R. N. J Appl Polym Sci 1989, 37, 443.
18. Datta, R. N.; Das, P. K.; Basu, D. K. Rubber Chem Technol 1986, 59, 525.
19. Datta, R. N.; Das, M. M.; Basu, D. K.; Chaudhuri, A. K. Rubber Chem Technol 1984, 57, 879.
20. Haehl, A. Rubber Chem Technol 1954, 27, 147.
21. Henry, R. A.; Dehn, W. M. J Am Chem Soc 1950, 72, 2806.
22. Bristow, G. M.; Wistall, B. T. J Appl Polym Sci 1965, 9, 495.
23. Mullins, L. J Appl Polym Sci 1959, 2, 1.
24. (a) Mooney, M. J Appl Phys 1940, 11, 582; (b) Rivlin, R. S.; Saunders, D. W. Philos Trans R Soc London Ser A 1951, 243, 251.
25. Saville, B.; Watson, A. A. Rubber Chem Technol 1967, 40, 100.
26. Campbell, D. S. J Appl Polym Sci 1969, 13, 1201.
27. Campbell, D. S.; Saville, B. Proc Int Rubber Conf 1958, 5, 1967.
28. White, D. C. Mikrochim Acta 1962, 5, 807.
29. Datta, R. N.; Basu, D. K. Rubber Chem Technol 1986, 58, 27.
30. Datta, R. N.; Das, P. K.; Basu, D. K. J Appl Polym Sci 1986, 32, 5849.
31. Son, P. N. Rubber Chem Technol 1973, 46, 999.
32. Scheele, W. Rubber Chem Technol 1961, 34, 1306.